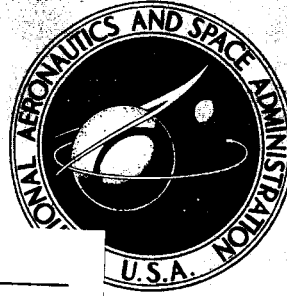


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**AN ANALYSIS OF THE COUPLED
CHEMICALLY REACTING BOUNDARY LAYER
AND CHARRING ABLATOR**

Part V

**A General Approach to the Thermochemical
Solution of Mixed Equilibrium-Nonequilibrium,
Homogeneous or Heterogeneous Systems**

by Robert M. Kendall

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ITEK CORPORATION, VIDYA DIVISION

Palo Alto, Calif.

for Manned Spacecraft Center

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for Manned Spacecraft Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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FOREWORD

The present report is one of a series of six reports, published simultaneously, which describe analyses and computational procedures for: 1) prediction of the in-depth response of charring ablation materials, based on one-dimensional thermal streamtubes of arbitrary cross-section and considering general surface chemical and energy balances, and 2) nonsimilar solution of chemically reacting laminar boundary layers, with an approximate formulation for unequal diffusion and thermal diffusion coefficients for all species and with a general approach to the thermochemical solution of mixed equilibrium-nonequilibrium homogeneous or heterogeneous systems. Part I serves as a summary report and describes a procedure for coupling the charring ablator and boundary layer routines. The charring ablator procedure is described in Part II, whereas the fluid-mechanical aspects of the boundary layer and the boundary-layer solution procedure are treated in Part III. The approximation for multicomponent transport properties and the thermochemistry model are described in Parts IV and V, respectively. Finally, in Part VI an analysis is presented for the in-depth response of charring materials taking into account char-density buildup near the surface due to coking reactions in depth.

The titles in the series are:

- Part I Summary Report: An Analysis of the Coupled Chemically Reacting Boundary Layer and Charring Ablator, by R. M. Kendall, E. P. Bartlett, R. A. Rindal, and C. B. Moyer.
- Part II Finite Difference Solution for the In-depth Response of Charring Materials Considering Surface Chemical and Energy Balances, by C. B. Moyer and R. A. Rindal.
- Part III Nonsimilar Solution of the Multicomponent Laminar Boundary Layer by an Integral Matrix Method, by E. P. Bartlett and R. M. Kendall.
- Part IV A Unified Approximation for Mixture Transport properties for Multicomponent Boundary-Layer Applications, by E. P. Bartlett, R. M. Kendall, and R. A. Rindal.
- Part V A General Approach to the Thermochemical Solution of Mixed Equilibrium-Nonequilibrium, Homogeneous or Heterogeneous Systems, by R. M. Kendall.
- Part VI An Approach for Characterizing Charring Ablator Response with In-depth Coking Reactions, by R. A. Rindal.

This effort was conducted for the Structures and Mechanics Division of the Manned Spacecraft Center, National Aeronautics and Space Administration under Contract No. NAS9-4599 to Vidya Division of Itek Corporation with Mr. Donald M. Curry and Mr. George Strouhal as the NASA Technical Monitors. The work was initiated by the present authors while at Vidya and was completed by Aerotherm Corporation under subcontract to Vidya (P.O. 8471 V9002) after Aerotherm purchased the physical assets of the Vidya Thermodynamics Department. Dr. Robert M. Kendall of Aerotherm was the Program Manager and Principal Investigator.

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ABSTRACT

A general equilibrium and nonequilibrium chemical state procedure is developed and applied mathematically to a number of open and closed thermodynamic systems. The conventional equilibrium relations are developed in terms of a set of base species. The base species concept is then extended in order to treat mixed equilibrium and nonequilibrium systems in a general fashion. The specification of controlling reactions is used to create non-redundant equation sets as equilibrium is approached.

