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TIGER COMPUTER PROGRAM DOCUMENTATION

Stanford Research Institute

PREPARED FOR
Naval Ordnance Laboratory
Picatinny Arsenal
California University

March 1974

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TIGER is a digital computer program written in FORTRAN IV for calculating the thermodynamic state attained in a heterogeneous system of known atomic composition containing gases, liquids, and solids with arbitrary equations of state. As currently arranged, the program is modular, includes 52 routines, and can be applied to systems containing up to 30 gaseous and 10 condensed constituents composed of up to 10 chemical elements. The memory required to perform a calculation depends on the computer. For example, on the CDC 6400

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STANFORD RESEARCH INSTITUTE
Menlo Park, California 94025 · U.S.A.

March 1974

TIGER

COMPUTER PROGRAM DOCUMENTATION

By: M. COWPERTHWAITE and W. H. ZWISLER

Prepared for:

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FOREWORD

The theoretical basis of the TIGER code for calculating the thermodynamic state in a nonideal heterogeneous mixture was formulated by Dr. S. R. Brinkley, Jr. The original version of the code was developed and documented from July 1966 to November 1968 at Stanford Research Institute by W. H. Zwisler, W. E. Wiebenson, and L. B. Seely for Ballistic Research Laboratories under Contract No. DA-04-200-AMC-3226(X) monitored by Dr. S. M. Taylor.

Development of the code after 1968 was supported by Lawrence Livermore Laboratory under Contract AT(04-3)-115, Agreement No. 89, P.O. No. 5411209, with Mr. M. Finger and Dr. E. Lee as Technical Monitors. New routines were also added to the code as a result of work performed for Picatinny Arsenal under Contract DAAA21-71-C-0454 monitored by Mr. J. Hershkowitz and work performed for Naval Ordnance Laboratory under Contract N60921-72-C-0013 monitored by Dr. S. J. Jacobs. The present documentation of TIGER was written for Lawrence Livermore Laboratory, for Naval Ordnance Laboratory, and for Picatinny Arsenal under the contracts cited above to provide an up to date version of the code.

GENERAL ABSTRACT

TIGER is a digital computer program written in FORTRAN IV for calculating the thermodynamic state attained in a heterogeneous system of known atomic composition containing gases, liquids, and solids with arbitrary equations of state. As currently arranged, the program is modular, includes 52 routines, and can be applied to systems containing up to 30 gaseous and 10 condensed constituents composed of up to 10 chemical elements. The memory required to perform a calculation depends on the computer. For example, on the CDC 6400 computer, 40K words are required. The input instructions are written in a quasi-free-field format to simplify the input of data into the computer.

The TIGER documentation consists of four volumes. Volume I presents the theoretical basis of the code and its application to the calculation of the detonation parameters of condensed explosives. The equations used by Brinkley to calculate the thermodynamic state in a nonideal heterogeneous system in chemical equilibrium are derived and extended to treat systems in partial equilibrium. A brief discussion of the Chapman-Jouguet (CJ) theory of detonation is followed by an account of the methods used to calculate conditions in the CJ wave and the properties of the detonation products along Hugoniot curves and isentropes. Volume II presents a summary of the formulas and relationships used in TIGER. Volume III presents the FORTRAN code and flow charts needed to understand the program in detail, and Volume IV is a user's guide that explains how to prepare input cards and interpret the output of a calculation.

VOLUME I

THEORETICAL AND MATHEMATICAL FORMULATIONS FOR THE TIGER COMPUTER PROGRAM

by

M. Cowperthwaite and W. H. Zwisler
Stanford Research Institute
Menlo Park, California
January 1973

VOLUME I

ABSTRACT

Volume I contains the theoretical basis of the TIGER code and its application to the calculation of the properties of detonating condensed explosives. The equations used by Brinkley to calculate the thermodynamic state in a nonideal heterogeneous system of known atomic composition in chemical equilibrium are derived and extended to treat such systems in partial equilibrium. A brief discussion of the Chapman-Jouguet (CJ) theory of detonation is followed by an account of the methods used to compute conditions in the CJ wave and the properties of the detonation products along Hugoniot curves and isentropes. The presentation in this volume will be of interest primarily to the reader concerned with understanding the theoretical background of the code rather than to the user of the program.

ACKNOWLEDGMENT

The authors wish to express their gratitude to Mrs. Jane Daly for her skill and patience in preparing the manuscript with its multitude of equations that constitute the theoretical basis of the TIGER code.

VOLUME I

CONTENTS

I-A. INTRODUCTION

TIGER is a digital computer code written in FORTRAN IV for calculating the thermodynamic state of a nonideal heterogeneous system of known composition. It was developed at Stanford Research Institute specifically for detonation calculations after experience with the RUBY code at Lawrence Livermore Laboratory and the BKW code at Los Alamos Scientific Laboratory had led to the conclusion that a more versatile code was required to perform routine and research calculations on condensed explosives. While RUBY is limited by its inability to treat certain explosive compositions, both RUBY and BKW are restricted by the inflexibility of their interlocking subroutines which, for example, prevent use of a new equation of state in a calculation without complete reprogramming.

The TIGER code was constructed to avoid the problems associated with interdependent subroutines. The program was written in modular form so that the thermodynamics used to calculate the state, the hydrodynamics used to calculate detonation parameters, and the equations of state used to describe the properties of the system are treated separately in different parts of the code. Because of this separation, TIGER can be best described as a general code for calculating the thermodynamic properties of a nonideal heterogeneous mixture, described by an arbitrary equation of state, with the capability of calculating detonation parameters provided by the hydrodynamic option. Whereas the hydrodynamic problems are computationally trivial and are solved in the executive part of the program, the thermodynamic problems are complex and are solved in the subroutines THERMØ and ECØMPØ, which constitute the largest part of the program. The gaseous and condensed equation of state subroutines are named STATE G and STATE C. They are called on by THERMØ and ECØMPØ in a thermodynamic calculation whenever equation of state data are required.

I-B. THEORETICAL BASIS OF TIGER FOR EQUILIBRIUM CALCULATIONS

1. Introduction

This section of the TIGER documentation presents the theoretical basis of the methods developed by R. S. Brinkley, Jr. to calculate the thermodynamic properties of a nonideal heterogeneous system of known atomic composition containing gaseous, liquid, and solid phases. The thermodynamics is formulated with an arbitrary equation of state to make TIGER applicable to a wide variety of problems, and the most suitable equation of state available should be used to perform the calculations in a particular application.

The heterogeneous system is assumed to be in mechanical and thermal equilibrium, but not necessarily in chemical equilibrium. Since pressure and temperature are well defined in this case, the thermodynamic state of the mixture can be defined by the values of the state variables, pressure p, temperature T, volume V, entropy S, internal energy E, and by the mole numbers of the constituents. Other thermodynamic variables such as the enthalpy H and the Gibbs free energy G, can then be calculated with thermodynamic identities. The problem addressed by Tiger is that of computing the thermodynamic state when the gross composition and a complete equation of state of the mixture are known. An assumption about the attainment of chemical equilibrium and the specification of two independent state variables are required to solve this problem. Section I-B presents methods used to calculate the thermodynamic state when the composition is assumed to be in a state of chemical equilibrium and the pair of variables can be chosen from the following set: [(p,T), (p,h), (p,s), (v,T), (v,e), (p,v), and (v,s)], where h, s, v, and e denote the specific values of the enthalpy, entropy, volume, and internal energy.

Section I-C presents the extension of these methods to nonequilibrium systems that are partially frozen and partially in chemical equilibrium, and Section I-D presents the method used to calculate the thermodynamic state in systems that are completely frozen in metastable equilibrium.

Assumptions about the composition are required to calculate the thermodynamic state when kinetic processes are not treated explicitly. The assumptions used in TIGER are related implicitly to rate processes and cover a wide spectrum of chemical kinetics. As a consequence, the results based on them provide a means of modeling chemical kinetic processes with the TIGER code. When the system is assumed to be in chemical equilibrium, the composition is unknown and must be determined in the calculations of the thermodynamic state. The equilibrium composition is calculated with the equilibrium conditions and the stoichiometric conditions that express the conservation of mass for the system in terms of its molecular and atomic composition. When the system is assumed to be frozen, the composition must be chosen to satisfy the stoichiometric conditions; when it is assumed to be in partial equilibrium, the frozen composition is chosen and the remainder is calculated with the equilibrium and stoichiometric conditions as in the previous case.

2. Description of the Composition in Terms of Components

It is convenient for computational purposes to formulate a general method for describing the composition of a heterogeneous system in terms of its gross composition. The possible species that make up the system are restricted to a set chosen on the basis of chemical intuition and from the results of previous calculations. We will consider the set of t possible species, s gaseous and $(t - s)$ condensed, formed from c different chemical elements. These species will be distinguished with a constituent index i and the elements with an atomic index k. Thus, the gaseous constituents are labelled with $i = 1, \ldots, s$, the condensed constituents with $i = s + 1, \ldots, t$, and the elements with $k = 1, \ldots, c$. Condensed species are assumed to be present as pure phases to exclude the consideration of solid and liquid solutions. The initial composition in a mass of mixture M_0 is described by parameters specifying the gross composition of the system. The final composition obtained by computing the thermodynamic state of the system is defined by the mole numbers $n_i (i = 1, \ldots, s)$ of the gaseous constituents and by the mole numbers $n_i^* (i = s + 1, \ldots, t)$ of the condensed species. The phase rule imposes a restriction on the number of the variables n_i^* that may be nonzero. When all the n_i^* are zero, the system is homogeneous and consists of a gaseous phase only.

The parameters used to describe the gross composition of the mixture are related to the mole numbers of the constituents by the law of conservation of mass, and such a relationship is used in the computation of the mole numbers n_i and n_i^* to ensure that mass is conserved in our closed system. Since iterative procedures are in general necessary to compute the composition, it is important to express the conservation of mass relationship in terms of the most suitable representation of the gross composition for performing the iterations. It has been found from experience that calculation of n_i and n_i^* usually proceeds most readily when the gross composition is expressed in terms of the most abundant species in the system.

Let M_k and Q_k denote the mass and number of gram atoms of element k present in a mass M_0 of our mixture. Then M_0 and the c values of Q_k are related by the equation

$$M_0 = \sum_{k=1}^{c} Q_k M_k \qquad \text{(I-B-1)}$$

expressing the conservation of mass. The gross composition of the system can be described by using the c values of Q_k as extensive variables or the $c - 1$ values of their ratios as intensive variables. For two mixtures with the same gross composition, the Q_k's are proportional to each other and the proportionality constant is the ratio of the masses of the two systems. Although the Q_k's are the natural parameters for describing the gross composition of the mixture, they are usually unsuitable for computing n_i and $n_i{*}$ because the elements are present in small quantities in many systems of interest. It is therefore convenient to formulate a general method for describing the gross composition of the mixture so that the conservation of mass can be expressed in terms of the most abundant species in the system.

The gross composition of the mixture will be expressed in terms of its constituents, and the constituents sufficient for its description will be called the components of the system. An analytic criterion will be formulated for selecting a set of components. The criterion is based on the assumption that the number of components is equal to the number of elements c. The components will be distinguished with an index j and labelled accordingly with $j = 1, \ldots, c$.

Since the species are labelled as constituents with $i = 1,2, \ldots t$, and as components with $j = 1,2, \ldots, c$, the index $i = i{*}(j)$ is introduced to show that the species labelled as the j^{th} component is also labelled as the $i = i{*}(j)^{th}$ constituent.

It is convenient to rewrite molecular formulae so that each species in the system can be represented as a vector. The molecular formula of the constituent labelled i is thus written as

$$Y^i = X^1_{\alpha_{i1}} \ldots X^k_{\alpha_{ik}} \ldots X^c_{\alpha_{ic}} \qquad \text{(I-B-2)}$$

where X^k denotes the element labelled k, and α_{ik} denotes the number of atoms of element k present in a molecule of species i. A vector representation of each species is then readily obtained by defining the formula vector of the constituent labelled i as,

$$y_i = (\alpha_{i1}, \ldots, \alpha_{ic}) \qquad i = 1, \ldots, t \qquad \text{(I-B-3)}$$

Consider, for example, a system containing nitrogen, oxygen, carbon, and hydrogen, labelled with k = 1, 2, 3, and 4 as $X^1 = N$, $X^2 = O$, $X^3 = C$, and $X^4 = H$. Suppose that carbon dioxide is labelled with i = 3 and water with i = 4. Then writing Eq. (I-B-2) for these species gives

$$CO_2 \equiv Y^3 = N_0O_2C_1H_0$$

with

$$\alpha_{31} = 0$$
$$\alpha_{32} = 2$$
$$\alpha_{33} = 1$$
$$\alpha_{34} = 0$$

and

$$H_2O \equiv Y^4 = N_0O_1C_0H_2$$

with

$$\alpha_{41} = 0$$
$$\alpha_{42} = 1$$
$$\alpha_{43} = 0$$
$$\alpha_{44} = 2$$

and Eq. (I-B-3) gives their corresponding vector representations as $y_3 = (0,2,1,0)$ and $y_4 = (0,1,0,2)$.

A necessary and sufficient condition for the selection of a proper set of components is that the formula vectors of the constituents selected as components be linearly independent. This condition implies that the determinant $|\alpha_{i*(j)k}|$ of the formula vectors of these constituents is nonzero. Let q_j denote the number of moles of the j^{th} component in mass M_0 of the hypothetical system consisting of components only. Then the condition for the hypothetical system of components to have the same gross composition as the system of interest follows from the law of conservation of mass as

$$\sum_{j=1}^{c} \alpha_{i*(j)k} q_j = Q_k \qquad k = 1, 2, \ldots, c \qquad \text{(I-B-4)}$$

The quantities $q_j (j = 1, 2, \ldots, c)$ are called the stoichiometric constants of the system for a particular choice of components. They provide an alternative specification of the gross composition of the system to that provided by the Q_k.

A choice of components is generally not unique. The elements always constitute a proper set of components. And in the case that they are chosen as components, Eq. (I-B-4) becomes

$$\sum_{j=1}^{c} \delta_{jk} q_j = Q_k \qquad \text{(I-B-5)}$$

where δ_{jk} is the Kronecker delta having the property that $\delta_{jk} = 1$ when $j = k$, and $\delta_{jk} = 0$ when $j \neq k$. However, if the elements are present in small quantities, as is usually the case, it is more convenient to choose components from the more abundant species in the system.

We are now in a position to formulate the procedure used to describe the composition of the system in terms of components. The procedure is based on the fact that the formula vector of the i^{th} constituent can be expressed as a linear combination of the formula vectors of the components as follows:

$$y_i = \sum_{j=1}^{c} \beta_{ij} y_{i*(j)} \qquad (i = 1,2, \ldots, t) \qquad \text{(I-B-6)}$$

If the dissociated elements are taken to be the components, then Eq. (I-B-6) reduces to Eq. (I-B-3) and $\beta_{ij} = \alpha_{ij}$. The expressions in Eq. (I-B-6) are the vector representations of the chemical reactions producing the constituents from the components; the corresponding expressions in terms of molecular formulae can be written formally as

$$Y^i = \sum_{j=1}^{c} \beta_{ij} Y^{i*(j)} \qquad (i = 1,2, \ldots, t) \qquad \text{(I-B-7)}$$

The expressions in Eq. (I-B-6) contain an identity for each constituent selected as a component. Although the expressions in Eq. (I-B-7) can always be written by inspection, using the customary rules for balancing chemical equations, it is convenient to develop a method for constructing the β_{ij} matrix that can be used in the computer. The coefficients in the β_{ij} matrix will be calculated using the coefficients α_{ik} of the formula vectors of the constituents.

The combination of Eqs. (I-B-3) and (I-B-6) leads to the following matrix equation

$$(\alpha_{ik}) = (\beta_{ij})(\alpha_{i*(j)k}) \qquad \text{(I-B-8)}$$

where $\alpha_{i*(j)k}$ is the matrix formed from the formula vectors of the components. Since $\alpha_{i*(j)k}$ is by definition nonsingular, Eq. (I-B-8) can be inverted to give the equation

$$(\beta_{ij}) = (\alpha_{ik})(\tilde{\alpha}_{kj}) \qquad \text{(I-B-9)}$$

where $(\tilde{\alpha}_{kj})$ denotes the inverse matrix $(\alpha_{i*(j)k})^{-1}$. Equation (I-B-9) can be rewritten in terms of the coefficients as

$$\beta_{ij} = \sum_{k=1}^{c} \alpha_{ik} \tilde{\alpha}_{kj} \qquad ((I-B-10)$$

Since the matrix (α_{ik}) is known, Eq. (I-B-9) can be used to construct the matrix (β_{ij}) if a procedure is formulated for constructing the matrix $(\tilde{\alpha}_{kj})$. The matrix $(\tilde{\alpha}_{kj})$ is constructed by selecting an appropriate set of linearly independent formula vectors and inverting the corresponding $(\alpha_{i*(j)k})$ matrix. The $(\tilde{\alpha}_{kj})$ matrix is constructed from the (α_{ik}) matrix with a method suitable for electronic computers. The selection of components and the computation of the $(\tilde{\alpha}_{kj})$ matrix are carried out concurrently.

The rows of the (α_{ik}) matrix are added to an initially null $c \times c$ matrix one at a time. After each such addition the rows are tested for linear independence. Linearly independent rows define components and are retained, linearly dependent rows are rejected, and the process is continued until a $c \times c$ matrix is obtained. The test for linear independence is made by beginning the reduction of the matrix to triangular form (by operations on rows) with the first such addition and by continuing it with each subsequent addition. After triangularizing, a row is linearly independent if it contains a nonzero element on the diagonal or to the right of the diagonal. The nonzero element is placed on the diagonal, if necessary. by rearrangement of columns. The $c \times c$ matrix is used to construct the $(\tilde{\alpha}_{kj})$ matrix by back substitution.

The $(\alpha_{i*(j)k})$, (α_{ik}), and (β_{ij}) matrices for a system containing C, H, O, and N (with C, CO_2, H_2, and N_2 considered as components) are given below to exemplify the method used in the TIGER code to describe the composition of a thermodynamic system:

COMPONENTS

		ELEMENTS			
		C	H	O	N
$\alpha_{i*(j)k}$	k =	1	2	3	4
i*(j)					
C	1	1	0	0	0
CO_2	3	1	0	2	0
H_2	4	0	2	0	0
N_2	6	0	0	0	2

CONSTITUENTS

		ELEMENTS			
		C	H	O	N
α_{ik}	k =	1	2	3	4
	i				
C	1	1	0	0	0
CO	2	1	0	1	0
CO_2	3	1	0	2	0
H_2	4	0	2	0	0
H_2O	5	0	2	1	0
N_2	6	0	0	0	2
O_2	7	0	0	2	0
O	8	0	0	1	0
OH	9	0	1	1	0
H	10	0	1	0	0

			COMPONENTS			
			C	CO_2	H_2	N_2
	β_{ij}		j = 1	2	3	4
		i				
CONSTITUENTS	C	1	1	0	0	0
	CO	2	$\frac{1}{2}$	$\frac{1}{2}$	0	0
	CO_2	3	0	1	0	0
	H_2	4	0	0	1	0
	H_2O	5	$-\frac{1}{2}$	$\frac{1}{2}$	1	0
	N_2	6	0	0	0	1
	O_2	7	-1	1	0	0
	O	8	$-\frac{1}{2}$	$\frac{1}{2}$	0	0
	OH	9	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0
	H	10	0	0	$\frac{1}{2}$	0

3. Thermodynamic Description of Nonideal Heterogeneous Systems

Section I-B-3 presents the thermodynamic description of nonideal heterogeneous systems used in the TIGER code. Systems in mechanical and thermal equilibrium, with condensed phases considered as pure substances to exclude solid and liquid solutions, are treated under the assumption that an equation of state exists for each phase. The equations of state are restricted only by thermodynamic identities and stability conditions. This description is convenient to use in calculations of the thermodynamic state of such systems at one of the following points, (p,T), (p,h), (p,s), (v,T), (v,e), (v,p) or (v,s), when the composition is in chemical equilibrium, in partial equilibrium, or completely frozen in metastable equilibrium. In the treatment of partial equilibrium, part of the composition is prescribed to be frozen and the remainder is assumed to be in chemical equilibrium. Calculation of the state at a point involves calculating the composition and evaluating the other state variables with thermodynamic identities. As stated in Section I-B-2, the composition is restricted a priori to s gaseous species with mole numbers $n_i (i = 1,2, \ldots, s)$, $t - s$ condensed species with mole numbers $n_i^* \; (i = s + 1, \ldots, t)$, and must satisfy the stoichiometric conditions expressing the law of conservation of mass for the system.

Calculation of the state is easiest when the composition is completely frozen because the mole numbers can be chosen to satisfy the stoichiometric conditions. The calculations are more complicated for the equilibrium cases because the composition must satisfy the equilibrium conditions as well as the stoichiometric conditions. Since calculation of the equilibrium composition is based a priori on the assumption that some of the condensed species are present and the remainder are absent, the results of the calculation must be used to test if this assumption satisfies the equilibrium conditions for condensed species. To satisfy these equilibrium conditions, the mole number of a species i assumed to be present must satisfy the condition $n_i^* \geq 0$, and the chemical potential of a species assumed to be absent must exceed its chemical potential in the gaseous phase.

a. The Stoichiometric Conditions

The stoichiometric conditions expressing the conservation of mass for the system will be formulated by expressing the formula vectors of the constituents in terms of the formular vectors of the components. A set of components is first chosen, and the corresponding stoichiometric constants are evaluated. The system is then transformed into a system containing only these components by expressing the constitutents as linear combinations of them. The stoichiometric conditions are then obtained by equating the mole numbers of the components in the transformed system to their stoichiometric constants. Following this procedure with the notation introduced previously in Section I-B-2 gives the stoichiometric conditions as

$$\sum_{i=1}^{s} \beta_{ij} n_i + \sum_{i=s+1}^{t} \beta_{ij} n_i^* = q_j \qquad j = 1, 2, \ldots, c \tag{I-B-11}$$

It is convenient to introduce the index $i'(m)$, with $m = 1, 2, \ldots, t - s$, so that the condensed species labeled as m is also labeled as the $i = i'(m)^{th}$ constituent. It is also convenient to denote the mole numbers of the condensed species by N_m so that

$$n_{i'(m)}^* = N_m \qquad m = 1, 2, \ldots, t - s \tag{I-B-12}$$

The condensed constituents assumed to be present and in equilibrium with the gaseous phase will always be chosen as components as in the original version of the TIGER code formulated by R. S. Brinkley, Jr. It is necessary to set $i*(j) = i'(m)$, and $n_{i'(m)}^* = N_j$ for $m = j = 1, 2, \ldots, p$ to make the i' map compatible with the $i*$ map introduced previously for mapping components into constituents. The condensed species assumed to be frozen and not in chemical equilibrium with the gaseous phase will be labeled with $m = p + 1, \ldots, p'$, and the remainder that are assumed to be absent (but to satisfy the equilibrium conditions) will be labeled with $m = p' + 1, \ldots, t - s$. Thus the mole numbers of the condensed species are subject to the following restrictions: $N_m = N_j \geq 0$ for $m \equiv j = 1, 2, \ldots, p$; $N_m \geq 0$ for $m = p + 1, \ldots, p'$; and $N_m = 0$ for $m = p' + 1, \ldots, t - s$. The summation term over the condensed species in Eq. (I-B-11) can therefore be rewritten as

$$\sum_{i=s+1}^{t} \beta_{ij} n_i^* = \sum_{m=1}^{p} \delta_{mj} N_m + \sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m \qquad j = 1, \ldots, c \tag{I-B-13}$$

It is convenient for comparative purposes to write an equation similar to (I-B-13) for the gaseous summation term in Eq. (I-B-11), although the gaseous species will not be treated with this equation in the code. Assume that s' of the gaseous species are in equilibrium while the remaining $s - s'$ are frozen, and introduce the index $\hat{i}(g)$ with $g = 1, \ldots, s$ to indicate that the gaseous species labeled as g is also labeled as the $i = \hat{i}(g)^{th}$ constituent. The gaseous species assumed to be components will be labeled with $g = 1, \ldots, c - p$, those assumed to be in equilibrium with $g = c - p + 1, \ldots, s'$, and those assumed to be frozen with $g = s' + 1, \ldots, s$. As in the treatment of the condensed species, it is necessary to set $\hat{i}(g) = i*(g + p)$ for $g = 1, \ldots, c - p$ to make the $\hat{i}$ map compatible with the $i*$ map for identifying components as constituents. With this notation the summation term over the gaseous species in Eq. (I-B-11) can be rewritten as

$$\sum_{i=1}^{s} \beta_{ij} n_i = \sum_{g=1}^{c-p} \delta_{g+p,j} n_{\hat{i}(g)} + \sum_{g=c-p+1}^{s'} \beta_{\hat{i}(g)j} n_{\hat{i}(g)} + \sum_{g=s'+1}^{s} \beta_{\hat{i}(g)j} n_{\hat{i}(g)} \tag{I-B-14}$$

with

$$j = 1, \ldots, c$$

Since $m = 1, \ldots, p$ and $m = p' + 1, \ldots, t - s$ are used to label the condensed species assumed to be in chemical equilibrium, and $m = p + 1, \ldots, p'$ are used to label the condensed species assumed to be frozen, the condition for all the condensed species to be in equilibrium is $p' = p$, and the conditions for them all to be frozen are $p = 0$ and $p' = t - s$. Similarly, since $g = 1, \ldots, s'$ are used to label the gaseous species in chemical equilibrium and $g = s' + 1, \ldots, s$ are used to label the frozen species, the condition for all the gaseous species to be in equilibrium is $s = s'$, and the condition for them all to be frozen is $s' = 0$. Thus $p = p'$ and $s = s'$ when the composition of the heterogeneous system is in complete equilibrium, and $p = s' = 0$ and $p' = t - s$ when it is completely frozen. When $t = s$, no condensed species are present and the system is a homogeneous gas phase. Furthermore, when $t = s = s'$, the composition of the gaseous mixture is in chemical equilibrium, and when $t - s = s' = 0$, it is completely frozen.

In calculations of the thermodynamic state, the mole numbers of the equilibrium species are calculated using the stoichiometric conditions and the equilibrium conditions. The $c - p$ gaseous components are chosen first from the gaseous constituents assumed to be in equilibrium; they must include frozen species when $s' < c - p$, and must be chosen from the frozen species when $s' = 0$. It is convenient for computational purposes to combine Eqs. (I-B-11) and (I-B-13) and rewrite the stoichiometric conditions as

$$\sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m + \sum_{i=1}^{s} \beta_{ij} n_i + N_j = q_j \qquad j = 1, 2, \ldots, p \qquad \text{(I-B-15)}$$

$$\sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m + \sum_{i=1}^{s} \beta_{ij} n_i = q_j \qquad j = p + 1, \ldots, c \qquad \text{(I-B-16)}$$

These equations are generalizations of the stoichiometric conditions formulated by Brinkley for the case of equilibrium, and thus they reduce to the stoichiometric conditions presented in the original documentation of the TIGER code when $p = p'$ and the first summation term vanishes. For the homogeneous system when $p' = p = 0$, Eq. (I-B-15) vanishes and Eq. (I-C-16) reduces to the stoichiometric conditions for the gaseous phase.

Let n denote the total number of moles of gas in our mixture of mass M_0 so that

$$n = \sum_{i=1}^{s} n_i \qquad \text{(I-B-17)}$$

It is useful for computational purposes to have another expression for n and such a relationship can be obtained by combining Eqs. (I-B-16) and (I-B-17). Thus, summing Eq. (I-B-16) over j and subtracting the result from Eq. (I-B-17) leads to the equation

$$n = q_g + \sum_{i=1}^{s} (1 - \beta_i) n_i - \sum_{m=p+1}^{p'} \beta_{i'(m)} N_m \qquad \text{(I-B-18)}$$

where q_g, β_i, and $\beta_{i(m)}$ are defined by the equations,

$$q_g = \sum_{j=p+1}^{c} q_j \qquad \text{(I-B-19)}$$

$$\beta_i = \sum_{j=p+1}^{c} \beta_{ij} \qquad \text{(I-B-20)}$$

$$\beta_{i'(m)} = \sum_{j=p+1}^{c} \beta_{i'(m)j} \qquad \text{(I-B-21)}$$

It is also useful to define the reference mass M_0 of the mixture in terms of the components as

$$M_0 = \sum_{j=1}^{c} q_j M_j \qquad \text{(I-B-22)}$$

where M_j is the molecular mass of the j^{th} component, and to normalize the system by choosing M_0 as 100 grams. Then the mass balance equation for the normalized system is

$$100 = \sum_{j=1}^{c} (100\, q_j/M_0) M_j \qquad \text{(I-B-23)}$$

and the corresponding stoichiometric coefficients are

$$q_j' = 100\, q_j/M_0 \qquad \text{(I-B-24)}$$

Thus, the equations for the normalized system are obtained from those for the reference system of mass M_0 by replacing q_J by $100\, q_J/M_0$.

If we consider the decomposition products of TNT, $C_7H_5O_6N_3$, as an example and choose C, CO, H_2, and N_2 as components according to the reaction

$$C_7H_5O_6N_3 \rightarrow C + 6\, CO + 5/2\, H_2 + 3/2\, N_2$$

then the normalized stoichiometric coefficients are $q'_c = 100/M$, $q'_{CO} = 600/M$, $q'_{H_2} = 250/M$, and $q'_{N_2} = 150/M$, where $M = 228.18$ is the molecular weight of TNT.

b. Equations of State

The gas phase is treated with an equation of state of the form,

$$p = p(\rho, T, n_1, \ldots, n_s) \qquad \text{(I-B-25)}$$

expressing the pressure as an explicit function of the gas density ρ, the temperature, and the mole numbers of the gaseous constituents. It is convenient to introduce the variable $\hat{\rho}$ through the identity

$$\frac{\hat{\rho}}{M_0} = \frac{\rho}{M_g} \qquad \text{(I-B-26)}$$

so that $1/\hat{\rho}$ is the volume of gas per unit mass of mixture, and $\rho = \hat{\rho}$ when $M_g = M_0$ and no condensed species are present. Equation (I-B-25) is then written more explicitly as

$$p = \frac{nRT}{M_0} \hat{\rho}\Phi(\hat{\rho}, T, n_1, \ldots, n_s) \qquad \text{(I-B-27)}$$

with Φ an imperfection term that approaches 1 as the gaseous mixture becomes ideal.

The chemical potential μ_i of the i^{th} gaseous constituent is written as

$$\mu_i/RT = \mu_i^o/RT + \xi_i + \Gamma_i + \pi_{c+1} \qquad i = 1, \ldots, s \qquad \text{(I-B-28)}$$

where $\mu_i^o = \mu_i^o(T)$ is the chemical potential of the i^{th} gaseous constituent in its standard state at unit pressure, and ξ_i, π_{c+1}, and Γ_i are defined by the equations

$$\xi_i = \ln n_i \qquad \text{(I-B-29)}$$

$$\pi_{c+1} = \ln (RT\hat{\rho}/M_o) \qquad \text{(I-B-30)}$$

$$\Gamma_i = \int_o^{\hat{\rho}} \left[\frac{M_o}{RT\hat{\rho}} \left(\frac{\partial p}{\partial n_i} \right) - 1 \right] \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-B-31)}$$

with the integration performed along an isotherm. The imperfection term Γ_i can be considered as the logarithm of an activity coefficient and can be written in terms of Φ as

$$\Gamma_i = \int_o^{\hat{\rho}} \left[\Phi + n \frac{\partial \Phi}{\partial n_i} - 1 \right] \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-B-32)}$$

The thermodynamic identity

$$\frac{d}{d \ln T} \left(\frac{\mu^o i}{RT} \right) = - \frac{H_i^o}{RT} \equiv - \chi_i^o \qquad i = 1, \ldots, s \qquad \text{(I-B-33)}$$

is used to introduce the molar enthalpy H_i^o and the reduced molar enthalpy χ_i^o of the i^{th} gaseous constituent in its standard state.

The condensed species are treated with equations of state of the form

$$V_i^* = V_i^*(T,p) \qquad i = s+1, \ldots, t \qquad \text{(I-B-34a)}$$

$$H_i^* = H_i^*(T,p) \qquad \text{(I-B-34b)}$$

where V_i^* and H_i^* denote the molar volume and molar enthalpy of the i^{th} condensed constituent. It is convenient to label these molar quantities with the index m introduced earlier for condensed species, so that

$$V_{i'(m)}^* = V_m^* \qquad m = 1, \ldots, t-s \qquad \text{(I-B-35a)}$$

$$H_{i'(m)}^* = H_m^* \qquad \text{(I-B-35b)}$$

and $i'(m) = i^*(j)$ for $m = j = 1,2, \ldots, p$. Use will be made of the derivatives

$$\alpha_m^*(T,p) = \left(\frac{\partial \ln V_m^*}{\partial \ln T}\right)_p \qquad \text{(I-B-36a)}$$

$$\beta_m^*(T,p) = \left(\frac{\partial \ln V_m^*}{\partial \ln p}\right)_T \qquad \text{(I-B-36b)}$$

and

$$\left(\frac{\partial H_m^*}{\partial T}\right)_p = C_{pm}^* \qquad \text{(I-B-37a)}$$

$$\left(\frac{\partial H_m^*}{\partial p}\right)_T = V_m^*(1 - \alpha_m^*) \qquad \text{(I-B-37b)}$$

The derivative α_m^* is related to the coefficient of thermal expansion at constant pressure and β_m^* to the coefficient of compression at constant temperature of the m^{th} condensed species; C_{pm}^* is the corresponding constant pressure molar heat capacity.

The chemical potentials of the condensed species, in contrast to the chemical potentials of the gaseous species, are functions only of temperature and pressure and will be written as either

$$\hat{\mu}_i = \hat{\mu}_i(T,p) \qquad i = s + 1, \ldots, t \qquad \text{(I-B-38)}$$

or

$$\mu^*_m = \mu^*_m(T,p) \qquad m = 1, \ldots, t - s \qquad \text{(I-B-39)}$$

with $i'(m) = i^*(j)$ and $\hat{\mu}_{i'(m)} = \mu^*_m$ for $m = j = 1, \ldots, p$. The chemical potentials of these species in the gaseous phase are denoted by μ_i with $i = s + 1, \ldots, t$. It is important to note that the index i on the gaseous potential μ_i has the range $i = 1, \ldots, t$ and covers all the constituents, even though the species labeled with $i = s + 1, \ldots, t$ are assumed <u>a priori</u> to be condensed constituents. It is convenient for computational purposes to define the reduced molar volume φ^*_m and the reduced molar enthalpy χ^*_m of the condensed species with the thermodynamic identities

$$p \frac{\partial}{\partial p}\left(\frac{\mu^*_m(p,T)}{RT}\right) = \frac{pV^*_m}{RT} \equiv \varphi^*_m \qquad \text{(I-B-40)}$$

and

$$T \frac{\partial}{\partial T}\left(\frac{\mu^*_m(p,T)}{RT}\right) = -\frac{H^*_m}{RT} \equiv -\chi^*_m \qquad \text{(I-B-41)}$$

Equations (I-B-26), (I-B-40), and (I-B-41) are used to obtain a convenient expression for the specific volume of the mixture. The volume V of the mixture is written as the sum of the volumes of the phases as

$$V = M_0/\hat{\rho} + \sum_{j=1}^{p} N_j V^*_j + \sum_{m=p+1}^{p'} N_m V^*_m \qquad \text{(I-B-42)}$$

by remembering that $m = j$ for $m = 1, \ldots, p$. The equation for the specific volume is obtained as

$$v = 1/\hat{\rho} + \frac{RT}{M_0 p}\left(\sum_{j=1}^{p} N_j \varphi_j + \sum_{m=p+1}^{p'} N_m \varphi^*_m\right) \qquad \text{(I-B-43)}$$

by dividing Eq. (I-B-42) by M_0.

4. Calculation of the Equilibrium Composition

a. Equilibrium Conditions and Iteration Parameters

It is convenient to consider the case of complete equilibrium when $p = p'$, $s = s'$, and the mixture contains no frozen constituents. Then equilibrium conditions must be formulated for the s gaseous constituents, for the p condensed constituents assumed to be present, and for the remaining $t - (s + p)$ condensed constituents assumed to be absent. Use will be made of the fact that the chemical potentials of the species in equilibrium satisfy the same equations as their formula vectors. Equation (I-B-6) is thus used to express the formula vectors of the constituents as linear combinations of the formula vectors of the components. The equations for the formula vectors are written as

$$y_i = \sum_{j=1}^{p} \beta_{ij} y_{i*(j)} + \sum_{j=p+1}^{c} \beta_{ij} y_{i*(j)} \qquad i = 1, \ldots, t \qquad \text{(I-B-44)}$$

because the p condensed constituents assumed to be present must be chosen as components. Replacing $y_{i*(j)}$ by $\mu_{i*(j)}$ in Eq. (I-B-44) and taking account of Eqs. (I-B-38) and (I-B-39) leads to the equation

$$\mu_i = \sum_{j=1}^{p} \beta_{ij} \mu_j^* + \sum_{j=p+1}^{c} \beta_{ij} \mu_{i*(j)} \qquad i = 1, \ldots, t \qquad \text{(I-B-45)}$$

Equation (I-B-45) expresses the chemical potential of each constituent in the gaseous phase in terms of the chemical potentials of the condensed and gaseous components. Thus for $i = 1, \ldots, s$ it is an expression for the gaseous constituents, but for $i = s + 1, \ldots, t$ it is an expression for the gaseous species assumed *a priori* to be condensed constituents.

Equation (I-B-45) contains c identities for the values of $i = i^*(j)$ labelling the constituents chosen as components. Introducing

$j' = 1, \ldots, c$ as a dummy component index so that $\beta_{i*(j')j} = \delta_{j'j}$, and setting $i = i*(j')$ in Eq. (I-B-45) gives these identities as

$$\mu_i = \mu_{i*(j)} = \mu_j^* \qquad j = 1, \ldots, p \qquad \text{(I-B-46a)}$$

$$\mu_i = \mu_{i*(j)} \qquad j = p + 1, \ldots, c \qquad \text{(I-B-46b)}$$

Whereas Eq. (I-B-46a) is the condition for a condensed constituent that is present to be in equilibrium with the gaseous phase, Eq. (I-B-46b) is an identity specifying the gaseous constituents chosen as components. We must now consider the condensed constituents assumed to be absent with $i \in s + 1, \ldots, t$ and $i = i*(m)$, $m = p + 1, \ldots, t - s$. The equilibrium condition for each of these species is that its chemical potential in the condensed phase must be greater than its chemical potential in the gaseous phase. Gibbs' conditions for chemical equilibrium in the heterogeneous mixture can thus be written as

$$\mu_i = \sum_{j=1}^{p} \beta_{ij}\mu_j^* + \sum_{j=p+1}^{c} \beta_{ij}\mu_{i*(j)} \qquad i = 1, \ldots, s \qquad \text{(I-B-47a)}$$

$$\mu_{i*(j)} = \mu_j^* \qquad j = 1, \ldots, p \qquad \text{(I-B-47b)}$$

$$\mu_{i'(m)} = \sum_{j=1}^{p} \beta_{i'(m)j}\mu_j^* + \sum_{j=p+1}^{c} \beta_{i'(m)j}\mu_{i*(j)} < \mu_m^*$$

$$\text{for} \qquad m = p + 1, \ldots, t - s \qquad \text{(I-B-47c)}$$

Thus the gaseous constituents in an equilibrium mixture must satisfy Eq. (I-B-47a), the condensed constituents assumed *a priori* to be present must satisfy Eq. (I-B-47b), and those assumed to be absent must satisfy Eq. (I-B-47c).

When a complete equation of state of the mixture is known, Eqs. (I-B-47) and the stoichiometric conditions obtained by setting $p = p'$ in Eqs. (I-B-15) and (I-B-16) are sufficient for calculating the equilibrium composition at any one of the following specified points (p, T), (p, h), (p, s), (v, T), (v, e), (v, p), or (v, s). Since μ_i is known as a function of the n_i's, the $s - c + p$ independent equilibrium conditions together with the c stoichiometric conditions constitute a set of $s + p$ equations for calculating the $s + p$ unknown mole numbers $n_i (i + 1, \ldots, s)$ and $N_j (j = 1, \ldots, p)$. The computed compositions must be checked, however, to test the validity of the a priori assumptions that had to be made about the presence $(N_j \geq 0$ for $j = 1, \ldots, p)$ and the absence $(N_m = 0$ for $m = p + 1, \ldots, t - s)$ of condensed constituents. The assumptions are valid when the calculated composition satisfies the condition $N_j \geq 0$ and Eq. (I-B-47c), and they are invalid when the calculated composition does not satisfy these conditions. In the latter case, the assumptions must be changed and the composition must be recalculated until $N_j \geq 0$ and Eq. (I-B-47c) is satisfied.

The equations used in the TIGER code to compute the equilibrium composition will now be derived. The first step is to obtain an expression for the equilibrium conditions of the gaseous species in terms of their mole numbers. Thus substituting μ_i and $\mu_{i*(j)}$ given by Eq. (I-B-28) into Eq. (I-B-47a) and making use of Eq. (I-B-30) leads to the following equation for $\xi_i = \ln n_i (i = 1, \ldots, s)$,

$$\xi_i = - g_i - \Gamma_i + \sum_{j=1}^{p} \beta_{ij} \mu_j^* / RT + \sum_{j=p+1}^{c} \beta_{ij} \pi_j + (\beta_i - 1) \pi_{c+1} \qquad \text{(I-B-48)}$$

where

$$g_i = \mu_i^0 / RT - \sum_{j=p+1}^{c} \beta_{ij} \mu_{i*(j)}^0 / RT \qquad \text{(I-B-49)}$$

and

$$\pi_j = \xi_{i*(j)} + \Gamma_{i*(j)} \qquad j = p + 1, \ldots, c \qquad \text{(I-B-50)}$$

Equation (I-B-48) reduces to Eq. (I-B-50) for the gaseous constituents chosen as components because $\beta_{i*(j')j} = \delta_{jj'}$, $g_i = 0$, and $\beta_i = 1$ for $i = i*(j')(j' = p + 1, \ldots, c)$. The next step is to express the inequalities of Eq. (I-B-47c) in terms of the mole numbers of the gaseous species. The combination of Eq. (I-B-28) and (I-B-47c) leads to the expression

$$-g^*_m + \sum_{j=1}^{p}\beta_{i'(m)j}\mu^*_j + \sum_{j=p+1}^{c}\beta_{i'(m)j}\tau_j + \beta_{i'(m)}\tau_{c+1} < 0 \qquad \text{(I-B-51)}$$

$$\text{for} \qquad m = p + 1, \ldots, t - s$$

where

$$g^*_m = \mu^*_m/RT - \sum_{j=p+1}^{c}\beta_{i'(m)j}\mu^\circ_{i*(j)}/RT \qquad \text{(I-B-52)}$$

It is now convenient to simplify Eqs. (I-B-48) and (I-B-51) by introducing the parameters

$$\tau_j = \mu^*_j/RT \qquad j = 1, \ldots, p \qquad \text{(I-B-53)}$$

and

$$\beta_{i,c+1} = \beta_i - 1 \qquad \text{(I-B-54)}$$

For notational convenience, the index j used for the τ parameters will be extended from c to $c + 2$ so that Eq. (I-B-48) can be written as

$$\xi_i = -g_i - \Gamma_i + \sum_{j=1}^{c+1}\beta_{ij}\tau_j \qquad i = 1, \ldots, s \qquad \text{(I-B-55)}$$

and Eq. (I-B-51) can be written as

$$-g^*_m + \sum_{j=1}^{c+1}\beta_{i'(m)j}\tau_j + \tau_{c+1} < 0 \qquad m = p + 1, \ldots, t - s \qquad \text{(I-B-56)}$$

Other equations needed to compute the equilibrium composition are the stoichiometric conditions

$$\sum_{i=1}^{s} \beta_{ij} n_i + N_j = q_j \qquad j = 1, \ldots, p \qquad \text{(I-B-57)}$$

$$\sum_{i=1}^{s} \beta_{ij} n_i = q_j \qquad j = p + 1, \ldots, c \qquad \text{(I-B-58)}$$

obtained by setting $p = p'$ in Eqs. (I-B-15) and (I-B-16).