The treatment of open system mass balances within the basic framework of the state solution permits direct surface state calculations considering boundary-layer transfer relations and surface-condensed phase removal relations. The relations defining the state downstream of an oblique shock are also included in the basic solution procedure permitting direct evaluation of these relations without recourse to subordinate iterative schemes.

The factors affecting convergence within the framework of the Newton-Raphson iterative procedure are discussed and the techniques employed in the study are described. The means of evaluating state derivatives is described and relations presented for specific examples.

The computer program which performs the equilibrium state solutions according to the methods presented, the Aerotherm Chemical Equilibrium (ACE) program is described briefly. The program which contains some of the nonequilibrium features of the analysis, the ACE/KINET program is also introduced. The current operational status of both programs is presented.

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LIST OF SYMBOLS

A_m	affinity of reaction m (Eq. (54))
B_m	pre-exponential factor for kinetic reaction m
c_{kj}	number of atoms of element k in molecule j
C_M	mass transfer coefficient
C_p	heat capacity per unit mass
E_{a_m}	activation energy of kinetic reaction m
F_j	diffusion factor for species j
F_j^*	modified diffusion factor for species j
\bar{F}	mean F_j^* defined by Eq. (77)
G_j	partial free energy of species j at its partial pressure and temperature
G_j^0	standard state free energy of pure species j at the system temperature and one atmosphere pressure
H_j	enthalpy per mole of species j at system temperature
h	enthalpy of unit mass of system
j_i	mass flux of element i away from unit area of wall
k_{F_m}	forward reaction rate constant of reaction m
K_{P_j}	equilibrium constant for reaction j (or m)
\tilde{K}_i	"elemental" mass fraction of "element" i
\dot{m}	mass flow rate per unit surface area
m	molecular weight of system, total mass per moles of gas
m_g	molecular weight of gas phase, mass of gas per moles of gas
m_j	molecular weight of species j
n_j	moles of species j in unit mass of system
N_j	representing molecular formula of species j
N_b	number of base species (or "elements")
N_{bb}	number of base-base species

LIST OF SYMBOLS (Continued)

N_s	total number of species in system
p_j	partial pressure of gas phase species j
p_l	moles of condensed phase species l for P moles of gas or as defined by Eq. (66)
P	total system pressure
Q_{im}	defined by Eq. (50)
r_i	net rate of production of "element" i due to all kinetic reactions
R	universal gas constant
\bar{R}_m	net forward rate of reaction m
s	entropy of unit mass of system
S_j	entropy per mole of species j at its partial pressure and temperature
S_j^0	standard state entropy of a mole of pure species j at the system temperature and one atmosphere pressure
t	time
T	system temperature
u_e	velocity at boundary-layer edge
v	specific volume (Eq. (12) only), velocity normal to the wall
x_j	mole fraction of species j
\tilde{z}_i^*	diffusive fraction of element i (Eq. (73))
α_i	mole units of "element" i in unit mass of system
$\bar{\alpha}_i$	conserved quantity of "element" i per Eq. (82)
α_{Z_i}	conserved quantity of "element" i per Eq. (64)
$\gamma_h, \gamma_f, \gamma_k$	defined by Eqs. (83)-(85)
θ	angle between velocity vector and normal to shock wave
μ_w^R, μ_m^P	stoichiometric coefficients on reactants and products in kinetic reaction m

LIST OF SYMBOLS (Concluded)

μ_2	diffusive molecular weight defined by Eq. (74)
ν_{ij}	stoichiometric coefficient on base species i in formation reaction of species j
ρ	density of system
ρ_e	density at boundary-layer edge
ρ_ℓ	density of pure condensed species ℓ
σ_{ik}	stoichiometric coefficient on base-base species k in formation reaction of base species i
χ_{jk}	sum of all terms involving p_j in mass balance k

SUBSCRIPTS

c	char material
e	edge
F	at the fail state of a species
g	pyrolysis gas
i	base species or "elements"
j	gas phase species (including base species)
k	atomic elements or base-base species
ℓ	condensed species (including base species)
m	kinetic reaction index
r	condensed phase removal
w	wall
1	upstream of shock
2	downstream of shock