Equations (I-B-53), (I-B-55), (I-B-57), and (I-B-58) can be used to compute the equilibrium composition with a set of condensed components specified a priori by the assumption about the presence of condensed constituents, and then Eq. (I-B-56) can be used to test whether this assumption is valid. It is convenient to define π_{c+2} by the equation

$$\pi_{c+2} = \ln T \qquad \text{(I-B-59)}$$

For fixed values of π_{c+1} and π_{c+2}, Eqs. (I-B-53), (I-B-55), (I-B-57), and (I-B-58) constitute $(c + p + s)$ equations for the $(c + p + s)$ unknown quantities $\pi_j (j = 1, \ldots, c)$, $N_j (j = 1, \ldots, p)$, and $n_i (i = 1, \ldots, s)$. Equations (I-B-53), (I-B-55), and (I-B-58) can be used to determine the $c + s$ values of π_j and n_i, however, because N_j appears only in Eq. (I-B-57). Solving the former equations thus determines the composition of the gas phase at fixed temperature and density, provided that the condensed species assumed to be present satisfy the inequalities $N_j \geq 0 \; (j = 1, \ldots, p)$. And solving the latter equation for the N_j's with the calculated gaseous composition determines the composition of the condensed phases. According to Brinkley, this method of treating the equilibrium problem in terms of gaseous and condensed components is consistent with the Gibbs Phase Rule.

An iterative procedure is required for the simultaneous solution of the equilibrium and stoichiometric conditions because Eq. (I-B-58) is linear in the mole numbers of the gaseous species, but Eq. (I-B-55) is transcendental in these mole numbers and their logarithms. The η parameters are considered as independent variables in Brinkley's iterative procedure for solving the equilibrium problem at a specified point. It should be remembered that the index j originally introduced for components has the range $j = 1, \ldots, c + 2$ when used for the π parameters. That the $\pi_j (j = 1, \ldots, c + 2)$ parameters can be chosen as independent variables follows from the equations presented earlier in this volume. Specifically, Eq. (I-B-55) can be rewritten as

$$\xi_i + \Gamma_i = G_i(\pi_1, \ldots, \pi_{c+2}) \qquad \text{(I-B-60)}$$

with

$$G_i = -g_i + \sum_{j=1}^{c+1} \beta_{ij} \pi_j \qquad \text{(I-B-61)}$$

because g_i defined by Eq. (I-B-49) is a function of temperature only, and $\ln T = \pi_{c+2}$. Equation (I-B-60) can then be regarded as an expression

$$n_i = n_i(\pi_1, \ldots, \pi_{c+2}) \qquad \text{(I-B-62)}$$

defining the mole numbers of the gaseous species as implicit functions of the π_j because $\xi_i = \ln n_i$ and Γ_i is an explicit function of $\hat{\rho}$, T, and n_i,

$$\Gamma_i = \Gamma_i(n_1, \ldots, n_s, \pi_{c+1}, \pi_{c+2}) \qquad \text{(I-B-63)}$$

It follows from Eq. (I-B-62) that Eq. (I-B-57) can be regarded as an expression

$$N_j = N_j(\pi_1, \ldots, \pi_{c+2}) \qquad \text{(I-B-64)}$$

defining the mole numbers of the condensed species as implicit functions of the τ_j parameters.

Brinkley's approach to the equilibrium problem was to construct a set of $c + 2$ equations

$$F_j(\tau_1, \ldots, \tau_{c+2}) = 0 \qquad j = 1, \ldots, c + 2 \qquad \text{(I-B-65)}$$

so that the set of τ_j satisfying these equations defines the equilibrium composition. This set of τ_j that satisfies Eqs. (I-B-65) will be called the set of equilibrium values of τ_j. It is convenient to write the iterative equations used to solve (I-B-65) for the equilibrium values of τ_j with the Newton-Raphson technique as

$$\sum_{k=1}^{c+2} - \frac{\partial F_j}{\partial \tau_k}\left(\tau_1^i, \ldots, \tau_{c+2}^i\right)\Delta\tau_k = F_j(\tau_1^i, \ldots, \tau_{c+2}^i) \qquad \text{(I-B-66)}$$

where $\Delta\tau_k = \tau_k^{i+1} - \tau_k^i$ and τ_k^i is the i^{th} approximation to the equilibrium value of τ_k. It should be noted that the index k introduced originally for atoms is also being used as a dummy index for the iteration parameters in order to simplify the notation in the remainder of the documentation. The partial derivatives $\partial F_j/\partial\tau_k$ must be known as explicit functions of the τ_k parameters in order to generate a solution to Eqs. (I-B-65) with (I-B-66). This being the case, an initial approximation to the solution $(\tau_1^1, \ldots, \tau_{c+2}^1)$ is used to generate a second approximate solution $(\tau_1^2, \ldots, \tau_{c+2}^2)$ with (I-B-66), and the procedure is continued until preassigned conditions for convergence to the solution are satisfied. The conditions used to test for convergence in the present version of the code are $\sum_{j=1}^{p} F_j^2/p < \epsilon_1$, $\sum_{j=p+1}^{c} F_j^2/(c - p) \le \epsilon_2$, $F_{c+1}^2 < \epsilon_3$, and $F_{c+2}^2 \le \epsilon_4$ where ϵ_1, ϵ_2, ϵ_3, and ϵ_4 are preassigned small numbers. The Eqs. (I-B-53) and (I-B-58) were chosen to define c of the expressions in (I-B-65) as

$$F_j = \mu_j^*/RT - \pi_j = 0 \qquad j = 1, \ldots, p \qquad \text{(I-B-67)}$$

$$F_j = q_j - \sum_{i=1}^{s} \beta_{ij} n_i = 0 \qquad j = p + 1, \ldots, c \qquad \text{(I-B-68)}$$

and the remaining two equations

$$\begin{aligned} F_{c+1} &= 0 \\ F_{c+2} &= 0 \end{aligned} \qquad \text{(I-B-69)}$$

were used to define the constraints imposed by specifying the two independent state variables at the thermodynamic point of interest. The different expressions for F_{c+1} and F_{c+2} for the seven different point calculations considered earlier will be presented later. A double iterative scheme is required to solve Eqs. (I-B-67) and (I-B-68) for the equilibrium values of π_j because Eq. (I-B-60) must be solved for n_i in order to evaluate the F_j's and the partial derivatives

$$\frac{\partial F_j}{\partial \pi_k} = - \sum_{i=1}^{s} \beta_{ij} \frac{\partial \xi_i}{\partial \pi_k} n_i \qquad j = p + 1, \ldots, c \qquad \text{(I-B-70)}$$

obtained from the stoichiometric conditions expressed by (I-B-68).

The equilibrium values of π_j are determined in an outer iteration with Eqs. (I-B-67) to (I-B-69), using values of n_i calculated in an inner iteration with Eq. (I-B-60) and the Newton-Raphson technique. The equations in (I-B-60) were rewritten as

$$W_i(\xi_1, \ldots, \xi_s) = - \xi_i - \Gamma_i + G_i(\pi_1, \ldots, \pi_{c+2}) = 0 \qquad \text{(I-B-71)}$$

$$i = 1, \ldots, s$$

and solved for $\xi_i = \ln n_i$ to determine the mole numbers corresponding to a fixed set of the γ_j parameters in the inner iteration. The iterative equations used to solve (I-B-71) were written similarly to those used to solve (I-B-65) as

$$\sum_{r=1}^{s} - \frac{\partial W_i}{\partial \xi_r}(\xi_1^k, \ldots, \xi_s^k)\Delta\xi_r = W_i(\xi_1^k, \ldots, \xi_s^k) \qquad i = 1, \ldots, s \qquad \text{(I-B-72)}$$

with

$$\begin{aligned} \frac{\partial W_i}{\partial \xi_r} &= - \delta_{ir} - \left(\frac{\partial \Gamma_i}{\partial n_r}\right) n_r \\ \frac{\partial \Gamma_i}{\partial n_r} &= \int_0^{\hat{\rho}} \frac{M_0}{RT\hat{\rho}} \left(\frac{\partial^2 p}{\partial n_i \partial n_r}\right) \frac{d\hat{\rho}}{\hat{\rho}} \end{aligned} \qquad \text{(I-B-73)}$$

$\Delta\xi_r = \xi_r^{k+1} - \xi_r^k$, and ξ_r^k the k^{th} approximation to ξ_r.

When the equilibrium composition of the gaseous phase has been determined, the mole numbers of the condensed phases are calculated with Eq. (I-B-57), and Eq. (I-B-56) is used to test the validity of the *a priori* assumption about the condensed phases that is required to perform the equilibrium calculation. When the equilibrium composition of the mixture is known, the thermodynamic state at a specified point is computed with thermodynamic identities.

b. State Equations

The equations will now be presented for computing the thermodynamic state in the seven different point calculations after the equilibrium composition has been determined. The pressure p, the specific volume v, the specific enthalpy h, the specific Gibbs free energy g, the specific internal energy e, the specific entropy s, and their derivatives will all be regarded as implicit functions of the iteration parameters $(\eta_1, \ldots, \eta_{c+2})$. The partial derivatives of these variables with respect to η_j that are used in the iterations will be presented later.

The equation for the pressure is written as

$$p = \frac{nRT\hat{\rho}}{M_0} \Phi(\eta_1, \ldots, \eta_{c+2}) \qquad \text{(I-B-74)}$$

with Φ regarded as an implicit function of the iteration parameters instead of an explicit function $\Phi = \Phi(\hat{\rho}, T, n_1, \ldots, n_s)$ specified by the equation of state of the gaseous mixture. The equation for the specific volume of the equilibrium mixture is obtained by setting $p = p'$ in Eq. (I-B-42) as

$$v(\eta_1, \ldots, \eta_{c+2}) = 1/\hat{\rho} + 1/M_0 \left(\sum_{j=1}^{p} N_j V_j^* \right) \qquad \text{(I-B-75)}$$

The specific enthalpy h of the mixture is given by the expression,

$$M_0 h = \sum_{j=1}^{p} N_j H_j^* + \sum_{i=1}^{s} n_i H_i^\circ + pM_0/\hat{\rho} + RT(\epsilon - n) \qquad \text{(I-B-76)}$$

with the imperfection term ϵ defined by the following integral along an isotherm

$$\epsilon = \int_0^{\hat{\rho}} \frac{M_0}{RT\hat{\rho}} \left[p - T \frac{\partial p}{\partial T} \right] \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-B-77)}$$

Another expression for $h(\eta_1, \ldots, \eta_{c+2})$ with $\beta_{i,c+2} = X_i^\circ - \sum_{j=p+1}^{c} \beta_{ij} X_{i*(j)}^\circ$ is obtained as

$$M_0 h = \sum_{j=1}^{p} N_j H_j^* + \sum_{j=p+1}^{c} q_j H_{i*(j)}^\circ + RT \sum_{i=1}^{s} \beta_{i,c+2} n_i + pM_0/\hat{\rho} + RT(\epsilon - n) \qquad \text{(I-B-78)}$$

by multiplying Eq. (I-B-58) by $H_{i*(j)}^\circ$ and adding the resulting expression to Eq. (I-B-76). The frozen heat capacity of the mixture is given by the equation

$$c_f = \sum_{j=1}^{p} N_j C^*_{pj} + \sum_{j=p+1}^{c} q_j C^\circ_{pi*(j)} + \sum_{i=1}^{s} (\Delta_i C^\circ_p) n_i + R(\epsilon'_T - n) \qquad \text{(I-B-79)}$$

where $C^\circ_{pi} = dH^\circ_i/dT$ is the molar constant pressure heat capacity of the i^{th} gaseous constituent in its standard state,

$$\Delta_i C^\circ_p = C^\circ_{pi} - \sum_{j=p+1}^{c} \beta_{ij} C^\circ_{pi*(j)} \qquad \text{(I-B-80)}$$

and

$$\epsilon'_T = - \int_0^{\rho} \frac{M_0}{R\hat{\rho}} T \frac{\partial^2 p}{\partial T^2} \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-B-81)}$$

The quantity $R\epsilon'_T$ is the contribution to the constant volume heat capacity of a mixture of weight M_0 resulting from gas phase imperfections.

Summing the Gibbs free energy of the condensed and gaseous phases gives the equation for the specific Gibbs free energy of the mixture as

$$M_0 g = \sum_{j=1}^{p} N_j \mu^*_j + \sum_{i=1}^{s} n_i \mu_i \qquad \text{(I-B-82)}$$

An alternative expression for g in terms of the stoichiometric constant q_j is obtained as

$$M_0 g = \sum_{j=1}^{p} q_j \mu^*_j + \sum_{j=p+1}^{c} q_j \mu_{i*(j)} + \sum_{i=1}^{s} n_i \left[\mu_i - \sum_{j=1}^{p} \beta_{ij} \mu^*_j - \sum_{j=p+1}^{c} \beta_{ij} \mu_{i*(j)} \right] \qquad \text{(I-B-83)}$$

by multiplying Eq. (I-B-57) by μ^*_j and Eq. (I-B-58) by $\mu_{i*(j)}$ and adding the resulting expression to Eq. (I-B-82). Combining Gibbs' condition for chemical equilibrium Eq. (I-B-47a) with Eq. (I-B-83) gives the free energy of the equilibrium mixture as

$$M_0 g = \sum_{j=1}^{p} q_j \mu^*_j + \sum_{j=p+1}^{c} q_j \mu_{i*(j)} \qquad \text{(I-B-84)}$$

since the bracketed term in Eq. (I-B-83) vanishes. Combining Eq. (I-B-84) with Eqs. (I-B-28), (I-B-50), and (I-B-53) gives the equation for $g(\pi_1, \ldots, \pi_{c+2})$ in terms of π as

$$M_0 g/RT = \sum_{j=1}^{c} q_j \pi_j + \sum_{j=p+1}^{c} q_j \pi_{c+1} + \sum_{j=p+1}^{c} q_j \mu^0_{i*(j)}/RT \qquad \text{(I-B-85)}$$

The specific internal energy of the mixture is calculated with the thermodynamic identity

$$e(\pi_1, \ldots, \pi_{c+2}) = h - pv \qquad \text{(I-B-86)}$$

and specific entropy is calculated with the identity

$$s(\pi_1, \ldots, \pi_{c+2}) = (h - g)/T \qquad \text{(I-B-87)}$$

c. State Conditions

The state conditions expressed in Eq. (I-B-69) by $F_{c+1} = F_{c+2} = 0$ define which one of the seven pairs of state variables (p_0, T_0), (p_0, h_0), (p_0, s_0), (p_0, v_0), (v_0, T_0), (v_0, e_0), or (v_0, s_0) is specified at the thermodynamic point of interest. The case when the pressure p_0 is specified will be considered before the case when the specific volume v_0 is specified.

When the pressure of the system is specified as p_0, F_{c+1} is defined by the equation

$$F_{c+1} = \ln p_0 - \ln p = 0 \qquad \text{(I-B-88)}$$

and p is calculated with the gas phase equation of state. At (p_0, T_0) points, the condition π_{c+2} = constant is used to specific that $T = T_0$

and consequently the equation $F_{c+2} = 0$ is not required. The iteration procedure used to calculate the equilibrium composition is simplified because the rank of the Newton-Raphson matrix is reduced to $c + 1$ and the condition $\eta^{i+1}_{c+2} - \eta^{i}_{c+2} = 0$ is imposed at each iteration. At (p_0,h_0) and (p_0,s_0) points, F_{c+2} is defined, respectively, by the equations,

$$F_{c+2} = M_0(h_0 - h)/RT = 0 \tag{I-B-89}$$

and

$$F_{c+2} = M_0(s_0 - (h - g)/T)R = 0 \tag{I-B-90}$$

where h is evaluated with Eq. (I-B-78) and $p = p_0$. and g is evaluated with Eq. (I-B-85). At (p_0,v_0) points F_{c+2} is defined by the equation

$$F_{c+2} = p_0M_0(v_0 - v)/RT = 0 \tag{I-B-91}$$

and v is evaluated with Eq. (I-B-75).

When the specific volume v_0 is specified and the pressure is not, then F_{c+1} is defined by the equation

$$F_{c+1} = pM_0(v_0 - v)/RT = 0 \tag{I-B-92}$$

and v is evaluated with Eq. (I-B-75). At a (v_0,T_0) point, the temperature T_0 is specified in the same way as for the (p_0,T_0) point. At (v_0,e_0) and (v_0,s_0) points, F_{c+2} is defined respectively by the equations

$$F_{c+2} = M_0(e_0 - h + pv_0)/RT = 0 \tag{I-B-93}$$

and

$$F_{c+2} = M_0(s_0 - (h - g)/T)R = 0 \tag{I-B-94}$$

where h is evaluated with Eq. (I-B-78) and g is evaluated with Eq. (I-B-85).

d. Partial Derivatives with Respect to the Iteration Parameters

It is convenient for notational purposes to expand the expressions (I-B-65) in a linear Taylor series about an approximation $(\eta_1^o, \ldots, \eta_{c+2}^o)$ to the solution $(\eta_1, \ldots, \eta_{c+2})$ and write

$$\sum_{k=1}^{c+2} D_{jk}^o \Delta_k = F_j^o \qquad j = 1, \ldots, c + 2 \qquad \text{(I-B-95)}$$

with $D_{jk} = - \partial F_j / \partial \eta_k$, $\Delta_k = \eta_k - \eta_k^o$, and the superscript ^{o} used to denote that the quantity so designated is evaluated at the approximation to the state of the system. The equations for the partial derivatives of the state variables, obtained in the expressions for D_{jk} by differentiating F_j partially with respect to η_k according to the chain rule, will be presented before the expressions for D_{jk}.

(1) Partial Derivatives of the Mole Numbers

Equations for the partial derivatives of the mole numbers with respect to the iteration parameters are derived with Eq. (I-B-29) and (I-B-55). Differentiating Eqs. (I-B-29) and (I-B-55) with respect to η_k gives the equations

$$\frac{\partial n_i}{\partial \eta_k} = n_i \frac{\partial \xi_i}{\partial \eta_k} \qquad \text{(I-B-96)}$$

and

$$\frac{\partial \xi_i}{\partial \eta_k} = - \frac{\partial \Gamma_i}{\partial \hat{\rho}} \frac{\partial \hat{\rho}}{\partial \eta_k} - \frac{\partial \Gamma_i}{\partial T} \frac{\partial T}{\partial \eta_k} - \sum_{r=1}^{s} \frac{\partial \Gamma_i}{\partial n_r} \frac{\partial n_r}{\partial \eta_k} + \sum_{j=1}^{c+2} \beta_{ij} \delta_{jk} \qquad \text{(I-B-97)}$$

with $k = 1, \ldots, c + 2$, the partial derivatives $\partial \hat{\rho} / \partial \eta_k$ and $\partial T / \partial \eta_k$ given by the equations

$$\begin{aligned} \partial \hat{\rho} / \partial \eta_k &= \hat{\rho} (\delta_{c+1,k} - \delta_{c+2,k}) \\ \partial T / \partial \eta_k &= T \, \delta_{c+2,k} \end{aligned} \qquad \text{(I-B-98)}$$

and $\beta_{i,c+2}$ defined by the equation

$$-\beta_{i,c+2} = \frac{\partial g_i}{\partial \tau_{c+2}}, = T \frac{dg_i}{dT} \tag{I-B-99}$$

since g_i is a function of temperature only. It follows from Eq. (I-B-33) that $\beta_{i,c+2}$ can be expressed in terms of the reduced enthalpies of the gaseous species in their standard states as

$$\beta_{i,c+2} = \chi_i^{\circ} - \sum_{j=p+1}^{c} \beta_{ij} \chi_{i*(j)} \tag{I-B-100}$$

Setting $\partial n_r / \partial \tau_k = n_r \partial \xi_r / \partial \tau_k$ and $\gamma_{ir} = \partial \Gamma_i / \partial n_r$ in Eq. (I-B-97) and rearranging terms leads to the following equations with $i = 1, \ldots, s$:

$$\sum_{r=1}^{s} (\delta_{ir} + \gamma_{ir} n_r) \frac{\partial \xi_r}{\partial \tau_k} = \beta_{ik} \qquad k = 1, \ldots, c \tag{I-B-101}$$

$$\sum_{r=1}^{s} (\delta_{ir} + \gamma_{ir} n_r) \frac{\partial \xi_r}{\partial \tau_{c+1}} = \beta_{i,c+1} - \frac{\partial \Gamma_i}{\partial\, \ell n\, \hat{\rho}} \tag{I-B-102}$$

$$\sum_{r=1}^{s} (\delta_{ir} + \gamma_{ir} n_r) \frac{\partial \xi_r}{\partial \tau_{c+2}} = \beta_{i,c+2} + \frac{\partial \Gamma_i}{\partial\, \ell n\, \hat{\rho}} - \frac{\partial \Gamma_i}{\partial\, \ell n\, T} \tag{I-B-103}$$

where the derivatives of the activity coefficient Γ_i are given according to Eq. (I-B-31) by the equations,

$$\frac{\partial \Gamma_i}{\partial n_r} = \int_0^{\hat{\rho}} \frac{M_0}{RT\hat{\rho}} \frac{\partial^2 p}{\partial n_i \partial n_r} \frac{d\hat{\rho}}{\hat{\rho}} \tag{I-B-104}$$

$$\frac{\partial \Gamma_i}{\partial\, \ell n\, \hat{\rho}} = \frac{M_0}{RT\hat{\rho}} \frac{\partial p}{\partial n_i} - 1 \tag{I-B-105}$$

and

$$\frac{\partial \Gamma_i}{\partial \ln T} = \int_0^{\rho} \frac{M_c}{RT\rho} \left[T \frac{\partial^2 p}{\partial T \partial n_i} - \frac{\partial p}{\partial n_i} \right] \frac{d\hat{\rho}}{\rho} \qquad \text{(I-B-106)}$$

Although the integral expression for $\partial \Gamma_i / \partial \ln T$ is given here, this derivative can be readily obtained by differentiating the explicit expression for Γ_i directly.