SUPERSSCRIPTS

$ ^{-1}$	matrix inverse
$ ^T$	matrix transpose
o	standard state (pure and at one atmosphere) or trial value

A GENERAL APPROACH TO THE THERMOCHEMICAL SOLUTION
OF MIXED EQUILIBRIUM-NONEQUILIBRIUM, HOMOGENEOUS
OR HETEROGENEOUS SYSTEMS

SECTION 1
INTRODUCTION

In the study of high-energy boundary-layer phenomena, thermochemical processes can be of dominant importance. This is particularly true when these boundary layers interact with chemically active surfaces. In the present study, interest is directed toward the superorbital reentry of the Apollo vehicle and the thermochemical response of its heat shield. The requirements for evaluating the chemical state of homogeneous and heterogeneous systems in this study are extensive. These requirements include the determination of the chemical state after normal or oblique shock wave compression, during the isentropic expansion of the inviscid shock-layer gases, within the boundary layer and at the chemically active surface. In the last two instances these state calculations are coupled with complex mass-balance relations. Many chemical-state solution procedures have been documented to treat reasonably standard closed systems, such as those associated with expansion processes. (See, for example, Refs. 1 through 4.) For open systems, only a few direct solution procedures have been documented. The surface state calculation for a general chemical system described in Ref. 5 falls into a special class of open system problems. Because of the number of requirements imposed upon the chemical-state routines in the present study, the general treatment of a variety of chemical systems became a major effort. The inclusion of a general kinetic model, ionization, and the extensive bookkeeping associated with the downstream introduction of new species is of major importance in the formulation of the general problem necessary for thoroughly treating the coupled boundary-layer problem.

Starting from reasonably fundamental relations, the procedures adopted as a part of this research effort are described in this report. The basic relations are presented in the next section followed by sections on the solution procedure and the evaluation of thermodynamic properties.

These techniques have been built in greater or lesser extent into the Aerotherm Chemical Equilibrium (ACE) program and certain special modifications of it. The final section of this report specifies the exact status of these routines and the extent to which the general formulation presented herein has been implemented. The procedures are presently limited to equilibrium, except that selected homogeneous reactions can be considered frozen within the boundary layer and selected heterogeneous and surface catalyzed kinetically controlled reactions can proceed at the material surface.

SECTION 2
BASIC RELATIONS

In this section the relations which are required to specify the chemical state of a system are presented. Basically four types of relations can be considered in a general open system. These are the equilibrium relations applying to those reactions which can be considered as generally equilibrated, the nonequilibrium relations for those reactions which can be (but are not necessarily) out of equilibrium, the mass-balance relations, and those additional state constraints imposed on the system.

2.1 EQUILIBRIUM RELATIONS - TOTALLY EQUILIBRATED SYSTEMS

In a chemical system there will exist, in the general case, a set of independent equilibrium reactions. All other equilibrium reactions will be equivalent, both physically and mathematically, to this independent set. Consider for example the simple H, O, HO, H₂O, H₂, O₂, H₂O₂, O₃ system. Six independent equilibrium reactions can be written, for example



Other reactions such as



are merely linear combinations of the six (arbitrarily selected) independent equations (i.e., Eq. (7) = Eq. (2) - Eq. (3) - $\frac{1}{2}$ Eq. (4)). It can be shown that in a completely equilibrated system the number of independent equations is usually equal to the number of molecules less the number of elements.* The

*An exception occurs when two or more elements are in the same ratio in all molecules of a system, e.g., the system NO₂, N₂O₄ has one (not zero) independent equations.