The relationships in Eqs. (I-B-101) to (I-B-103) constitute $c + 2$ sets of s simultaneous linear equations for $\partial \xi_i / \partial \tau_k$ and can be solved for these derivatives when the mole numbers associated with a set $(\tau_1, \ldots, \tau_{c+2})$ of the iteration parameters have been calculated with Eq. (I-B-71) in the inner iteration. The corresponding derivatives of the gaseous mole numbers can then be calculated with Eq. (I-B-96).

The Eqs. (I-B-101) to (I-B-103) become simplified for an ideal gas mixture with $\Gamma_i = 0$, $i = 1, \ldots, s$. In this case, the matrix of Eqs. (I-B-101) to (I-B-103) reduces to the unit matrix, and the equations have the solution

$$\frac{\partial \xi_i}{\partial \tau_k} = \beta_{ik} \qquad \begin{array}{l} i = 1, \ldots, s \\ k = 1, \ldots, c + 2 \end{array} \qquad \text{(I-B-107)}$$

The abbreviation

$$C_{ik} = \frac{\partial \xi_i}{\partial \tau_k} = \frac{1}{n_i} \frac{\partial n_i}{\partial \tau_k} \qquad \begin{array}{l} i = 1, \ldots, s \\ k = 1, \ldots, c + 2 \end{array} \qquad \text{(I-B-108)}$$

is introduced for convenience in writing other derivatives of the state with respect to the iteration parameters. Differentiation of Eq. (I-B-57) gives the partial derivatives of the mole numbers of the condensed species N_j as

$$\frac{\partial N_j}{\partial \tau_k} = - \sum_{i=1}^{s} \beta_{ij} C_{ik} n_i \qquad \begin{array}{l} j = 1, \ldots, p, \\ k = 1, \ldots, c + 2 \end{array} \qquad \text{(I-B-109)}$$

and differentiation of Eq. (I-B-18) with $p = p'$ gives the derivatives of the total number of gaseous moles n as

$$\frac{\partial n}{\partial \eta_k} = - \sum_{i=1}^{s} \beta_{i,c+1} C_{ik} n_i \qquad k = 1, \ldots, c + 2 \qquad \text{(I-B-110)}$$

with $\beta_{i,c+1}$ defined by Eq. (I-B-54).

(2) Partial Derivatives of the Pressure

It is convenient to derive equations for these partial derivatives with Eq. (I-B-74) for the pressure rewritten as

$$\ln p = \ln \Phi + \ln n + \eta_{c+1} \qquad \text{(I-B-111)}$$

Differentiation of Eq. (I-B-111) with respect to η_k then leads to the following equations

$$\frac{\partial \ln p}{\partial \eta_k} = \frac{\partial \ln \Phi}{\partial \eta_k} + \frac{1}{n} \frac{\partial n}{\partial \eta_k} \qquad k = 1, \ldots, c \qquad \text{(I-B-112)}$$

$$\frac{\partial \ln p}{\partial \eta_{c+1}} = \frac{\partial \ln \Phi}{\partial \eta_{c+1}} + \frac{1}{n} \frac{\partial n}{\partial \eta_{c+1}} + 1 \qquad \text{(I-B-113)}$$

$$\frac{\partial \ln p}{\partial \eta_{c+2}} = \frac{\partial \ln \Phi}{\partial \eta_{c+2}} + \frac{1}{n} \frac{\partial n}{\partial \eta_{c+2}} \qquad \text{(I-B-114)}$$

where Φ is considered to be a function of $\eta_1, \ldots, \eta_{c+2}$. Differentiating Φ by the chain rule and making use of Eqs. (I-B-98) and (I-B-108) leads to the following expressions for the partial derivatives of Φ

$$\frac{\partial \ln \Phi}{\partial \eta_k} = \sum_{i=1}^{s} \frac{\partial \ln \Phi}{\partial \ln n_i} C_{ik} \qquad k = 1, \ldots, c \qquad \text{(I-B-115)}$$

$$\frac{\partial \ln \Phi}{\partial \eta_{c+1}} = \sum_{i=1}^{s} \frac{\partial \ln \Phi}{\partial \ln n_i} C_{i,c+1} + \frac{\partial \ln \Phi}{\partial \ln \beta} \qquad \text{(I-B-116)}$$

$$\frac{\partial \ln \Phi}{\partial \eta_{c+2}} = \sum_{i=1}^{s} \frac{\partial \ln \Phi}{\partial \ln n_i} C_{i,c+2} - \frac{\partial \ln \Phi}{\partial \ln p} + \frac{\partial \ln \Phi}{\partial \ln T} \qquad \text{(I-B-117)}$$

Equations (I-B-112) to (I-B-114) for the partial derivatives of the pressure are evaluated with the aid of Eq. (I-B-110) for the derivatives of n and Eqs. (I-B-115) to (I-B-117) for the derivatives of Φ.

(3) Partial Derivatives for the Condensed Phases

The thermodynamic properties of a condensed phase are assumed to be explicit functions of temperature and pressure specified by its complete equation of state. They can therefore be regarded as implicit functions of the iteration parameters because of the implicit dependence of the pressure on these parameters. The partial derivatives of the thermodynamic properties of a condensed phase with respect to η_k are derived because they are required to calculate the partial derivatives of the mixture.

The partial derivatives of the molar volume V^*_j and the molar enthalpy H^*_j of the j^{th} condensed component are expressed in terms of the identities contained in Eqs. (I-B-36), (I-B-37), and (I-B-40) with $j = 1, \ldots, p$ as

$$\frac{p}{RT} \frac{\partial}{\partial \eta_k} V^*_j(p,T) = \beta^*_j \varphi^*_j \frac{\partial \ln p}{\partial \eta_k} \qquad k = 1, 2, \ldots, c+1 \qquad \text{(I-B-118)}$$

$$\frac{p}{RT} \frac{\partial}{\partial \eta_{c+2}} V^*_j(T,p) = \alpha^*_j \varphi^*_j + \beta^*_j \varphi^*_j \frac{\partial \ln p}{\partial \eta_{c+2}} \qquad \text{(I-B-119)}$$

and

$$\frac{1}{RT} \frac{\partial}{\partial \eta_k} H^*_j(p,T) = \varphi^*_j (1 - \alpha^*_j) \frac{\partial \ln p}{\partial \eta_k} \qquad k = 1, \ldots, c+1 \qquad \text{(I-B-120)}$$

$$\frac{1}{RT} \frac{\partial}{\partial \eta_{c+2}} H^*_j(p,T) = \frac{C^*_{pj}}{R} + \varphi^*_j (1 - \alpha^*_j) \frac{\partial \ln p}{\partial \eta_{c+2}} \qquad \text{(I-B-121)}$$

The partial derivatives of the reduced chemical potential μ_J^*/RT of the J^{th} condensed component are expressed in terms of the identities in Eqs. (I-B-40) and (I-B-41) with $J = 1, \ldots, c$ as

$$\frac{\partial}{\partial \eta_k} \frac{\mu_J^*(p,T)}{RT} = \varphi_J^* \frac{\partial \ln p}{\partial \eta_k} \qquad k = 1, 2, \ldots, c+1 \qquad \text{(I-B-122)}$$

$$\frac{\partial}{\partial \eta_{c+2}} \frac{\mu_J^*(p,T)}{RT} = -\chi_J^* + \varphi_J^* \frac{\partial \ln p}{\partial \eta_{c+2}} \qquad \text{(I-B-123)}$$

In a point calculation with the pressure specified to be p_0, the properties of the condensed phases can be evaluated in each iteration with p_0 instead of with the current value of the pressure calculated with the gaseous equation of state. In this case, the properties of the condensed phases can be regarded as a function of temperature only, and the equations for the partial derivatives of V_J^*, H_J^*, and μ_J^*/RT are obtained by setting $\partial \ln p/\partial \eta_k = 0$ $(k = 1, \ldots, c+2)$ in Eqs. (I-B-118) to (I-B-123).

(4) Partial Derivatives of the Specific Volume of the Mixture

The partial derivatives of the specific volume with respect to the iteration parameters can be written as

$$\frac{pM_0}{RT} \frac{\partial v}{\partial \eta_k} = \sum_{J=1}^{P} \varphi_J^* \frac{\partial N_J}{\partial \eta_k} + \sum_{J=1}^{P} N_J \frac{p}{RT} \frac{\partial V_J^*}{\partial \eta_k} \qquad k = 1, \ldots, c \qquad \text{(I-B-124)}$$

and

$$\frac{pM_0}{RT} \frac{\partial v}{\partial \eta_{c+1}} = \sum_{J=1}^{P} \varphi_J^* \frac{\partial N_J}{\partial \eta_{c+1}} + \sum_{J=1}^{P} N_J \frac{p}{RT} \frac{\partial V_J^*}{\partial \eta_{c+1}} - \frac{pM_0}{RT\rho} \qquad \text{(I-B-125)}$$

$$\frac{pM_0}{RT} \frac{\partial v}{\partial \eta_{c+2}} = \sum_{J=1}^{P} \varphi_J^* \frac{\partial N_J}{\partial \eta_{c+2}} + \sum_{J=1}^{P} N_J \frac{p}{RT} \frac{\partial V_J^*}{\partial \eta_{c+2}} + \frac{pM_0}{RT\rho} \qquad \text{(I-B-126)}$$

These equations can be rewritten with Eqs. (I-B-118) and (I-B-119) as

$$\frac{pM_0}{RT}\frac{\partial v}{\partial n_k} = \sum_{j=1}^{p} \varpi^*_j \frac{\partial N_j}{\partial n_k} + \frac{\partial\, \ln p}{\partial n_k} \sum_{j=1}^{p} N_j \beta^*_j \varpi^*_j \qquad k = 1, 2, \ldots, c \qquad \text{(I-B-127)}$$

$$\frac{pM_0}{RT}\frac{\partial v}{\partial n_{c+1}} = \sum_{j=1}^{p} \varpi^*_j \frac{\partial N_j}{\partial n_{c+1}} + \frac{\partial\, \ln p}{\partial n_{c+1}} \sum_{j=1}^{p} N_j \beta^*_j \varpi^*_j - \frac{pM_0}{RT\beta} \qquad \text{(I-B-128)}$$

and

$$\frac{pM_0}{RT}\frac{\partial v}{\partial n_{c+2}} = \sum_{j=1}^{p} \varpi^*_j \frac{\partial N_j}{\partial n_{c+2}} + \frac{\partial\, \ln p}{\partial n_{c+2}} \sum_{j=1}^{p} N_j \beta^*_j \varpi^*_j + \sum_{j=1}^{p} N_j \alpha^*_j \varpi^*_j + \frac{pM_0}{RT\beta} \qquad \text{(-B-129)}$$

The Eqs. (I-B-127) to (I-B-129) are used to evaluate the derivatives of F_{c+1} and F_{c+2} at a point where the specific volume of the mixture is specified to be v_0.

(5) Partial Derivatives of the Specific Enthalpy of the Mixture

The identity

$$\frac{\partial \epsilon}{\partial n_i} = -\frac{\partial \Gamma_i}{\partial\, \ln T} \qquad \text{(I-B-130)}$$

together with Eqs. (I-B-120) and (I-B-121) for the derivatives of H^*_j, Eq. (I-B-110) for the derivatives of n, and Eq. (I-B-79) for the frozen heat capacity, are used to express the partial derivatives of the specific enthalpy as

$$\frac{M_0}{RT}\frac{\partial h}{\partial n_k} = \sum_{j=1}^{p} \chi^*_j \frac{\partial N_j}{\partial n_k} - \frac{\partial\, \ln p}{\partial n_k} \sum_{j=1}^{p} N_j \alpha^*_j \varpi^*_j + \frac{M_0 pv}{RT}\,\frac{\partial\, \ln p}{\partial n_k}$$

$$+ \sum_{i=1}^{s} \left(\beta_{i,c+1} + \beta_{i,c+2} - \frac{\partial \Gamma_i}{\partial\, \ln T}\right) C_{ik} n_i \qquad \text{(I-B-131)}$$

for $k = 1, 2, \ldots, c$ and

$$\frac{M_0}{RT}\frac{\partial h}{\partial \eta_{c+1}} = \sum_{j=1}^{p} \chi_j^* \frac{\partial N_j}{\partial \eta_{c+1}} - \frac{\partial \ln p}{\partial \eta_{c+1}} \sum_{j=1}^{p} N_j \alpha_j^* \sigma_j^* + \frac{M_0 pv}{RT}\frac{\partial \ln p}{\partial \eta_{c+1}}$$

$$+ \sum_{i=1}^{s}\left(\beta_{i,c+1} + \beta_{i,c+2} - \frac{\partial \Gamma_i}{\partial \ln T}\right) C_{i,c+1} n_i - \frac{M_0 p}{RT\rho} - \frac{n\Phi\theta \ln \Phi}{\partial \ln T} \qquad \text{(I-B-132)}$$

and

$$\frac{M_0}{RT}\frac{\partial h}{\partial \eta_{c+2}} = \sum_{j=1}^{p} \chi_j^* \frac{\partial N_j}{\partial \eta_{c+2}} - \frac{\partial \ln p}{\partial \eta_{c+2}} \sum_{j=1}^{p} N_j \alpha_j^* \sigma_j^* + \frac{M_0 pv}{RT}\frac{\partial \ln p}{\partial \eta_{c+2}}$$

$$+ \sum_{i=1}^{s}\left(\beta_{i,c+1} + \beta_{i,c+2} - \frac{\partial \Gamma_i}{\partial \ln T}\right) C_{i,c+2} n_i \qquad \text{(I-B-133)}$$

$$+ \frac{M_0 p}{RT\rho} + \frac{n\Phi\theta \ln \Phi}{\partial \ln T} + \frac{c_f}{R}$$

The equations for the derivatives $\partial h/\partial \eta_k$ at a point where the pressure is specified to be p_0 can be obtained by setting $\partial \ln p/\partial \eta_k = 0$ ($k = 1, \ldots, c + 2$) in Eqs. (I-B-131) to (I-B-132) because in this case H_j^* is a function of temperature only.

(6) Partial Derivatives of the Specific Free Energy of the Mixture

The derivatives $\partial (M_0 g/RT)/\partial \eta_k$ are readily obtained by differentiating Eq. (I-B-85) as

$$\frac{\partial}{\partial \eta_k}\frac{M_0 g}{RT} = q_k \qquad \text{for} \qquad k = 1, 2, \ldots, c \qquad \text{(I-B-134)}$$

and

$$\frac{\partial}{\partial \eta_{c+1}}\frac{M_0 g}{RT} = \sum_{j=p+1}^{c} q_j \qquad \text{(I-B-135)}$$

and

$$\frac{\partial}{\partial \eta_{c+2}}\frac{M_0 g}{RT} = - \sum_{j=p+1}^{c} q_j \chi_{i*(j)}^0 \qquad \text{(I-B-136)}$$

(7) Partial Derivatives of the Specific Energy and Specific Entropy of the Mixture

The equations for the derivatives $\partial e/\partial \pi_k$ and $\partial s/\partial \pi_k$ are obtained by differentiating the identity for e Eq. (I-B-86) and the identity for s Eq. (I-B-87) and substituting the equations for the resulting derivatives that have already been presented.

(8) Equations for the D_{jk} Derivatives

The partial derivatives of the state variables with respect to the iteration parameters presented in the previous paragraphs can now be used to formulate the equations for the D_{jk} derivatives. The equations for the condensed components $(j = 1, \ldots, p)$ will be presented first, then the equations obtained from the stoichiometric conditions $(j = p + 1, \ldots, c)$, and then those obtained from the state conditions $(j = c + 1, c + 2)$.

The equations for D_{jk} with $j = 1, \ldots, p$ are obtained as

$$D_{jk} = \delta_{jk} - \frac{\partial}{\partial \pi_k} \frac{\mu_j^*}{RT} \qquad k = 1, \ldots, c + 2 \qquad \text{(I-B-137)}$$

by differentiating Eq. (I-B-67) partially with respect to π_k. Combining Eq. (I-B-137) with Eqs. (I-B-122) and (I-B-123) gives the equations

$$D_{jk} = \delta_{jk} - \omega_j^* \frac{\partial \ln p}{\partial \pi_k} \qquad k = 1, 2, \ldots, c + 1 \qquad \text{(I-B-138)}$$

and

$$D_{j,c+2} = \chi_j^* - \omega_j^* \frac{\partial \ln p}{\partial \pi_{c+2}} \qquad \text{(I-B-139)}$$

which reduce to the equations

$$D_{jk} = \delta_{jk} \qquad k = 1, 2, \ldots, c + 1 \qquad \text{(I-B-140)}$$

and

$$D_{j,c+2} = X_j^* \qquad \text{(I-B-141)}$$

for the point calculations when the pressure of the system is specified to be p_0.

The equations for D_{jk} with $j = p + 1, \ldots, c$ are obtained as

$$D_{jk} = \sum_{i=1}^{s} \beta_{ij} \frac{\partial n_i}{\partial \eta_k} \qquad k = p + 1, \ldots, c + 2 \qquad \text{(I-B-142)}$$

by differentiating Eq. (I-B-68), and they are rewritten as

$$D_{jk} = \sum_{i=1}^{s} \beta_{ij} C_{ik} n_i \qquad k = p + 1, \ldots, c + 2 \qquad \text{(I-B-143)}$$

with the Eq. (I-B-108).

The equations used in the seven different point calculations for D_{jk} with $j = c + 1, c + 2$ are obtained by differentiating the state conditions. The case when the pressure of the system is specified to be p_0 will again be considered before the case when the specific volume is specified to be v_0.

At points where $p = p_0$, the equations for $D_{c+1,k}$ are obtained as

$$D_{c+1,k} = \frac{\partial \ln p}{\partial \eta_k} \qquad k = 1, 2. .., c + 2 \qquad \text{(I-B-144)}$$

by differentiating Eq. (I-B-88) partially with respect to η_k, and the derivatives are evaluated with Eqs. (I-B-112) to (I-B-114). At (p_0, T_0) points, the $D_{c+2,k}$ derivatives are not required because the condition $\Delta_{c+2} = 0$ is employed. The equations for $D_{c+2,k}$ are obtained at (p_0, h_0) points as

$$D_{c+2,k} = \frac{M_0}{RT}\left(\frac{\partial h}{\partial \eta_k}\right)_0 \qquad k = 1, 2, \ldots, c+1 \qquad \text{(I-B-145)}$$

and

$$D_{c+2,c+2} = \frac{M_0}{RT}\left[\left(\frac{\partial h}{\partial \eta_{c+2}}\right)_0 + (h_0 - h)\right] \qquad \text{(I-B-146)}$$

by differentiating Eq. (I-B-89); at (p_0, s_0) points as

$$D_{c+2,k} = \frac{M_0}{RT}\left(\frac{\partial h}{\partial \eta_k}\right)_0 - \frac{\partial}{\partial \eta_k}\frac{M_0 g}{RT} \qquad k = 1, 2, \ldots, c+1 \qquad \text{(I-B-147)}$$

and

$$D_{c+2,c+2} = \frac{M_0}{RT}\left[\left(\frac{\partial h}{\partial \eta_{c+2}}\right)_0 - h\right] - \frac{\partial}{\partial \eta_{c+2}}\frac{M_0 g}{RT} \qquad \text{(I-B-148)}$$

by differentiating Eq. (I-B-90); and at (p_0, v_0) points as

$$D_{c+2,k} = \frac{p_0 M_0}{RT}\left(\frac{\partial v}{\partial \eta_k}\right)_0 \qquad k = 1, 2, \ldots, c+1 \qquad \text{(I-B-149)}$$

and

$$D_{c+2,c+2} = \frac{p_0 M_0}{RT}\left[\left(\frac{\partial v}{\partial \eta_{c+2}}\right)_0 + (v_0 - v)\right] \qquad \text{(I-B-150)}$$

by differentiating Eq. (I-B-91). The $(\partial h/\partial \eta_k)_0$ and $(\partial v/\partial \eta_k)_0$ derivatives are evaluated with the equations obtained by setting $(\partial \ln p/\partial \eta_k) = 0$ in Eqs. (I-B-131) to (I-B-133) and in Eqs. (I-B-127) to (I-B-129), and the $\partial(M_0 g/RT)/\partial \eta_k$ derivatives are evaluated with Eqs. (I-B-134) to (I-B-136).

At points where $v = v_0$ and the pressure is not specified, the equations for $D_{c+1,k}$ are obtained as

$$D_{c+1,k} = \frac{pM_0}{RT}\left[\frac{\partial v}{\partial \eta_k} - (v_0 - v)\frac{\partial \ln p}{\partial \eta_k}\right] \qquad k = 1, \ldots, c+1 \qquad \text{(I-B-151)}$$

and

$$D_{c+1,c+2} = \frac{pM_0}{RT}\left[\frac{\partial v}{\partial \pi_{c+2}} + (v_0 - v)\left(1 - \frac{\partial \ln p}{\partial \pi_{c+2}}\right)\right] \tag{I-B-152}$$

by differentiating Eq. (I-B-92), and the derivatives are evaluated with Eqs. (I-B-112) to (I-B-114) and Eqs. (I-B-127) to (I-B-129). At (v_0, T_0) points, the $D_{c+2,k}$ derivatives are not required because the condition $D_{c+2} = 0$ is employed. The $D_{c+2,k}$ are obtained at (v_0, e_0) points as

$$D_{c+2,k} = \frac{M_0}{RT}\left[\frac{\partial h}{\partial \pi_k} - pv_0 \frac{\partial \ln p}{\partial \pi_k}\right] \qquad k = 1, \ldots, c+1 \tag{I-B-153}$$

and

$$D_{c+2,c+2} = \frac{M_0}{RT}\left[\frac{\partial h}{\partial \pi_{c+2}} - pv_0 \frac{\partial \ln p}{\partial \pi_{c+2}} + (e_0 - h + pv_0)\right] \tag{I-B-154}$$

by differentiating Eq. (I-B-93), and at (v_0, s_0) points as

$$D_{c+2,k} = \frac{M_0}{RT}\frac{\partial h}{\partial \pi_k} - \frac{\partial}{\partial \pi_k}\frac{M_0 g}{RT} \qquad k = 1, c+1 \tag{I-B-155}$$

and

$$D_{c+2,c+2} = \frac{M_0}{RT}\left(\frac{\partial h}{\partial \pi_{c+2}} - h - \frac{\partial}{\partial \pi_{c+2}}\frac{M_0 g}{RT}\right) \tag{I-B-156}$$

by differentiating Eq. (I-B-94).

e. The Equilibrium Partial Derivatives

Equations will be derived for a complete set of equilibrium first-order partial derivatives of the system so that the equations for any other equilibrium partial derivative can be obtained with thermodynamic identities.

A convenient set of complete derivatives for use in hydrodynamic calculations consists of the equilibrium specific heat capacity at constant volume

$$C_v = \left(\frac{\partial e}{\partial T}\right)_v = \left(\frac{\partial h}{\partial T}\right)_v - v\left(\frac{\partial p}{\partial T}\right)_v \tag{I-B-157}$$

and the following derivatives of the equilibrium (e-p-v) equation of state

$$\alpha = \frac{1}{p}\left(\frac{\partial e}{\partial v}\right)_p = \frac{T}{p}\left(\frac{\partial s}{\partial v}\right)_p - 1 = \frac{C_p}{p}\left(\frac{\partial T}{\partial v}\right)_p - 1 \tag{I-B-158}$$

$$\beta = \frac{1}{v}\left(\frac{\partial e}{\partial p}\right)_v = \frac{T}{v}\left(\frac{\partial s}{\partial p}\right)_v = \frac{C_v}{v}\left(\frac{\partial T}{\partial p}\right)_v \tag{I-B-159}$$

The adiabatic exponent $\varkappa$ used in hydrodynamic calculations is related to α and β by the identities

$$\varkappa = -\left(\frac{\partial\, \ln\, p}{\partial\, \ln\, v}\right)_s = \frac{\alpha + 1}{\beta} \tag{I-B-160}$$

It is convenient to rewrite the Eqs. (I-B-157) to (I-B-159) and change the independent variables to η_{c+1} and η_{c+2} with the identities

$$\left(\frac{\partial}{\partial v}\right)_T = \left(\frac{\partial}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \Bigg/ \left(\frac{\partial v}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-161}$$

$$T\left(\frac{\partial}{\partial T}\right)_v = \left(\frac{\partial}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} - \left(\frac{\partial}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \left(\frac{\partial v}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} \left(\frac{\partial v}{\partial \eta_{c+1}}\right)^{-1}_{\eta_{c+2}} \tag{I-B-162}$$

so that the quantities C_v, α, and β can be evaluated with the partial derivatives presented in Section d. Care must be taken however to remember that $(\partial/\partial\eta_{c+1})_{\eta_{c+2}}$ and $(\partial/\partial\eta_{c+2})_{\eta_{c+1}}$ are equilibrium partial derivatives related to the frozen derivatives $\partial/\partial\eta_k$ $(k = 1, \ldots, c + 2)$ by the equations

$$(\partial/\partial\eta_{c+1})_{\eta_{c+2}} = \sum_{k=1}^{c}(\partial/\partial\eta_k)(\partial\eta_k/\partial\eta_{c+1})_{\eta_{c+2}} + \partial/\partial\eta_{c+1} \qquad \text{(I-B-163)}$$

$$(\partial/\partial\eta_{c+2})_{\eta_{c+1}} = \sum_{k=1}^{c}(\partial/\partial\eta_k)(\partial\eta_k/\partial\eta_{c+2})_{\eta_{c+1}} + \partial/\partial\eta_{c+2} \qquad \text{(I-B-164)}$$

and that the equilibrium derivatives of the iteration parameters $\eta_k (k = 1, \ldots, c)$ are required for their evaluation. The derivatives $(\partial\eta_k/\partial\eta_{c+1})_{\eta_{c+2}}$ denote the rates of change of the η_k parameters with respect to η_{c+1} when η_{c+2} is kept constant and the system remains in chemical equilibrium. Similarly, the $(\partial\eta_k/\partial\eta_{c+2})_{\eta_{c+1}}$ derivatives denote the rates of change of the η_k parameters with respect to η_{c+2} when η_{c+1} is kept constant and the system remains in chemical equilibrium. The equations for C_v, α, and β are rewritten as

$$\frac{M_0 C_v}{R} = \frac{M_0}{R}\left(\frac{\partial h}{\partial T}\right)_v - \left(\frac{M_0 pv}{RT}\right)\left[T\left(\frac{\partial \ln p}{\partial T}\right)_v\right] \qquad \text{(I-B-165)}$$

$$\alpha = \frac{1}{p}\left(\frac{\partial h}{\partial v}\right)_T - 1 - \left[\frac{M_0}{R}\left(\frac{\partial h}{\partial T}\right)_v\right]\left[\frac{RT}{M_0 p}\left(\frac{\partial \ln p}{\partial v}\right)_T\right]\left[T\left(\frac{\partial \ln p}{\partial T}\right)_v\right]^{-1} \qquad \text{(I-B-166)}$$

and

$$\beta = \frac{RT}{M_0 pv}\left[\frac{M_0 C_v}{R}\right]\left[T\left(\frac{\partial \ln p}{\partial T}\right)_v\right]^{-1} \qquad \text{(I-B-167)}$$

and the identities (I-B-161) and (I-B-162) are used to express the partial derivatives appearing in these equations in terms of η_{c+1} and η_{c+2} as

$$\frac{RT}{M_o p}\left(\frac{\partial \ln p}{\partial v}\right)_T = \left(\frac{\partial \ln p}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \Big/ \left(\frac{M_o p}{RT}\frac{\partial v}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-168}$$

$$T\left(\frac{\partial \ln p}{\partial T}\right)_v = \left(\frac{\partial \ln p}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} - \left(\frac{\partial \ln p}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \left(\frac{M_o p}{RT}\frac{\partial v}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} \Big/ \left(\frac{M_o p}{RT}\frac{\partial v}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-169}$$

and

$$\frac{1}{p}\left(\frac{\partial h}{\partial v}\right)_T = \left(\frac{M_o}{RT}\frac{\partial h}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \Big/ \left(\frac{M_o p}{RT}\frac{\partial v}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-170}$$

$$\frac{M_o}{R}\left(\frac{\partial h}{\partial T}\right)_v = \left(\frac{M_o}{RT}\frac{\partial h}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} - \left(\frac{M_o}{RT}\frac{\partial h}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \left(\frac{M_o p}{RT}\frac{\partial v}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} \Big/ \left(\frac{M_o p}{RT}\frac{\partial v}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-171}$$

The application of Eqs. (I-B-163) and (I-B-164) to the pressure, the specific volume, and the enthalpy then gives the equations relating the equilibrium partial derivatives to the frozen derivatives presented in Section d. The equations for the derivatives of the pressure are written as

$$\left(\frac{\partial \ln p}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} = \frac{\partial \ln p}{\partial \eta_{c+1}} + \sum_{k=1}^{c} \frac{\partial \ln p}{\partial \eta_k}\left(\frac{\partial \eta_k}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-172}$$

and

$$\left(\frac{\partial \ln p}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} = \frac{\partial \ln p}{\partial \eta_{c+2}} + \sum_{k=1}^{c} \frac{\partial \ln p}{\partial \eta_k}\left(\frac{\partial \eta_k}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} \tag{I-B-173}$$

with the frozen derivatives of the pressure given by the Eqs. (I-B-112) to (I-B-114). The equations for the derivatives of the specific volume of the mixture and written as

$$\frac{M_0 p}{RT}\left(\frac{\partial v}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} = \frac{M_0 p}{RT}\,\frac{\partial v}{\partial \eta_{c+1}} + \sum_{k=1}^{c} \frac{M_0 p}{RT}\,\frac{\partial v}{\partial \eta_k}\left(\frac{\partial \eta_k}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-174}$$

and

$$\frac{M_0 p}{RT}\left(\frac{\partial v}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} = \frac{M_0 p}{RT}\,\frac{\partial v}{\partial \eta_{c+2}} + \sum_{k=1}^{c} \frac{M_0 p}{RT}\,\frac{\partial v}{\partial \eta_k}\left(\frac{\partial \eta_k}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} \tag{I-B-175}$$

with the frozen derivatives given by the Eqs. (I-B-127) to (I-B-129), and those for the specific enthalpy as

$$\frac{M_0}{RT}\left(\frac{\partial h}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} = \frac{M_0}{RT}\,\frac{\partial h}{\partial \eta_{c+1}} + \sum_{k=1}^{c} \frac{M_0}{RT}\,\frac{\partial h}{\partial \eta_k}\left(\frac{\partial \eta_k}{\partial \eta_{c+1}}\right)_{\eta_{c+2}} \tag{I-B-176}$$

and

$$\frac{M_0}{RT}\left(\frac{\partial h}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} = \frac{M_0}{RT}\,\frac{\partial h}{\partial \eta_{c+2}} + \sum_{k=1}^{c} \frac{M_0}{RT}\,\frac{\partial h}{\partial \eta_k}\left(\frac{\partial \eta_k}{\partial \eta_{c+2}}\right)_{\eta_{c+1}} \tag{I-B-177}$$

with the frozen derivatives given by Eqs. (I-B-131) to (I-B-133). The equations for the equilibrium derivatives of the iteration parameters $\eta_k (k = 1, \ldots, c)$, $(\partial\eta_k/\partial\eta_{c+1})_{c+2}$, and $(\partial\eta_k/\partial\eta_{c+2})_{c+1}$ are obtained for $j = 1, \ldots, c$ by differentiating Eqs. (I-B-67) and (I-B-68) and setting $\partial F_j/\partial\eta_k = -D_{jk}$ as

$$-\sum_{k=1}^{c} D_{jk}(\partial\eta_k/\partial\eta_{c+1})_{\eta_{c+2}} = D_{j,c+1} \tag{I-B-178}$$

and

$$-\sum_{k=1}^{c} D_{jk}(\partial\tau_k/\partial\tau_{c+2})_{\tau_{c+1}} = D_{j,c+2} \qquad \text{(I-B-179)}$$

expressions for D_{jk} for the condensed components $j = 1, \ldots, p$ are given by Eqs. (I-B-138) and (I-B-139), and expressions for D_{jk} for the gaseous components $j = p + 1, \ldots, c$ are given by Eq. (I-B-143). Equations (I-B-178) and (I-B-179) are solved for the equilibrium derivatives with the values of D_{jk} obtained by solving Eq. (I-B-95) for the equilibrium composition with the Newton-Raphson method.

Equations (I-B-165) to (I-B-179) are used to evaluate the complete set of derivatives (C_v, α, β) at a point where the system has attained chemical equilibrium without a condensed component changing phase.

f. Phase Change of a Condensed Component

The foregoing treatment of condensed species cannot be used to solve the equilibrium problem when the condensed species are considered capable of existing in different phases. The treatment must be extended to determine when a condensed species is present as a single phase or as an equilibrium mixture of the phases. The important practical case of melting when the phases are solid and liquid is presented to illustrate the basic method used to solve this type of problem.

Gibbs' conditions for equilibrium used previously to test the a priori assumption made about the presence of condensed constituents must now be used to determine the relative stabilities of the liquid and solid phases of a condensed component. Let μ^*_{sj} and $\mu^*_{\ell j}$ denote the chemical potentials of the solid and liquid phases of the j^{th} condensed component, N^*_{sj} and $N^*_{\ell j}$ denote their respective mole numbers, $T^*_j = T^*_j(p)$ denote the Clausius-Clapeyron equations for the variation of melting points with pressure, and f_ℓ denote the fraction of liquid present at the melting point. Gibbs' conditions for equilibrium of the solid and liquid phases can then be written for $j = 1, \ldots, p$ as

$$\mu^*_{sj}(p, T < T^*_j) < \mu^*_{\ell j}(p, T < T^*_j) \qquad \text{(I-B-180)}$$

$$\mu^*_{\ell j}(p, T > T^*_j) < \mu^*_{sj}(p, T > T^*_j) \qquad \text{(I-B-181)}$$

$$\mu^*_{sj}(p, T = T^*_j) = \mu^*_{\ell j}(p, T = T^*_j) \qquad \text{(I-B-182)}$$

with $j = 1, \ldots, p$. Equation (I-B-180) gives the stability condition for the solid, Eq. (I-B-181) the stability condition for the liquid, and Eq. (I-B-182) the stability condition for a mixture of solid and liquid at a melting point. In an equilibrium mixture the j^{th} condensed component will exist as a solid with $f_\ell = 0$ when Eq. (I-B-180) is satisfied, as a liquid with $f_\ell = 1$ when Eq. (I-B-181) is satisfied, and as a mixture of solid and liquid with $0 \le f_\ell \le 1$ when Eq. (I-B-182) is satisfied.

The Eqs. (I-B-180) to (I-B-182) apply to all condensed components, but at this stage melting of only one of them, the j^{th}, will be considered. It is then convenient to write the following equations for the properties of the j^{th} condensed component constituent.

$$\alpha^*_j = f_\ell \alpha^*_{\ell j} + (1 - f_\ell)\alpha^*_{sj} \qquad \text{(I-B-183)}$$

$$\beta^*_j = f_\ell \beta^*_{\ell j} + (1 - f_\ell)\beta^*_{sj} \qquad \text{(I-B-184)}$$

$$\varphi^*_j = f_\ell \varphi^*_{\ell j} + (1 - f_\ell)\varphi^*_{sj} \qquad \text{(I-B-185)}$$

$$\frac{\mu^*_j}{RT} = \frac{f_\ell \mu^*_{\ell j}}{RT} + (1 - f_\ell)\frac{\mu^*_{sj}}{RT} \qquad \text{(I-B-186)}$$

$$X_J^* = f_\ell X_{\ell J}^* + (1 - f_\ell) X_{sJ}^* \qquad \text{(I-B-187)}$$

$$\frac{C_{pJ}^*}{R} = \frac{f_\ell C_{p\ell}^*}{R} + (1 - f_\ell) \frac{C_{psJ}^*}{R} \qquad \text{(I-B-188)}$$

$$\Delta\mu_J^* = \mu_{\ell J}^* - \mu_{sJ}^* \qquad \text{(I-B-189)}$$

Equations (I-B-183) to (I-B-189) are used with those already presented for the mixture to calculate the equilibrium thermodynamic state at a specified point when the J^th^ condensed component can occur as a liquid, a solid, or a mixture of liquid and solid at the melting point. As in the previous treatment of the equilibrium problem with condensed species, the validity of the calculated state is determined by its compatibility with the assumptions required to perform the calculations. It should be remembered, however, that the question whether a condensed species is present as a liquid or a solid is not a problem in a (p,T) calculation because the phase is determined by the specified values of p and T and the Clausius-Clapeyron equation. In the particular case when the free energies of the solid and liquid are found to be equal, the (p,T) calculation is performed at the solid phase boundary with $f_\ell = 0$.

Consider the other six point calculations when the phase assumption is fixed by the values of T and p, say (T_0, p_0), chosen to start the iterative procedure to determine the thermodynamic state. Only the case when the choice of the solid as a component is valid and $N_{sJ}^* \geq 0$ will be considered. Suppose further that $\Delta\mu_J^*(T_0, p_0) > 0$ so that the calculation is performed with $f_\ell = 0$, and let T_c and p_c denote the values of temperature and pressure resulting from the calculation. Since the point calculation was performed with $f_\ell = 0$, it is necessary to check that the calculated state is compatible with this phase assumption. The calculated state is an equilibrium state when either $\mu_j^*(T_c,p_c) > 0$ and the solid is more stable than the liquid, or $\Delta\mu_j^*(T_c,p_c) = 0$ and the solid is in equilibrium with the liquid at the solid phase boundary. But it is not an equilibrium state when $\Delta\mu_j^*(T_c,p_c) < 0$ and the liquid is more stable than the solid, for then the phase assumption and the calculated state are incompatible. When $\Delta\mu_j^*(T_c,p_c) < 0$, values of T_0 and p_0 are chosen so that $\Delta\mu_j^*(T_0,p_0) < 0$ and the point calculation is performed again with $f_\ell = 1$. Now with $_{\ell j}^* \geq 0$, the calculated state is an equilibrium state when $\Delta\mu_j^*(T_c,p_c) \leq 0$ and the liquid is more stable than the solid or is in equilibrium with the solid at the liquid phase boundary, but not when $\Delta\mu_j^*(T_c,p_c) > 0$ and the solid is more stable than the liquid. When $\Delta\mu_j^*(T_c,p_c) > 0$, it follows that $\Delta\mu_j^* = 0$ at the point of interest, and the thermodynamic state must be in the mixed phase region with f_ℓ in the range $0 < f_\ell < 1$.

When $\Delta\mu_j^* = 0$, the value of f_ℓ in the mixed phase region must be determined to perform a point calculation except at a (p,T) point where $T_j^* = T_j^*(p)$ and the value of f_ℓ can be chosen at will. Since $\Delta\mu_j^* < 0$ in the first calculation with $f_\ell = 0$, and $\Delta\mu_j^* > 0$ in the second calculation with $f_\ell = 1$, it is convenient to use the equilibrium condition $\Delta\mu_j^* = 0$ to determine the equilibrium value of f_ℓ. Since f_ℓ lies in the range $0 < f_\ell < 1$, a bounded linear approximation is used in the iteration scheme to determine the value of f_ℓ that satisfies the equation $\Delta\mu_j^* = 0$.

The order of the procedure must obviously be changed when the j^{th} condensed component is first assumed to be present as a liquid and not as a solid. The development of a general procedure for solving the equilibrium problem when more than one of the condensed species can melt will be based on the treatment for one species presented in this section.

g. Determination of a Mixed Phase Line

The routine for performing mixed phase line calculations is called MIXXED. The mixed phase line $T_J^* = T_J^*(p)$ of a condensed species in the (p-T) plane is determined by solving the following equation

$$\mu_{sJ}^*(T,p) = \mu_{\ell J}^*(T,p) \qquad \text{(I-B-190)}$$

expressing the equilibrium condition for the solid and liquid phases. If values of temperature are specified, then Eq. (I-B-190) is solved with a Newton-Raphson iteration scheme to determine the corresponding values of pressure. Similarly, if values of pressure are specified, Eq. (I-B-190) is solved to determine the corresponding values of temperature.

The thermodynamic state in a mixture containing a melting component can be calculated readily when the mixed phase line of this component has been determined. The calculation is performed at a (p,T) point on the mixed phase line with a specified value of f_ℓ. However, calculations of only two of these equilibrium states, namely, those with $f_\ell = 0$ and $f_\ell = 1$, have been programmed into the code. These values of f_ℓ were chosen purposely to define the phase boundaries and the mixed phase region of the thermodynamic system in the pressure-volume (p-v) plane.

h. Phase Changes of Condensed Species

The treatment of melting developed for one species was extended to $t - s$ species to obtain a more realistic treatment of thermodynamic systems containing multiple condensed phases. The equilibrium conditions expressed by Eqs. (I-B-180) to (I-B-182) must now be used to test the phase assumptions for $t - s$ species rather than for one. A calculated state is an equilibrium state when it satisfies the phase assumptions required to make the calculation. As discussed in I-B-4f, however, there is no problem in (p,T) calculations because the phases are determined by the specified values of p and T and by the Clausius-Clapeyron equations for the species.

Consider the other six point calculations when the phase assumptions are fixed by the values of T_0 and p_0 chosen to start the iterative procedure to determine the thermodynamic state. It is convenient to label those species set as solids with $m = 1, \ldots, a$ and those set as liquids with $m = a + 1, \ldots, a' \leq t - s$, so that the point calculation is performed with $f_{\ell m} = 0$ for $m = 1, \ldots, a$ and with $f_{\ell m} = 1$ for $m = a + 1, \ldots, a'$. It follows from Section I-B-4f that a calculated state is an equilibrium state when it satisfies the conditions $\Delta\mu^*_m(T_c,p_c) \geq 0$ for $m = 1, \ldots, a$, and $\Delta\mu^*_m(T_c,p_c) \leq 0$ for $m = a + 1, \ldots, a'$. When any one of these conditions is not satisfied, the calculated state is not an equilibrium state and it is necessary to choose new values of T_0 and p_0, say $(T_0{}',p_0{}')$, and repeat the point calculation with the new phase assumptions determined by the Clausius-Clapeyron equations. The values of $T_0{}'$ and $p_0{}'$ are based on the results of the last calculation and on the fact that the phase line of each species with an incorrect phase assumption intersects the line segment joining (p_0,T_0) and (p_c,T_c) in the $(p - T)$ plane. These points of intersection are first determined, and the values of T_c' and p_0' are chosen to change the phase assumption of the particular species whose intersection point lies closest to (p_0, T_0). Thus the phase assumption of only one species is changed by this procedure, and (p_0, T_0) lies on one side of its phase line and (p_0', T_0') lies on the other. Calculation of the state now gives new values of T_c and p_c, say (T'_c, p_c'), and the procedure is continued until the calculated state agrees with the phase assumptions used to perform the calculation. If the phase assumptions for a particular species, say with $m = b$, are found to be incorrect in two successive point calculations, the state must lie in the mixed phase region of this species with $0 < f_{\ell b} < 1$. In this case, the phases of the other condensed species are fixed, and the thermodynamic state in the mixed phase region is calculated using the method presented previously in Section I-B-4f.

i. The Equilibrium Partial Derivatives in a Mixed Phase Region

This section will be completed at a later date.