modification of this relation for systems that are not completely equilibrated will be considered in Section 2.2. The selection of this set of independent reactions can be done arbitrarily, but it is convenient to establish some consistent technique. Most such techniques are based on the pre-selection of a set of species usually equal in number to the number of elements. The formation reactions of all other species from this base set represent the independent set of equilibrium reactions. The base species must be selected in such a fashion that no reaction can be written wherein reactants and products are all base species. Thus in the above set HO and H₂O₂ represent an invalid base set whereas HO and O, HO and H, etc., represent valid sets. It has been reasonably common practice to select the monatomic gases as base species (Ref. 3, for example) since the formulation of the formation reactions is particularly convenient. There are advantages, however, in selecting a more general set, particularly when chemical kinetics are important. Considering a set of base species N_i, formation reactions for the remaining N_j species are of the form, indicated for example in Ref. 4,

$$\sum_i v_{ji} N_i \rightleftharpoons N_j \quad (8)$$

where the v_{ji} are the stoichiometric coefficients of the formation reactions. In the preceding example with H and O as N₁ and N₂, respectively, the v_{ji} would be

i \ j	1	2	3	4	5	6	7	8
	H	O	HO	H ₂ O	H ₂	O ₂	H ₂ O ₂	O ₃
1 H	1	0	1	2	2	0	2	0
2 O	0	1	1	1	0	2	2	3

while with H₂O and O₂ as N₁ and N₂, the v_{ji} would be

i \ j	1	2	3	4	5	6	7	8
	H ₂ O	O ₂	H	O	HO	H ₂	H ₂ O ₂	O ₃
1 H ₂ O	1	0	.5	0	.5	1	1	0
2 O ₂	0	1	-.25	.5	.25	-.5	.5	1.5

Mathematically, the v_{ji} are obtained implicitly from the c_{kj} (the atoms of element k in molecule j) by

$$\sum_i c_{ki} v_{ji} = c_{kj} \quad (9)$$

which for the latter table with $j = 7$ (i.e., H_2O_2) indicates

$$\text{for } k \text{ representing hydrogen } 2 \times 1 + 0 \times .5 = 2$$

$$\text{for } k \text{ representing oxygen } 1 \times 1 + 2 \times .5 = 2$$

In matrix form

$$|v_{ji}|^T = |c_{ki}|^{-1} |c_{kj}| \quad (10)$$

where the superscript T denotes transpose. Note that the square array c_{ki} can be considered as a subset of the larger rectangular array c_{kj} .

The set of independent formation reactions (Eq. (8)) for j ranging from $N_b + 1$ to N_s , where N_b is the number of base species and N_s is the total number of species, can be used to formulate a set of equilibrium constraints.

At equilibrium, the second law requires that these independent reactions occur without change in free energy. Therefore

$$G_j = \sum_i v_{ji} G_i \quad (11)$$

where the G_j are the partial molar free energies of the species (also referred to as the chemical potentials). The change in free energy is, by definition, equal to the isothermal reversible work performed by a steady flowing system in passing from one state to another. On this basis it is possible to relate the G_j to the standard-state free energies, G_j° , that is, the free energy of the species at the same temperature but undiluted and at one atmosphere pressure. Thus

$$G_j - G_j^\circ = \left[- \int_{p^\circ}^P v dp \right]_{\text{isothermal, reversible}} \quad (12)$$

where p° is one atmosphere. For a gas obeying the perfect gas law

$$G_j - G_j^\circ = - RT \ln p_j \quad (13)$$

if p_j is in units of atmospheres. Likewise, for an incompressible condensed phase containing only one species

$$G_\ell - G_\ell^\circ = \frac{1 - P}{\rho_\ell} \quad (14)$$

When more than one condensed species coexists in a phase, the work of mixing must be included. For an ideal mixture*

$$G_\ell - G_\ell^\circ = \frac{1 - P}{\rho_\ell} - RT \ln x_\ell \quad (15)$$

where x_ℓ is the mole fraction of species ℓ in the mixture.