I-C. THEORETICAL BASIS FOR NONEQUILIBRIUM CALCULATIONS IN PARTIALLY FROZEN SYSTEMS

1. Introduction

The theoretical basis for making nonequilibrium calculations is an extension of that developed by R. S. Brinkley, Jr. for making equilibrium calculations.* Methods are presented here for calculating the thermodynamic state of a nonideal heterogeneous system in partial equilibrium when the pair of state variables can be chosen from the following set: [(p,T), (p,h), (p,s), (v,T), (v,e), (p,v), and (v,s)]. The nonequilibrium states considered are those in mechanical and thermal equilibrium, with part of the composition frozen and part of it in chemical equilibrium. Frozen species are defined as species with mole numbers that are fixed and do not change in calculations of the thermodynamic state. But frozen condensed species are allowed to change phase according to their equations of state as in equilibrium calculations. In calculating the thermodynamic state of such a system, the mole numbers of the frozen species must be specified, and the mole numbers of the other species must be calculated using the equilibrium conditions and the stoichiometric conditions given in Section I-B of the TIGER documentation. It is important to note however that the choice of the frozen composition may not be compatible with the total stoichiometry of the system. The frozen species should be chosen so that the mass balance equation for the system can be satisfied. In other words, it is necessary to ensure that there is a feasible solution to the mass balance equations for the nonfrozen species. This problem was treated in a way similar to that used for the linear programming

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* Presented earlier in Section I-B-4.

problem, and a routine called FEASIB was written to determine the choice of frozen constituents compatible with the total stoichiometry of the system.

It is important to remember that the description of the composition presented in Sections I-B-2 and I-B-3a applies equally well to nonequilibrium system as to equilibrium system because it was formulated with the conservation of mass, which is valid for all thermodynamic systems. In fact, it was for this reason that the notation for labelling frozen constituents was introduced in Section I-B rather than in I-C. The discussion of equations of state presented in I-B-3b is also valid for our system in partial equilibrium because the pressure and temperature are well defined by the assumptions of mechanical and thermal equilibrium.

For convenience in presentation, the treatment given in this section of systems in partial equilibrium will parallel that given in section I-B for systems in chemical equilibrium. Consequently, equations that are the same as those in Section I-B will be repeated in special cases only.

2. Calculations with a Partially Frozen Composition

a. Equilibrium Conditions and Iteration Parameters

When the system is assumed to be in partial equilibrium, the frozen composition is chosen and the remainder is calculated with the equilibrium and stoichiometric conditions. These conditions will be expressed in terms of the notation for frozen constituents introduced in Section I-B-3a. The condensed constituents assumed to be present and in equilibrium with the gaseous phase are labelled with $j = 1, 2, \ldots, p$. These constituents will always be chosen as components. The condensed constituents assumed to be frozen and not in chemical equilibrium are labelled with $m = p + 1, \ldots, p'$, and the remainder that are assumed to be absent (but to satisfy the equilibrium conditions) with $p' + 1, \ldots, t - s$. The gaseous species assumed to be components and in equilibrium with the rest of the system are labelled with $g = 1, \ldots, c - p$, the remaining equilibrium species are labelled with $g = c - p + 1, \ldots, s'$, and those assumed to be frozen with $g = s' + 1, \ldots, s$.

The stoichiometric conditions for the mixture are written with the $i'(m)$ subscript introduced on page I-B-12, and with terms summed from $p + 1$ to p' to account for frozen condensed species as

$$\sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m + \sum_{i=1}^{s} \beta_{ij} n_i + N_j = q_j \qquad j = 1, 2, \ldots, p \qquad \text{(I-C-1)}$$

$$\sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m + \sum_{i=1}^{s} \beta_{ij} n_i = q_j \qquad j = p + 1, \ldots, c \qquad \text{(I-C-2)}$$

The conditions for the chemical potentials of gaseous constituents are written as

$$\mu_{\hat{i}(g)} = \sum_{j=1}^{p} \beta_{\hat{i}(g)j} \mu_j^* + \sum_{j=p+1}^{c} \beta_{\hat{i}(g)j} \mu_{\hat{i}(j)}^* \qquad g = 1, \ldots, s' \qquad \text{(I-C-3)}$$

and

$$\mu_{\hat{i}(g)} \neq \sum_{j=1}^{p} \beta_{\hat{i}(g)j} \mu_j^* + \sum_{j=p+1}^{c} \beta_{\hat{i}(g)j} \mu_{\hat{i}(j)}^* \qquad g = s' + 1, \ldots, s \qquad \text{(I-C-4)}$$

The first of these expressions is used to obtain equilibrium conditions, and the second is included to account for the fact that $s - s'$ gaseous species are frozen and are not in chemical equilibrium with the remainder of the system. Remembering that Eq. (I-C-3) contains $c-p$ identities for the constituents chosen as components, the equations for the chemical potentials of the species in our partially frozen mixture can be written as:

$$\mu_{\hat{i}(g)} = \sum_{j=1}^{p} \beta_{\hat{i}(g)j} \mu_j^* + \sum_{j=p+1}^{c} \beta_{\hat{i}(g)j} \mu_{\hat{i}(j)} \qquad g = 1, \ldots, s' \qquad \text{(I-C-5a)}$$

$$\mu_{\hat{i}(g)} \neq \sum_{j=1}^{p} \beta_{\hat{i}(g)j}\mu^*_j + \sum_{j=p+1}^{c} \beta_{\hat{i}(g)j}\mu_{\hat{f}(j)} \qquad g = s' + 1, \ldots, s \qquad \text{(I-C-5b)}$$

$$\mu^*_{i(j)} = \mu^*_j \qquad j = 1, \ldots, p \qquad \text{(I-C-5c)}$$

$$\mu_{i'(m)} = \sum_{j=1}^{p} \beta_{i'(m)j}\mu^*_j + \sum_{j=p+1}^{c} \beta_{i'(m)j}\mu_{\hat{f}(j)} \neq \mu^*_m \qquad m = p + 1, \ldots, p' \qquad \text{(I-C-5d)}$$

$$\mu_{i'(m)} = \sum_{j=1}^{p} \beta_{i'(m)j}\mu^*_j + \sum_{j=p+1}^{c} \beta_{i'(m)j}\mu_{\hat{f}(j)} < \mu^*_m \qquad m = p' + 1, \ldots, t - s \qquad \text{(I-C-5e)}$$

The gaseous constituents in equilibrium must satisfy (I-C-5a), and those that are not in equilibrium must satisfy (I-C-5b). The condensed constituents assumed a priori to be present and in equilibrium must satisfy (I-C-5c), the frozen condensed species must satisfy (I-C-5d), and those assumed to be absent must satisfy (I-C-5e). Equations (I-C-1), (I-C-2), and (I-C-5) are sufficient for calculating the equilibrium composition in the mixture at one of our specified state points when the mole numbers of the frozen species ($N_m \geq 0$, $m = p + 1, \ldots, p'$ and $n_{\hat{f}(g)}$, $g = s' + 1, \ldots, s$) have been properly assigned and a complete equation of state of the mixture is known.

Since μ_i is known as a function of the n_i's, the $s' - c + p$ independent equilibrium conditions together with the c stoichiometric conditions constitute a set of $s' + p$ equations for calculating the $s' + p$ unknown equilibrium mole numbers. With regard to the previous treatment, note that the number of equilibrium conditions and the number of unknown mole numbers for the gaseous species are both reduced by $s - s'$ by the inclusion of $s - s'$ frozen species. Here again, the computed equilibrium composition must be checked to test the validity of the a priori assumptions made about the presence ($N_j \geq 0$, $j = 1, \ldots, p$) and the absence ($N_m = 0$, $m = p + 1, \ldots, t - s$) of condensed constituents.

The assumptions are valid when the computed equilibrium composition is found to satisfy the condition $N_j \geq 0$ and that expressed by Eq. (I-C-5c).

Most of the equations for calculating the equilibrium gaseous composition (Section I-B-4a) can be used for our system in partial equilibrium when the constituent indices are changed to account for the presence of frozen species. It is necessary to change the index i with values $i = 1, \ldots, s$ to $\hat{i}(g)$, with $g = 1, \ldots, s'$, and to change the values of m to range from $m = p + 1, \ldots, t - s$ to $m = p' + 1, \ldots, t - s$. There is no need to change the j index, however, because it refers to components.

Thus the equations for $\xi_{\hat{i}(g)} = \ln n_{\hat{i}(g)}$ $(g = 1, \ldots, s')$ are obtained by substituting $\hat{i}(g)$ for i in Eqs. (I-B-48), (I-B-49), (I-B-55), (I-B-60), and (I-B-61). The expressions for g^*_m are obtained by substituting p' for p in Eqs. (I-B-51), (I-B-52), and (I-B-56). The equations (I-B-50), (I-B-53), (I-B-54), and (I-B-59) used to define π_j, $\beta_{i,c+1}$, and π_{c+2} remain the same. Similarly, the equations for $n_{\hat{i}(g)}$ and $\Gamma_{\hat{i}(g)}$ are obtained by changing i to $\hat{i}(g)$ in Eqs. (I-B-62) and (I-B-63), but Eq. (I-B-64) for N_j is unchanged.

The equation modifications required to make the iterative procedures for calculating the equilibrium composition applicable to a system in partial equilibrium will now be discussed. Recall that Brinkley's approach to the equilibrium problem was to construct a set of $c + 2$ equations

$$F_j(\pi_1, \ldots, \pi_{c+2}) = 0 \qquad \text{(I-C-6)}$$

so that the set of π_j satisfying these equation defines the equilibrium composition. The definitions of F_j for the system in partial equilibrium are as follows:

$$F_j = \mu_j^*/RT - \eta_j = 0 \qquad j = 1, \ldots, p \qquad \text{(I-C-7)}$$

$$F_j = q_j - \sum_{i=1}^{s} \beta_{ij} n_i + \sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m \qquad j = p+1, \ldots, c \qquad \text{(I-C-8)}$$

$$\left.\begin{aligned} F_{c+1} &= 0 \\ F_{c+2} &= 0 \end{aligned}\right\} \qquad \text{(I-C-9)}$$

These equations differ from those used for the system in chemical equilibrium only by the summation term for the frozen condensed species in Eq. (I-C-8). The iterative equations for F_j are the same as those presented in (I-B-66), but the following equations for their derivatives, corresponding to those given in (I-B-70),

$$\frac{\partial F_j}{\partial \eta_k} = -\sum_{g=1}^{s} \beta_{\hat{i}(g)j} \frac{\partial \xi_{\hat{i}(g)}}{\partial \eta_k} n_{\hat{i}(g)} \qquad j = p+1, \ldots, c \qquad \text{(I-C-10)}$$

must be modified with the conditions,

$$\frac{\partial \xi_{\hat{i}(g)}}{\partial \eta_k} = 0 \qquad g = s'+1, \ldots, s \qquad \text{(I-C-11)}$$

to ensure that the concentrations of the frozen gaseous species do not change when the composition of the part of the system in equilibrium is calculated. The equations for $W_{\hat{i}(g)}$, corresponding to those presented for W_i in (I-B-71) to (I-B-73), are as follows:

$$\begin{aligned} W_{\hat{i}(g)}\left(\xi_{\hat{i}(1)}, \ldots, \xi_{\hat{i}(s')}\right) = & -\xi_{\hat{i}(g)} - \Gamma_{\hat{i}(g)} \\ & + G_{\hat{i}(g)}(\eta_1, \ldots, \eta_{c+2}) = 0 \qquad \text{(I-C-12)} \\ & g = 1, \ldots, s' \end{aligned}$$

$$\sum_{r=1}^{s'} -\frac{\partial W_{\hat{i}(g)}}{\partial \xi_{\hat{i}(r)}}\left(\xi^k_{\hat{i}(1)}, \ldots, \xi^k_{\hat{i}(s)}\right) \Delta\xi_{\hat{i}(r)} = W_{\hat{i}(g)}\left(\xi^k_{i(1)}, \ldots, \xi^k_{\hat{i}(s')}\right) \qquad g = 1, \ldots, s' \qquad \text{(I-C-13)}$$

$$\frac{\partial w_{\hat{i}(g)}}{\partial \xi_{\hat{i}(r)}} = -\delta_{\hat{i}(g)\hat{i}(r)} - \left(\frac{\partial \Gamma_{\hat{i}(g)}}{\partial n_{\hat{i}(r)}}\right) n_{\hat{i}(r)}$$

$$\frac{\partial \Gamma_{\hat{i}(g)}}{\partial n_{\hat{i}(r)}} = \int_{0}^{\hat{\rho}} \frac{M_0}{RT\hat{\rho}} \left(\frac{\partial^2 p}{\partial n_{\hat{i}(g)} \partial n_{\hat{i}(r)}}\right) \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-C-14)}$$

b. <u>State Equations</u>

The state equations are used to calculate the thermodynamic state of our system in partial equilibrium when its equilibrium composition has been determined. Only the equations differing from those presented in Section I-B-4b will be given.

The equation for the specific volume of the mixture is written as

$$v(\pi_1, \ldots, \pi_{c+2}) = \frac{1}{\hat{\rho}} + \frac{1}{M_0}\left(\sum_{j=1}^{p} N_j V_j^* + \sum_{m=p+1}^{p'} N_m V_m^*\right) \qquad \text{(I-C-15)}$$

and the corresponding equation for the specific enthalpy as

$$M_0 h = \sum_{j=1}^{p} N_j H_j^* + \sum_{m=p+1}^{p'} N_m H_m^* + \sum_{i=1}^{s} n_i H_i^0 + pM_0/\hat{\rho} + RT(\epsilon - n) \qquad \text{(I-C-16)}$$

with the imperfection term defined by Eq. (I-B-77). The alternative expression for $h(\pi_1, \ldots, \pi_{c+2})$ is

$$M_0 h = \sum_{j=1}^{p} N_j H_j^* + \sum_{m=p+1}^{p'} N_m H_m^* + \sum_{j=p+1}^{c} H_{i*(j)}\left(q_j - \sum_{m=p+1}^{p'} \beta_{i'(m)j} N_m\right)$$
$$+ RT \sum_{i=1}^{s} \beta_{i,c+2} n_i + pM_0/\hat{\rho} + RT(\epsilon - n) \qquad \text{(I-C-17)}$$

and the equation for the frozen heat capacity of the mixture is

$$c_f = \sum_{j=1}^{p} N_j C^*_{pj} + \sum_{m=p+1}^{p'} N_m C^*_{pm} + \sum_{j=p+1}^{c} C^\circ_{pi*(j)}\left(q_j - \sum_{m=p+1}^{p'} \beta_{i(m)j} N_m\right)$$

$$+ \sum_{i=1}^{s} (\Delta_i C^\circ_p) n_i + R(\epsilon'_T - n) \qquad \text{(I-C-18)}$$

Equations (I-B-82) through (I-B-85) for the specific free energy must be altered because part of the composition is frozen. Summing the Gibbs' free energy of the condensed and gaseous phases of the mixture gives the specific free energy of the mixture as

$$M_0 g = \sum_{j=1}^{p} N_j \mu^*_j + \sum_{m=p+1}^{p'} N_m \mu^*_m + \sum_{i=1}^{s} n_i \mu_i \qquad \text{(I-C-19)}$$

Following a procedure with Eq. (I-C-19) similar to that presented for Eq. (I-B-82) gives the following expressions for the free energy

$$M_0 g = \sum_{j=1}^{p} \mu_j q_j + \sum_{j=p+1}^{c} \mu^*_{i(j)} q_j + \sum_{m=p+1}^{p'} N_m\left(\mu^*_m - \sum_{j=1}^{p} \beta_{i'(m)j} \mu^*_j - \sum_{j=p+1}^{c} \beta_{i'(m)j} \mu_{i*(j)}\right)$$

$$+ \sum_{g=s'+1}^{s} n_{\ell(g)}\left(\mu_{\ell(g)} - \sum_{j=1}^{p} \beta_{\ell(g)j} \mu^*_j - \sum_{j=p+1}^{c} \beta_{\ell(g)j} \mu_{i*(j)}\right) \qquad \text{(I-C-20)}$$

$$M_0 g/RT = \sum_{j=1}^{c} q_j \pi_j + \sum_{j=p+1}^{c} q_j (\pi_{c+1} + \mu^\circ_{i(j)}/RT)$$

$$+ \sum_{m=p+1}^{p'} N_m\left(\mu^*_m/RT - \sum_{j=1}^{c+1} \beta_{i'(m)j} \pi_j - \sum_{j=p+1}^{c} \beta_{i(m)j} \mu^\circ_{i*(j)}/RT\right) \qquad \text{(I-C-21)}$$

$$+ \sum_{g=s'+1}^{s} n_{\ell(g)}\left(\mu_{\ell(g)}/RT - \sum_{j=1}^{c+1} \beta_{\ell(g)j} \pi_j - \sum_{j=p+1}^{c} \beta_{\ell(g)j} \mu^\circ_{i*(j)}/RT\right)$$

The last two summation terms in Eqs. (I-C-20) and (I-C-21) are for the frozen species, and they disappear if the system is allowed to come to equilibrium.

c. State Conditions

The state conditions expressed in (I-C-9) by $F_{c+1} = F_{c+2} = 0$ define which one of the seven pairs of state variables (p_o, T_o), (p_o, h_o), (p_o, s_o), (p_o, v_o), (v_o, T_o), (v_o, e_o), or (v_o, s_o) is specified in the thermodynamic calculation. The equations used to define F_{c+1} and F_{c+2} for these seven different point calculations are obviously the same as those already presented in Section I-B-4c of the TIGER documentation and will therefore not be given here.

d. Partial Derivatives with Respect to the Iteration Parameters

Partial derivatives with respect to the iteration parameters are required to evaluate the derivatives $F_j/\partial\eta_k = -D_{jk}$ in the equation

$$\sum_{k=1}^{c+2} D^o_{jk}\Delta_k = F^o_j \qquad \text{(I-C-22)}$$

which are used to solve the set $F_j = 0 (j = 1, \ldots, c + 2)$ with the Newton-Raphson technique in the TIGER code.

(1) Partial Derivatives of the Mole Numbers

The equations for these partial derivatives are derived from the relationships

$$\xi_{\hat{i}(g)} = \ln n_{\hat{i}(g)} \qquad g = 1, \ldots, s' \qquad \text{(I-C-23)}$$

$$\xi_{\hat{i}(g)} = - g_{\hat{i}(g)} - \Gamma_{\hat{i}(g)} + \sum_{j=1}^{c+1} \beta_{\hat{i}(g)j}\eta_j \qquad g = 1, \ldots, s' \qquad \text{(I-C-24)}$$

by the procedure given in Section I-B-4d-1 of the TIGER documentation. They are therefore essentially the same as the equations given in I-B-4d-1 and can be readily obtained from them by changing i to $\hat{i}(g)$, with $g = 1, \ldots, s'$, and r to $\hat{i}'(r)$, with $r = 1, \ldots, s'$, where necessary, and including the additional conditions for the frozen species. It is necessary to change the i index in Eqs. (I-B-96), (I-B-97), (I-B-99) through (I-B-103), (I-B-107), and (I-B-108), the r index in Eqs. (I-B-101) through Eq. (I-B-103), and to add the following equations for frozen species,

$$\frac{\partial n_{\hat{i}(g)}}{\partial \eta_k} = 0 \qquad g = s' + 1, \ldots, s \qquad \text{(I-C-25)}$$

$$C_{\hat{i}(g),k} = 0 \qquad \begin{array}{l} g = s' + 1, \ldots, s \\ k = 1, \ldots, c + 2 \end{array} \qquad \text{(I-C-26)}$$

$$\frac{\partial N_m}{\partial \eta_k} = 0 \qquad \begin{array}{l} m = p + 1, \ldots, p' \\ k = 1, \ldots, c + 2 \end{array} \qquad \text{(I-C-27)}$$

It should be noted that although the subscript $\hat{i}(g)$ could be used in (I-B-110), there is no need to change the notation because the summation is taken over all the gaseous species.

(2) Partial Derivatives of the Pressure

The equations (I-B-111) through (I-B-117) for the pressure derivatives derived previously for systems in chemical equilibrium are also used for systems in partial equilibrium.

(3) Partial Derivatives for the Condensed Phases

The partial derivatives of the molar volume, molar enthalpy, and chemical potential of the condensed species in a partially frozen system are obtained by adding the derivatives of the frozen species to those given for the equilibrium species in (I-B-118) through (I-B-123). The equations for the frozen species are generated from Eq. (I-B-118) through Eq. (I-B-123) by changing $j(j = 1, \ldots, p)$ to $m(m = p + 1, \ldots p')$. The equations for V_m^* are given as an example.

$$\frac{p}{RT} \frac{\partial}{\partial \eta_k} V^*_m(p,T) = \beta^*_m \varphi_m \frac{\partial \ell n\, p}{\partial \eta_k} \qquad \begin{array}{l} k = 1,2, \ldots, c+1 \\ m = p+1, \ldots, p' \end{array} \qquad \text{(I-C-28)}$$

$$\frac{p}{RT} \frac{\partial}{\partial \eta_{c+2}} V^*_m(p,T) = \alpha^*_m \varphi^*_m + \beta^*_m \varphi^*_m \frac{\partial \ell n\, p}{\partial \eta_{c+2}} \qquad \ell n = p+1, \ldots, p' \qquad \text{(I-C-29)}$$

(4) Partial Derivatives of the Specific Volume of the Mixture

The derivatives of the specific volume are obtained by differentiating Eq. (I-C-15) with respect to the iteration parameters. They differ from the derivatives for the equilibrium mixture by a summation term over the condensed frozen species as shown, for example, in the following equations corresponding to Eqs. (I-B-127) through (I-B-129).

$$\frac{pM_O}{RT} \frac{\partial v}{\partial \eta_k} = \sum_{j=1}^{p} \varphi^*_j \frac{\partial N_j}{\partial \eta_k} + \frac{\partial \ell n\, p}{\partial \eta_k} \left(\sum_{j=1}^{p} N_j \beta^*_j \varphi^*_j + \sum_{m=p+1}^{p'} N_m \beta^*_m \varphi^*_m \right) \qquad \text{(I-C-30)}$$

$$\frac{pM_O}{RT} \frac{\partial v}{\partial \eta_{c+1}} = \sum_{j=1}^{p} \varphi^*_j \frac{\partial N_j}{\partial \eta_{c+1}} + \frac{\partial \ell n\, p}{\partial \eta_{c+1}} \left(\sum_{j=1}^{p} N_j \beta^*_j \varphi^*_j + \sum_{m=p+1}^{p'} N_m \beta^*_m \varphi^*_m \right) - \frac{pM_O}{RT\hat{\rho}} \qquad \text{(I-C-31)}$$

$$\begin{aligned} \frac{pM_O}{RT} \frac{\partial v}{\partial \eta_{c+2}} = {} & \sum_{j=1}^{p} \varphi^*_j \frac{\partial N_j}{\partial \eta_{c+2}} + \frac{\partial \ell n\, p}{\partial \eta_{c+2}} \left(\sum_{j=1}^{p} N_j \beta^*_j \varphi^*_j + \sum_{m=p+1}^{p'} N_m \beta^*_m \varphi^*_m \right) \\ & + \sum_{j+1}^{p} N_j \alpha^*_j \varphi^*_j + \sum_{m=p+1}^{p'} N_m \alpha^*_m \varphi^*_m + \frac{pM_O}{RT\overset{*}{\rho}} \end{aligned} \qquad \text{(I-C-32)}$$

(5) Partial Derivatives of the Specific Enthalpy of the Mixture

Here again, the partial derivatives of the specific enthalpy of the partially frozen mixture differ from those for the equilibrium mixture by summation terms for the frozen species. The equations are readily obtained by adding $-\partial \ln p/\partial\eta_k\left(\sum_{m=p+1}^{p'} N_m \alpha^*_m \sigma^*_m\right)$ to Eq. (I-B-131), by adding $-\partial \ln p/\partial\eta_{c+1}\left(\sum_{m=p+1}^{p'} N_m \alpha^*_m \sigma^*_m\right)$ to Eq. (I-B-132) and by adding $-\partial \ln p/\partial\eta_{c+2}\left(\sum_{m=p+1}^{p'} N_m \alpha^*_m \sigma^*_m\right)$ to Eq. (I-B-133).

(6) Partial Derivatives of the Specific Free Energy of the Mixture

The derivatives $\partial(M_0 g/RT)/\partial\eta_k$ are obtained by differentiating (I-C-21) as

$$\frac{\partial}{\partial\eta_k}\frac{M_0 g}{RT} = q_k + \sum_{m=p+1}^{p'} N_m\left(\frac{\partial \ln p}{\partial\eta_k}\sigma^*_m - \beta_{i'(m)k}\right) + \sum_{g=s'+1}^{s} n_{\hat{i}(g)}\left(\frac{\partial\Gamma_{\hat{i}(g)}}{\partial\eta_k} - \beta_{ik}\right) \qquad \text{(I-C-33)}$$

$$k = 1, \ldots, c$$

$$\frac{\partial}{\partial\eta_{c+1}}\frac{M_0 g}{RT} = \sum_{j=p+1}^{c} q_j + \sum_{m=p+1}^{p'} N_m\left(\frac{\partial \ln p}{\partial\eta_{c+1}}\sigma^*_m - \beta_{i'(m)c+1} - 1\right) + \sum_{g=s'+1}^{s} n_{\hat{i}(g)}\left(\frac{\partial\Gamma_{\hat{i}(g)}}{\partial\eta_{c+1}} - \beta_{\hat{i}(g)c+1}\right) \qquad \text{(I-C-34)}$$

$$\frac{\partial}{\partial\eta_{c+2}}\frac{M_0 g}{RT} = -\sum_{i=p+1}^{c} q_i\chi^\circ_{i*(j)} + \sum_{m=p+1}^{p'} N_m\left(\frac{\partial \ln p}{\partial\eta_{c+2}}\sigma^*_j - \chi^*_m + \sum_{j=p+1}^{c}\beta_{i'(m)j}\chi^\circ_{i*(j)}\right) + \sum_{g=s'+1}^{s} n_{\hat{i}(g)}\left(\frac{\partial\Gamma_{\hat{i}(g)}}{\partial\eta_{c+2}} - \chi^\circ_{\hat{i}(g)} + \sum_{j=p+1}^{c}\beta_{\hat{i}(g)j}\chi^\circ_{i*(j)}\right) \qquad \text{(I-C-35)}$$

e. The Nonequilibrium Partial Derivatives

The identities for the complete set of partial derivatives (C_v, α, β) given in Section I-B-4e of the TIGER documentation apply to any system whose thermodynamic state can be described by two independent variables. Consequently the equations given in I-B-4e in terms of the iteration parameters can be used to evaluate these derivatives for the system in partial equilibrium when care is taken to account for the fact that part of the composition is frozen. This fact is automatically taken account of in TIGER, however, because the derivatives $(\partial\eta_k/\partial\eta_{c+2})_{\eta_{c+1}}$ and $(\partial\eta_k/\partial\eta_{c+1})_{\eta_{c+2}}$ used in the evaluation are themselves evaluated with the values of C_{ik} calculated for the equilibrium species and with the values of $C_{ik} = 0$ for the frozen species.

f. Phase Changes

The treatment of phase changes for systems in partial equilibrium is exactly the same as that presented for equilibrium systems in Sections I-B-4f through I-B-4h of the TIGER documentation.

I-D. THEORETICAL BASIS FOR NONEQUILIBRIUM CALCULATIONS IN COMPLETELY FROZEN SYSTEMS

1. Introduction

The method for computing the thermodynamic state of a nonideal heterogeneous system with a frozen composition will be considered as a limiting case of the method described in Section I-C for computing the state in systems with a partially frozen composition. Here again the nonequilibrium states are considered to be in mechanical and thermal equilibrium and the condensed species are allowed to change phase as in equilibrium calculations, but the mole numbers of all the species are fixed. In any one of the seven point calculations for determining the thermodynamic state, the composition is chosen to satisfy the stoichiometric conditions, and the calculation is performed with the concentrations of the species fixed.

2. Calculations with a Completely Frozen Composition

The completely frozen system is described in terms of the indices introduced to label species in Section I-B-3 of the TIGER documentation by the conditions $p = s' = 0$ and $p' = t - s$. Consequently, the equations used to perform point calculations for completely frozen systems are readily obtained by setting $p = s' = 0$ and $p' = t - s$ in the equations presented in Section I-C-2 for the partially frozen system. For this reason they will not be given here. The equations for C_v, α, and β are the same as those presented in Section I-B-4e of the documentation for equilibrium systems. In this case, however, the derivatives are evaluated with $C_{ik} = 0$ for $i = 1, \ldots, s$ and $k = 1, \ldots, c + 2$ because all the species are frozen.

I-E. INCORPORATION OF AN EQUATION OF STATE INTO TIGER

1. Gaseous Equation of State

The incorporation of a nonideal gaseous equation of state into TIGER to perform the calculations discussed in the previous sections is by no means a trivial task. It is necessary to use the imperfection term Φ to derive expressions for the thermodynamic quantities required to perform the calculations. These quantities include the frozen partial derivatives of Φ, $\partial \ln \Phi/\partial \ln T$, $\partial \ln \Phi/\partial \ln \hat{\rho}$, and $\partial \ln \Phi/\partial n_i$; the imperfection integrals ϵ and ϵ'_T; and the activity coefficients Γ_i and their frozen partial derivatives. Equations for these quantities are derived with the Becker, Kistiakowsky, Wilson (BKW) relationship to demonstrate the incorporation of a nonideal equation of state into the code. The corresponding expressions for the JCZ2 and JCZ3 equations of state developed by Jacobs, Cowperthwaite, and Zwisler are well documented in the final report, "Improvement and Modification to TIGER Code" written under Contract N60921-72-C-0013, and will therefore not be presented here.

The form of the Becker equation of state proposed by Halford, Kistiakowsky, and Wilson[1] and modified by Fickett and Cowan[2] has become known as the BKW equation of state. It is written here in terms of the universal constants $\hat{\alpha}$, $\hat{\beta}$, and $\hat{\theta}$ as

$$\begin{aligned} p &= nRT\hat{\rho}\Phi/M_0 \\ \Phi &= \Phi(x) = 1 + xe^{\hat{\beta}x} \\ x &= k\hat{\rho}/M_0(T + \hat{\theta})^{\hat{\alpha}} \end{aligned} \qquad \text{(I-E-1)}$$

and

$$k = \hat{\kappa} \sum_{i=1}^{s} n_i k_i \qquad \text{(I-E-2)}$$

where $\hat{\kappa}$ is a scale factor introduced for computational convenience, $\hat{\kappa} k_i$ denotes the covolume constant of the i^{th} gaseous constituent, and k denotes the covolume of the mixture. Differentiating Eq. (I-E-1) leads to the following equations for the frozen derivatives of Φ,

$$\frac{\partial \ln \Phi}{\partial \ln T} = -\frac{\hat{\alpha} T}{(T + \hat{\theta})} \frac{d \ln \Phi}{d \ln x} = \frac{\partial \ln p}{\partial \ln T} - 1 \qquad \text{(I-E-3)}$$

$$\frac{\partial \ln \Phi}{\partial \ln \hat{\rho}} = \frac{d \ln \Phi}{d \ln x} = \frac{\partial \ln p}{\partial \ln \hat{\rho}} - 1 \qquad \text{(I-E-4)}$$

$$\frac{n \partial \ln \Phi}{\partial n_i} = \frac{n \hat{\kappa} k_i}{k} \frac{d \ln \Phi}{d \ln x} = n \frac{\partial \ln p}{\partial n_i} - 1 \qquad \text{(I-E-5)}$$

with

$$\frac{d \ln \Phi}{d \ln x} = \frac{(1 + \hat{\beta} x) x e^{\hat{\beta} x}}{1 + x e^{\hat{\beta} x}} \qquad \text{(I-E-6)}$$

Let e_g denote the internal energy of the gas mixture contained in a unit mass of mixture, and let E_i^0 denote the molar internal energy of the i^{th} constituent in its standard state taken as the hypothetical ideal gas at unit pressure. Then the imperfection integral ϵ for the gas mixture[3] can be written as

$$\epsilon = \frac{M_0}{RT}\left(e_g - e_g^0\right) = \frac{M_0}{RT} \int_0^{\hat{\rho}} \frac{p}{\hat{\rho}} \left[1 - \frac{\partial \ln p}{\partial \ln T}\right] \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-E-7)}$$

with

$$e_g^0 = \frac{1}{M_0} \sum_{i=1}^{s} n_i E_i^0 \qquad \text{(I-E-8)}$$

and the integration performed along an isotherm with the composition fixed as that of the mixture.*

Performing the integration in Eq. (I-E-7) with Eqs. (I-E-1) to (I-E-3) gives the imperfection integral ϵ for the BKW equation of state as

$$\epsilon = \frac{n\hat{\alpha}T}{T+\hat{\theta}} \int_1^{\Phi} \alpha\Phi = \frac{n\hat{\alpha}T}{T+\hat{\theta}}\, xe^{\hat{\beta}x} \qquad \text{(I-E-9)}$$

and the corresponding imperfection integral ϵ_T' is obtained by differentiating (Eq. I-E-9) partially with respect to T as

$$\epsilon_T' = \frac{n\hat{\alpha}T}{T+\hat{\theta}} \left[2 - \frac{T}{T+\hat{\theta}} (1 + \hat{\alpha} + \hat{\alpha}\hat{\beta}x)\right] xe^{\hat{\beta}x} \qquad \text{(I-E-10)}$$

The expression for the activity coefficient is derived with the following equation introduced earlier

$$\Gamma_i = \int_0^{\hat{\rho}} \left[\frac{M_O}{RT\hat{\rho}} \frac{\partial p}{\partial n_i} - 1\right] \frac{d\hat{\rho}}{\hat{\rho}} \qquad \text{(I-E-11)}$$

Performing the integration in Eq. (I-E-11) with Eqs. (I-E-1), (I-E-2), and (I-E-5) gives the activity coefficient Γ_i for the BKW equation of state as

$$\Gamma_i = \frac{1}{\hat{\beta}} (e^{\hat{\beta}x} - 1) + \frac{n\hat{\chi}k_i}{k}\, xe^{\hat{\beta}x} \qquad \text{(I-E-12)}$$

And differentiation of Eq. (I-E-12) gives the corresponding equations for the partial derivatives of Γ_i needed for the equilibrium calculation as

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* See Ref. 3 for a careful discussion of nonideal mixtures and the standard state.

$$\frac{\partial\Gamma_i}{\partial \ln T} = -\frac{\hat{\alpha}T}{T+\hat{\theta}}\left[1+\frac{n\alpha k_i}{k}(1+\hat{\beta}x)\right]xe^{\hat{\beta}x} \quad \text{(I-E-13)}$$

$$\frac{\partial\Gamma_i}{\partial \ln \hat{\rho}} = \left[1+\frac{n\hat{\alpha}k_i}{k}(1+\hat{\beta}x)\right]xe^{\hat{\beta}x} \quad \text{(I-E-14)}$$

and

$$\frac{\partial\Gamma_i}{\partial n_{i'}} = \left[\frac{\hat{\alpha}(k_i + k_{i'})}{k} + \frac{n\hat{\alpha}^2 k_i k_{i'}}{k^2}\hat{\beta}x\right]xe^{\hat{\beta}x} \quad \text{(I-E-15)}$$

The thermodynamic identities

$$\frac{\partial\Gamma_i}{\partial \ln \hat{\rho}} = \frac{M_0 p}{RT\hat{\rho}}\frac{\partial \ln p}{\partial n_i} - 1 \quad \text{(I-E-16)}$$

$$\frac{\partial\epsilon}{\partial \ln \hat{\rho}} = \frac{M_0 p}{RT\hat{\rho}}\left[1 - \frac{\partial \ln p}{\partial \ln T}\right] \quad \text{(I-E-17)}$$

and

$$\frac{\partial\epsilon}{\partial n_i} = -\frac{\partial\Gamma_i}{\partial \ln T} \quad \text{(I-E-18)}$$

are useful for checking the expressions derived for Γ_i and ϵ with a particular $p = p(\hat{\rho}, T, n_1, \ldots, n_s)$ equation of state.

2. Condensed Equations of State

Since routines for condensed equations of state are still being developed, this section will be completed at a later date.

REFERENCES I-E

1. Kistiakowsky, G. B., and Wilson, E. B. Jr., OSRD Report No. 114 (1941).
2. Cowan, R. O., and Fickett, W. T., Chem. Phys. <u>24</u>, 932 (1956).
3. Beattie, T. A., Chem. Rev. <u>44</u>, 141 (1941).

I-F. ONE-DIMENSIONAL DETONATION

1. Chapman-Jouguet Theory of Detonation

a. Brief History

The one-dimensional model of a detonation wave was formulated by D. Chapman,[1] and independently by E. Jouguet,[2] at the turn of the century. Its purpose was to account for wave propagation in combustible gases at speeds of the order of 2000 meters per second. Since experiments had shown the propagation to be supersonic, the front of the detonation wave was assumed to be a reactive shock discontinuity. The exothermic process in the discontinuity was viewed as maintaining the velocity of the wave, and a thermodynamic-hydrodynamic theory based on this assumption was developed to calculate that velocity. The theory combines the energy yield of the combustion reaction with the conservation laws of mass, momentum and energy. These well established laws, together with the equation of state and the Chapman-Jouguet hypothesis, define the problem and allow completion of the calculations.

Calculated velocities in gaseous explosives[3] are in good agreement with experiment, which is partly to be explained by the fact that the perfect gas equation of state can be validly applied. Successful calculations of detonation velocity in gases led Schmidt[4] to apply the Chapman-Jouguet theory to condensed explosives. Here, however, an equation of state at several hundred kilobars is required, but in general no satisfactory equations are available in this pressure range.

b. Rankine-Hugoniot Relationships

The Rankine-Hugoniot relationships express the continuity of mass, momentum, and energy across a shock discontinuity. Since the relationships are well known,[5] they will be presented without derivation. Let D, u, and $\rho = 1/v$ denote shock velocity, particle velocity, and density, and let the subscripts 0 and 1 denote values at the bottom and top of the shock discontinuity. Then the Rankine-Hugoniot relationships for a shock propagating at velocity D in a stationary material $(u_0 = 0)$ can be written as

$$\rho_0 D = \rho_1 (D - u_1) \qquad \text{(I-F-1)}$$

$$p_1 - p_0 = \rho_0 D u_1 \qquad \text{(I-F-2)}$$

$$p_1 u_1 = \rho_0 D (e_1 - e_0 + \tfrac{1}{2} u_1^2) \qquad \text{(I-F-3)}$$

Equation (I-F-1) expresses the conservation of mass, Eq. (I-F-2) expresses the balance of momentum, and Eq. (I-F-3) expresses the first law of thermodynamics under the assumption that the shock process is adiabatic. Moreover, since the shock process is irreversible, the second law of thermodynamics is expressed by the following inequality for the specific entropy, $s_1(e_1, \rho_1) > s_0(e_0, \rho_0)$. Combination of Eqs. (I-F-1) and (I-F-2) gives the equation

$$p_1 - p_0 = (D/v_0)^2 (v_0 - v_1) \qquad \text{(I-F-4)}$$

for a straight line in the $(p - v)$ plane that passes through the initial conditions (p_0, v_0) and is called the Rayleigh line. Combination of Eqs. (I-F-1), (I-F-2) and (I-F-3) gives the equation

$$e_1 - e_0 = \tfrac{1}{2} (p_1 + p_0)(v_0 - v_1) \qquad \text{(I-F-5)}$$

which relates the thermodynamic variables across the shock and is called the Hugoniot equation. An initial condition (e_0, p_0, v_0), an (e-p-v) equation of state of shocked material, and the Hugoniot equation define a curve in the (p-v) plane called the Hugoniot curve centered at (p_0, v_0). The compressive portion of the Hugoniot curve specifies the locus of states attainable from an initial state (e_0, p_0, v_0) by shocks with different velocities. For a nonreactive shock, the Hugoniot curve passes through its center point (p_0, v_0), but this is not so for a reactive shock because of the energy change in the reaction process. In calculating Hugoniot curves with Eq. (I-F-5), the heat of reaction is automatically accounted for by the difference in the specific internal energies of the standard states of the reactants and the products of combustion.

For exothermic waves, the compressive part of the Hugoniot curve is called the detonation branch of the Hugoniot, and the expansive part is called the deflagration branch. Since a shocked state must satisfy Eqs. (I-F-4) and (I-F-5), the intersection of the Hugoniot curve centered at (p_0, v_0) and the Rayleigh line of slope $-(D/v_0)^2$ passing through (p_0, v_0) defines the thermodynamic state (e_1, p_1, v_1) behind either a nonreactive or reactive shock discontinuity traveling with constant velocity D in stationary material with pressure p_0 and specific volume v_0.

Since the slope of the Rayleigh line must be positive to satisfy the conservation of mass, and momentum however, the detonation branch of the Hugoniot curve is terminated at the point where $e_1 = e_0$ and $v_1 = v_0$, and the deflagration branch of the Hugoniot curve is terminated at the point where $h_1 = h_0$ and $p_1 = p_0$. These termination points are for obvious reasons called the constant volume explosion point, and the constant pressure combustion point, and will be denoted by the superscripts e and c. The pressure at the constant volume explosion point can then be written formally as $p_e = p(e_0, v_0)$, and the volume at the constant pressure combustion point as $v_c = v(h_0, p_0)$.

c. Chapman-Jouguet Hypothesis

Since the states on a Hugoniot curve centered at (p_0, v_0) represent the locus of states connected to an initial state (e_0, p_0, v_0) by shocks traveling at different velocities, an additional condition is needed to determine a unique detonation velocity. In other words, the three conservation laws, together with a complete equation of state for detonation products in chemical equilibrium, are insufficient to calculate the variables D, u_1, p_1, ρ_1, e_1, which characterize the detonation process. Since there are five unknowns, but only four equations to calculate them, an additional equation is needed to complete the theory. The fifth equation, known as the Chapman-Jouguet condition

$$D = u_1 + c_1 \qquad \text{(I-F-6)}$$

where c_1 is the velocity of sound in the detonation products at the top of the shock discontinuity, follows directly from the Chapman-Jouguet hypothesis that the head of a rarefaction wave at the shock discontinuity travels at the same speed as the shock itself.