In environments of general concern in high-temperature thermodynamics, Eqs. (13) and (14) are generally employed and, in addition, $(1 - P)/\rho_\ell$ is assumed negligible in relation to the gas-phase work terms. On this basis, simplified equilibrium constant relations are obtained from Eqs. (11) and (13) for gas and condensed species (sub j or ℓ),

$$\ln K_{P_j} = - \frac{\Delta G_j^\circ}{RT} = \ln p_j - \sum_i \nu_{ji} \ln p_i \quad (16)$$

where the standard-state free energy change of the formation reaction for species j (or ℓ) is defined by

$$\Delta G_j^\circ = G_j^\circ - \sum_i \nu_{ji} G_i^\circ \quad (17)$$

and the partial pressure of condensed species will be taken as one atmosphere in order that Eq. (13) will indicate no work of compression.

The standard state free energy is a function of temperature only and is obtained for each molecular species from

$$G_j^\circ = H_j^\circ - TS_j^\circ \quad (18)$$

where enthalpies are obtained relative to some chemical base state, often the elements in their most natural form at 298°K and one atmosphere (JANAF base

*The ideal mixture assumption is satisfied by a mixture above which vapor pressures are proportional to mixture mole fractions and whose vapors obey the perfect gas law.

state). If any other base state is consistently adopted, the ΔG_j° will be unaffected.

The stationary condition of the free energy at equilibrium expressed in Eq. (11) is consistent with the minimum free energy statement often utilized in seeking the equilibrium state. Although the formulation followed here differs from those followed in free-energy minimization approaches, the ultimate numerics can reduce to an identical iterative solution procedure.

The solution of the set of algebraic equations (Eq. (16)) must be considered in conjunction with other constraints including the pressure balance

$$\sum_j P_j = P \quad (19)$$

where the summation is over all gas-phase species. The detailed solution procedure will be considered only after all relations have been presented.

2.2 MIXED EQUILIBRIUM-NONEQUILIBRIUM RELATIONS

When some reactions fail to equilibrate it is necessary to approach the selection of the independent set of equilibrium reactions with greater caution. In a general chemical system, certain sets of molecules can be treated as always equilibrated. Between these sets certain independent equilibrium and kinetically-controlled interchange reactions may exist. A procedure for treating mixed equilibrium-nonequilibrium systems is presented in this section.

The following rules are established in order to organize the logic:

1. Every species is assigned to one and only one set of molecules.
2. A set may contain as few as one species.
3. Each set has its own base species, i.e., that minimum number of species from which all other members of the set may be formed.
4. Within each set all possible reactions between member species are equilibrated.
5. Equilibrium interchange reactions involve species from more than one set.

Consider the eight species of the O-H system considered in Section 2.1; O, H₂O; H; H₂; O₂, O₃; HO, H₂O₂ where five sets are divided by semicolons. For these sets, the following base species are appropriate: O, H₂O; H; H₂; O₂; HO where only the first set requires more than one base species. At this juncture only two independent equilibrium reactions have been formulated, namely



Two independent equilibrium interchange reactions might be included in this system, for example



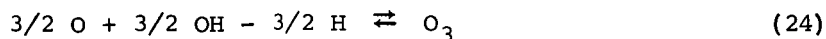
The effect of these reactions is to reduce the number of base species by two. For example H_2 and O_2 can be deleted. The remaining base species and the array of formation reactions coefficients, v_{ji} , are therefore

i \ j	1	2	3	4	5	6	7	8
	O	H ₂ O	H	OH	H ₂	O ₂	H ₂ O ₂	O ₃
1	0	1	0	0	-1	1	0	1.5
2	H ₂ O	0	1	0	0	0	0	0
3	H	0	0	1	0	-1	0	-1.5
4	OH	0	0	0	1	1	2	1.5

in the general relation

$$\sum_i v_{ji} N_i \rightleftharpoons N_j \quad (8)$$

To illustrate, the equilibrium formation reaction for O_3 (i.e., $j = 8$ in the above table) from the base species is given by