It follows from the Chapman-Jouguet condition that the stable detonation wave is represented in the (p-v) plane by the Rayleigh line (see Figure I-1) through (p_0, v_0) that has a point of tangency with the Hugoniot curve. This point of tangency defines the compressed state at the front of the detonation wave and is called the Chapman-Jouguet point. It is of interest to derive these properties of the Chapman-Jouguet detonation. Subjecting the differential forms of the (e-p-v) equation of state and the Hugoniot Eq. (I-F-5) to the condition that de is a perfect differential gives the following equation for the slope of a Hugoniot curve centered at (p_0, v_0):

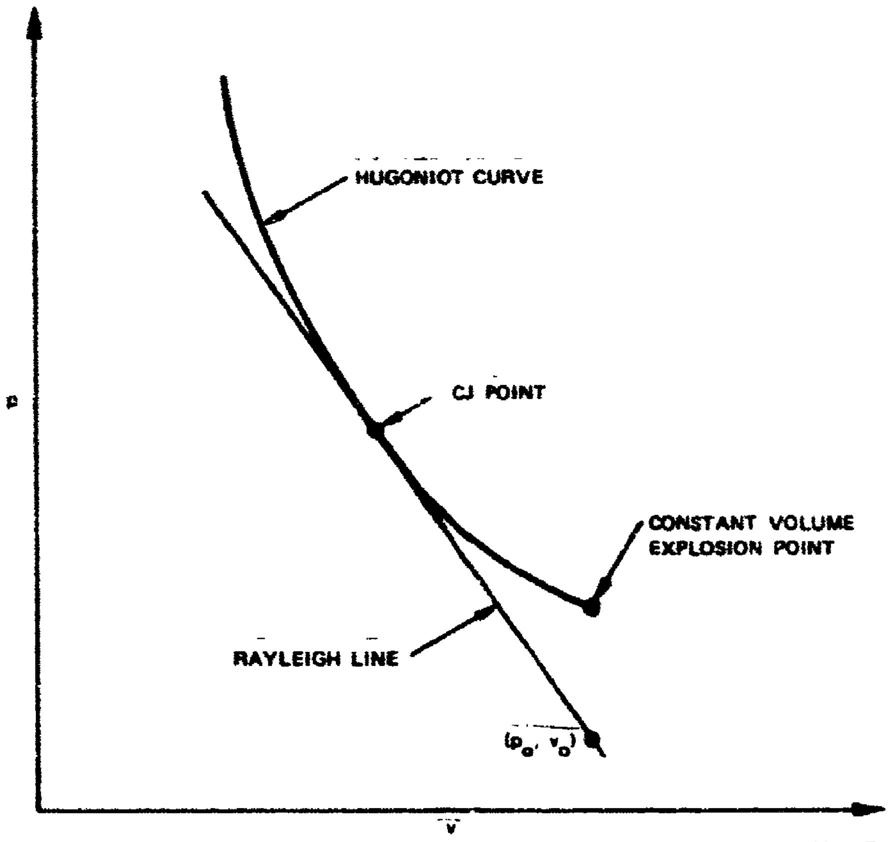

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FIGURE I-1 TANGENCY OF THE RAYLEIGH LINE TO THE PRODUCT HUGONIOT CURVE AT THE CHAPMAN-JOUGUET (CJ) POINT

$$\frac{dp}{dv} = -\frac{(\partial e/\partial v)_p + \frac{1}{2}(p_1 + p_0)}{(\partial e/\partial p)_v - \frac{1}{2}(v_0 - v_1)} \qquad \text{(I-F-7)}$$

Equation (I-F-7) gives $(\partial e/\partial p)_v - \frac{1}{2}(v_0 - v_1) \neq 0$ as a necessary condition for the slope of the Hugoniot curve to be finite. Elimination of $(\partial e/\partial v)_p$ and $(p_1 + p_0)$ from Eq. (I-F-7) with the identity

$$\left(\frac{c}{v}\right)^2 = -\left(\frac{\partial p}{\partial v}\right)_s = \frac{p + (\partial e/\partial v)_p}{(\partial e/\partial p)_v} \qquad \text{(I-F-8)}$$

and the equations for the Rayleigh line written as

$$(p_1 - p_0) = \{(D - u_1)/v_1\}^2 (v_0 - v_1)$$

gives the equation

$$\frac{dp}{dv} = -\frac{(c_1/v_1)^2(\partial e/\partial p)_v - [(D - u_1)/v_1]^2 \frac{1}{2}(v_0 - v_1)}{(\partial e/\partial p)_v - \frac{1}{2}(v_0 - v_1)} \qquad \text{(I-F-9)}$$

Since $(\partial e/\partial p)_v - \frac{1}{2}(v_0 - v_1) \neq 0$, combining Eq. (I-F-9) with the Chapman-Jouguet condition Eq. (I-F-6), and Eq. (I-F-8) gives the equation

$$\frac{dp}{dv} = -\left(\frac{c_1}{v_1}\right)^2 = \left(\frac{\partial p}{\partial v}\right)_s \qquad \text{(I-F-10)}$$

Thus, the Rayleigh line through (p_0, v_0) that satisfies the Chapman-Jouguet condition is tangent to the Hugoniot curve centered at (p_0, v_0) and is tangent also to the isentrope passing through the Chapman-Jouguet point. In other words, the Hugoniot curve has a first-order point of contact with the isentrope passing through the Chapman-Jouguet point. It follows from the tangency condition that the Chapman-Jouguet detonation wave propagates with a minimum velocity. The Chapman-Jouguet hypothesis leads to the conclusion that all unsupported reactive shock discontinuities satisfying the conservation laws of mass, momentum, and energy are unstable with respect to the discontinuity propagating at the lowest velocity.

2. States Attainable from the Chapman-Jouguet State

Other processes resulting from the interaction of a detonation wave with its surroundings are important for understanding the behavior of explosives. A particular interest in states attained by the reflection of a shock on the one hand, and of a rarefaction wave on the other hand, into a detonation leads, respectively, to the construction of the Hugoniot curve of detonation products centered at the Chapman-Jouguet point and to the isentrope of detonation products through the Chapman-Jouguet point. This Hugoniot curve centered at the Chapman-Jouguet point specifies the maximum pressure in detonations reflected from metals with increasing shock impedance; the isentrope specifies the succession of states attained in detonation products expanding into the atmosphere.

3. Equilibrium Chapman-Jouguet Calculations with an Arbitrary Equation of State

Our treatment of CJ states will be based on more general expressions of the jump conditions than those given in Section I-D-1b. Let w denote the mass velocity with respect to the reactive shock discontinuity, and let the subscripts $_0$ and $_1$ again denote conditions at the bottom and the top of this discontinuity. Then the Rankine-Hugoniot jump conditions expressing the balance of mass, momentum, and energy across the discontinuity can be written as:

$$\rho_1 w_1 = \rho_0 w_0 \qquad \text{(I-F-11)}$$

$$p_1 + \rho_1 w_1^2 = p_0 + \rho_0 w_0^2 \qquad \text{(I-F-12)}$$

$$h_1 + \tfrac{1}{2} w_1^2 = h_0 + \tfrac{1}{2} w_0^2 \qquad \text{(I-F-13)}$$

The Chapman-Jouguet condition is expressed by the equation

$$w_1^2 = c_1^2 \qquad \text{(I-F-14)}$$

with the sound speed c defined by the equations

$$c^2 = -v^2(\partial p/\partial v)_s = \varkappa pv \qquad \text{(I-F-15)}$$

and the adiabatic index $\varkappa$ related to the thermodynamic coefficients α and β by the following expression given previously in Section I-B-4e,

$$\varkappa = -\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_s = -\frac{C_p}{C_v}\,\frac{v}{p}\left(\frac{\partial p}{\partial v}\right)_T = \frac{\alpha + 1}{\beta} \qquad \text{(I-F-16)}$$

Combination of Eqs. (I-F-11) and (I-F-12) leads to the equation

$$1 - \frac{p_0}{p_1} = \frac{w_1^2}{p_1 v_1}\left(\frac{v_0}{v_1} - 1\right) \qquad \text{(I-F-17)}$$

and combination of Eqs. (I-F-11) through (I-F-13) leads to the Hugoniot equation (I-F-5), ${}_1 - e_0 = \frac{1}{2}(p_1 + p_0)(v_0 - v_1)$, relating the thermodynamic states connected by the shock discontinuity. Equations (I-F-14), (I-F-15), and (I-F-17) can then be combined to give the following expression

$$v_1 = v_0\left[\frac{1}{\varkappa_1}\left(1 - \frac{p_0}{p_1}\right) + 1\right]^{-1} \qquad \text{(I-F-18)}$$

for the CJ condition in terms of thermodynamic quantities only. Chapman-Jouguet states can therefore be considered as thermodynamic states defined by the Eqs. (I-F-5) and (I-F-18). Since TIGER was designed to perform thermodynamic calculations, these equations are used to compute CJ points in the code, but an iterative procedure must be used to solve them because e_1 and $\varkappa_1$ cannot be evaluated at a (p_1, v_1) point unless the composition is known.

The equations used to step forward from one equilibrium thermodynamic point calculation to the next in the iterative scheme will now be derived. Let superscript prime denote a point where the thermodynamic state has been calculated and the values of $\{e_1', p_1', v_1', T_1', \alpha_1', \beta_1', \ldots\}$ are known. Then Eq. (I-F-18) and an approximation to the Hugoniot equation are used with these values to generate the two state variables that are required to perform the next thermodynamic point calculation. Let $\Delta p = p_1 - p_1'$ and $\Delta v = v_1 - v_1'$, then combination of Eq. I-F-5) with the Taylor series expansion for e_1 about the point (p_1', v_1'),

$$e_1 = e_1' + \alpha_1' p_1' \Delta v + \beta_1' v_1' \Delta p \qquad \text{(I-F-19)}$$

gives the equation

$$2(e_1' - e_0) - (p_1' + p_0)(v_0 - v_1') = [v_0 - v_1' - 2\beta_1' v_1']\Delta p - [p_0 + p_1' + 2\alpha_1' p_1']\Delta v - \Delta p \Delta v \qquad \text{(I-F-20)}$$

which on rearrangement gives the approximation to the Hugoniot equation that is used in the code

$$\Delta p = \frac{2(e_1' - e_0) - (p_1' + p_0)(v_0 - v_1) + 2p_1' \alpha_1' \Delta v}{v_0 - v_1 - 2v_1' \beta_1'} \qquad \text{(I-F-21)}$$

Equation (I-F-21) is used to step forward in pressure, and Eq. (I-F-18) written as

$$v_1 = v_0 \left[\frac{1}{\chi_1'}\left(1 - \frac{p_0}{p_1'}\right) + 1\right]^{-1} \qquad \text{(I-F-22)}$$

is used to step forward in volume in performing the sequence of thermodynamic calculations to determine the CJ point.

The procedure for calculating the CJ point on the detonation branch of an equilibrium products Hugoniot curve of a condensed explosive is described below. The case when no problems are encountered in the calculations is discussed first, and then the types of problems that arise in such calculations.

derived. Let superscript prime denote a point where the thermodynamic state has been calculated and the values of $\{e_1', p_1', v_1', T_1', \alpha_1', \beta_1', \ldots\}$ are known. Then Eq. (I-F-18) and an approximation to the Hugoniot equation are used with these values to generate the two state variables that are required to perform the next thermodynamic point calculation. Let $\Delta p = p_1 - p_1'$ and $\Delta v = v_1 - v_1'$, then combination of Eq. I-F-5) with the Taylor series expansion for e_1 about the point (p_1', v_1'),

$$e_1 = e_1' + \alpha_1' p_1' \Delta v + \beta_1' v_1' \Delta p \qquad \text{(I-F-19)}$$

gives the equation

$$\begin{aligned} 2(e_1' - e_0) - (p_1' + p_0)(v_0 - v_1') &= [v_0 - v_1' - 2\beta_1' v_1']\Delta p \\ &\quad - [p_0 + p_1' + 2\alpha_1' p_1']\Delta v - \Delta p \Delta v \end{aligned} \qquad \text{(I-F-20)}$$

which on rearrangement gives the approximation to the Hugoniot equation that is used in the code

$$\Delta p = \frac{2(e_1' - e_0) - (p_1' + p_0)(v_0 - v_1) + 2p_1'\alpha_1'\Delta v}{v_0 - v_1 - 2v_1'\beta_1'} \qquad \text{(I-F-21)}$$

Equation (I-F-21) is used to step forward in pressure, and Eq. (I-F-18) written as

$$v_1 = v_0\left[\frac{1}{\chi_1}\left(1 - \frac{p_0}{p_1'}\right) + 1\right]^{-1} \qquad \text{(I-F-22)}$$

is used to step forward in volume in performing the sequence of thermodynamic calculations to determine the CJ point.

The procedure for calculating the CJ point on the detonation branch of an equilibrium products Hugoniot curve of a condensed explosive is described below. The case when no problems are encountered in the calculations is discussed first, and then the types of problems that arise in such calculations.

Determination of the CJ point involves the sequential performance of an (e,v) point calculation, a (T,v) point calculation, and a series of (p,v) point calculations. The (e,v) calculation is performed first with $e_1 = e_0$ and $v_1 = v_0$ to obtain the constant volume explosion point $(e_0, v_0, p_e', T_e', \alpha_e', \beta_e', \ldots)$ as a first approximation to the CJ point. The (T,v) calculation is then performed to obtain a better approximation to it. Originally the (T,v) calculation was performed with $T_1 = T_e'$ and $v_1 = v_0 \chi_e'/(\chi_e' + 1)$, obtained by ignoring the pressure term p_0/p_e' in Eq. (I-F-22), but experience has shown that a better approximation to the CJ state is obtained by choosing $T_1 = T_e'$ and $v_1 \geq 0.85\ v_0$.

The series of (p,v) calculations are performed next to determine the CJ point. The first (p,v) point calculation is performed with values of p_1 and v_1 generated from Eq. (I-F-22) and with the values of the thermodynamic variables obtained in the (T,v) calculation. Specifically, Eq. (I-F-22) is first used to calculate v_1, and then Eq. (I-F-21) is used to calculate the corresponding value of p_1. The state variables calculated at the first (p,v) point are then substituted into Eqs. (I-F-22) and (I-F-21) to generate the values of p_1 and v_1 for the second (p,v) calculation, and the process is contained until the CJ point is obtained. When $|\Delta v/v_1| < 10^{-8}$ and $|\Delta p/p_1| \leq 10^{-8}$ between successive calculations, it is assumed that the CJ point has been calculated successfully. It is clear that the method for calculating the CJ point on the detonation branch of the Hugoniot can easily be modified to calculate the CJ point on the deflagration branch of the Hugoniot curve.

The original iterative scheme for determining CJ points by performing a series of (p,v) point calculations was developed for gases by S. R. Brinkley, Jr. A series of computational problems encountered with

CJ calculations when the code was being developed, however, led to the conclusion that this scheme was unsatisfactory for condensed explosives. L. B. Seely solved these problems by introducing the (T,v) point calculation to obtain a better approximation to the CJ point in the early stages of the iterative procedure.

Calculation of the CJ point becomes a problem when the code cannot compute the constant volume explosion state or the state at one of the (p,v) points in the series of (p,v) calculations. The constant volume explosive state could not be computed for nonideal explosive compositions because it lay in the mixed phase region of one of the condensed constituents. No difficulties have been found with these compositions, however, since the revision of the routine for handling systems containing multiple condensed species capable of changing phase.

Difficulties in the (p,v) points calculations were found to arise for the following reasons: (1) the π's do not converge, (2) the temperature is out of range, (3) the n_i's do not converge, (4) the code cannot find a set of condensed components, and (5) the set of equations, $F_j = 0$ with $j = 1, \ldots, c + 2$, has no solution because of a local minimum. In the first three cases, the step size Δv taken to reach the incalculable point is halved until convergence is obtained, and then the series of (p,v) point calculations is continued. The last two cases arise when the values p and v chosen for the (p,v) calculation are incompatible with the equilibrium states of the system. In either case, a (p,T) calculation is performed to obtain an equilibrium (p,v) point, and the iterative procedure with (p,v) points is continued.

4. Construction of the Hugoniot Curve for an Arbitrary Equation of State

The iterative procedure for constructing a point on the Hugoniot curve by performing a series of (p,v) calculations when either the volume or pressure is specified is based on Eq. (I-F-20).

Consider first the case when the thermodynamic state at a (p′,v′) point is known, and the Hugoniot point at a specified volume v_1 is required. Equation (I-F-21) is used to generate the first approximation to the Hugoniot point. Then the equation

$$\Delta p = \frac{2(e_1{}' - e_0) - (p_1{}' + p_0)(v_0 - v_1)}{v_0 - v_1(1 + 2\beta_1{}'} \qquad \text{(I-F-23)}$$

obtained by setting $\Delta v = 0$ in Eq. (I-F-21) is used to generate subsequent approximations. The iteration process is started by substituting the known values of Δv, e', p', α', and β' into Eq. (I-F-21) to obtain the value of p_1 for the next (p_1, v_1) calculation. This procedure is continued, using Eq. (I-F-23), until the Hugoniot point is obtained. When $|\Delta p/p_1| \leq 10^{-6}$ between successive calculations, it is assumed that the Hugoniot point has been calculated successfully. The Hugoniot curve passing through the point calculated at v_1 can be readily constructed by performing a series of such calculations for different values of v. But then it is convenient to use the equation

$$\Delta p = \frac{[p_1{}'(1 + 2\alpha_1{}') + p_0]\ \Delta v}{v_0 - v_1(1 + 2\ \beta_1{}')} \qquad \text{(I-F-24)}$$

rather than Eq. (I-F-22) to find the value of p_1 for the first (p,v) calculation because the original state that is known lies on the Hugoniot curve.

Now consider the case when the thermodynamic state at a (p', v') point is known and the Hugoniot point at a specified pressure p_1 is required. A similar procedure is followed with p_1 fixed and values of v_1 evaluated, using the equations for Δv obtained from (I-F-20). The value of v_1 for the first (p_1, v_1) calculation is obtained from the equation

$$\Delta v = \frac{(p_1 + p_0)(v_0 - v_1') - 2(e_1' - e_0 + \beta_1' v_1' \Delta p)}{p_0 + p_1 + 2\alpha_1' p_1'} \qquad \text{(I-F-25)}$$

corresponding to Eq. (I-F-21), and values of v for subsequent (p_1, v) calculations are obtained from the equation

$$\Delta v = \frac{(p_1 + p_0)(v_0 - v_1') - 2(e_1' - e_0)}{p_0 + p_1(1 + 2\alpha_1')} \qquad \text{(I-F-26)}$$

corresponding to Eq. (I-F-23). When the known point lies on the Hugoniot curve, the value of v for the first (p_1, v) calculation is obtained from the equation

$$\Delta v = \frac{[v_0 - v_1'(1 + 2\beta_1')]\Delta p}{p_0 + p_1(1 + 2\alpha_1')} \qquad \text{(I-F-27)}$$

corresponding to Eq. (I-F-24). As in the previous case, Hugoniot points are assumed to be determined when $|\Delta v/v_1| \le 10^{-8}$ between successive (p_1, v_1) calculations.

Construction of the Hugoniot curve becomes a problem when a (p, v) point is incalculable because of discontinuities associated with a condensed species disappearing from the system. In one case, the incalculability arises because the code cannot find a set of condensed components; in the other, because there is no solution to the set of $F_J = 0$ equations for the specified values of p and v. In either case, the values of p and v chosen for the (p,v) calculation are incompatible with the equilibrium states of the system, and the problem is treated in the same way as in the CJ routine. A (p,T) calculation is performed to obtain an equilibrium (p,v) point, and then the iterative procedure with (p,v) points is continued.

5. Construction of an Isentrope for an Arbitrary Equation of State

An isentrope is readily constructed by performing either a series of (s,v) or a series of (s,p) point calculations with a constant value of s. The CJ isentrope is obtained by starting the calculations at the CJ point.

6. Frozen Chapman-Jouguet Calculations with an Arbitrary Equation of State

Frozen CJ states are readily calculated in TIGER by performing nonequilibrium point calculations in the CJ routine with the partial freeze options described in Section I-C of the TIGER documentation. The frozen CJ states calculated are therefore those in mechanical and thermal equilibrium, with part of the composition frozen and part of it in chemical equilibrium. The mole numbers of the frozen species are fixed, but frozen condensed species are allowed to change phases according to their equations of state as in equilibrium calculations. Frozen calculations can easily be performed without phase changes by removing the equation of state of one of the phases from the library.

The SPECIAL routine for computing nonequilibrium CJ states with two frozen constituents was developed to provide Picatinny Arsenal with a capability to investigate nonideal explosives. It was developed primarily for computing frozen CJ states with part of the explosive composition unreacted, but it can obviously be used for computing CJ states when the explosive is completely decomposed and two of the reaction products are frozen. The reaction coordinates λ_1 and λ_2 were introduced to describe the partially frozen nonequilibrium states. The coordinates $\lambda_i (i = 1,2)$ were chosen to satisfy the conditions $0 \le \lambda_i < 1$ by setting $\lambda_i = a_i/m_i$, where a_i denotes the mass of species i frozen in 1 kgm of mixture, and m_i denotes the largest value of a_i that will be used in calculations with the particular composition. Since m_i can be chosen to be larger or smaller than the equilibrium mass of species i, frozen CJ states containing more or less of species i than the equilibrium CJ state can be considered.

SPECIAL was written to provide a complete thermodynamic description of frozen CJ states with different values of λ_1 and λ_2. Included in this description are the parameters listed in the equilibrium CJ routine, the rate of entropy production, two additional quantities $\mathcal{O}_1$ and $\mathcal{O}_2$ (which can be preselected), the first and second derivatives of these quantities with respect to volume along a frozen Hugoniot curve, and the first derivatives along the loci of frozen CJ states. These first and second directional derivatives are approximated by differencing techniques when their explicit expressions are not available.

REFERENCES I-F

1. Chapman, D. L., Phil. Mag. 47 90 (1899).
2. Jouguet, E., J. Maths. Pures. Appl. 6 (Series II), 5 (1906).
3. Lewis, B., and Friauf, J. B., J. Am. Chem. Soc. 52, 3905 (1930).
4. Schmidt. A., Z. ges. Schiess- u. Sprengstoffw 31, 8, 37, 80, 114 (1936).
5. Zeldovich, Ya. B., and Kompaneets, A. S., Theory of Detonation, Academic Press, New York and London, 1960.