If it is assumed that all other interchange reactions are frozen, the formulation of the equilibrium-nonequilibrium aspects of the program are complete. In the totally equilibrated chemical system, conservational constraints

are often applied to the elements. In the system just presented, however, additional conservational constraints are required. In general these constraints take the form

$$\sum_j v_{ji} n_j = \alpha_i \quad (25)$$

where n_j is the number of moles of species j in a unit mass of system and α_i is a conserved variable relating to the "elemental" composition of a unit mass of the system. One such constraint is applied for each base species. To check the validity of this relation, consider the effect of a unit reduction in n_j . According to Eq. (8) the n_i will increase by $v_{j,i}$. Thus in Eq. (25) two terms are modified, namely, $v_{ii} n_i$ and $v_{j,i} n_j$. Since $v_{ii} = 1.0$, it is apparent that the increase in the latter term exactly balances the decrease in the former. In effect, the base species become the elements of the system, and their total masses can be treated as the conserved variable of the system. This generalized concept of the conserved "elements" of the system is extremely important to the present development and thus further examples are appropriate. In the completely equilibrated system previously presented, it is easy to accept that

$$\sum_j c_{kj} n_j = \alpha'_k \quad (26)$$

where α'_k , the total number of atoms of element k in a unit mass, is a conserved variable. If we premultiply both sides of this expression by the inverse $|c_{ki}|^{-1}$, there results from Eq. (10)

$$\sum_i v_{ji} n_i = |c_{ki}|^{-1} \alpha'_k = \alpha_i \quad (27)$$

Therefore if the α'_k are conserved then the α_i will be conserved. In the system of Eqs. (1) through (6), this is tantamount to naming a new set of elements which are, in effect, the base species. The term "element" (in quotes) will be used henceforth in this report to refer to those atoms or groupings of atoms (i.e. grouped according to the base species formulae) which according to the equilibrium relations are conserved.

In the general nonequilibrium system, certain kinetically-controlled reactions will be important. For example, in the H-O system



are three reactions of possible interest, M being any third body. The rates of these reactions can be related to the partial pressures of the reactants and products, the ultimate equilibrium constraint appropriate to the reaction, and the kinetic coefficient. With the general kinetic reaction in the form



its rate can be expressed generally by

$$\bar{R}_m = k_{Fm} \left[\prod_j p_j^{\mu_{jm}^R} - \frac{1}{K_{Pm}} \prod_j p_j^{\mu_{jm}^P} \right] \quad (32)$$

or by

$$\bar{R}_m = k_{Fm} \left[\exp \sum_j \mu_{jm}^R \ln p_j - \exp \left(\sum_j \mu_{jm}^P \ln p_j - \ln K_{Pm} \right) \right] \quad (33)$$

where

$$\ln K_{Pm} = - \frac{\Delta G_m^0}{RT} \equiv \frac{1}{RT} \left[\sum_j (\mu_{jm}^P - \mu_{jm}^R) G_j^0 \right] \quad (34)$$

The net effect of these reactions is the modification of the "elemental" makeup of the system. The kinetic reactions will cause a net increase rate (moles per unit volume)

$$r_i = \sum_m \sum_j (\mu_{jm}^P - \mu_{jm}^R) \nu_{ji} \bar{R}_m \quad (35)$$

of "element" i. It is this relation which will be introduced into the conservational equations in order to establish the local state of the reacting chemical system. Certain additional data must be provided in order to perform the kinetic calculations. First, the specification of the stoichiometry serves to establish not only the effect of the reaction but also the reaction order. For example



and



are equivalent stoichiometrically, the asterisk designating condensed-phase material. However, in Eq. (32), the former relation results in a half order reaction ($p_{C^*} \equiv 1.0$)*, whereas the latter results in a first-order reaction. The forward rate constant k_{F_m} , hopefully based on experimental data, is represented with an Arrhenius^m type function

$$k_{F_m} = B_m \exp \left(E_{a_m} / RT \right) \quad (38)$$

where the exponential factor establishes the probability of a collision having energy in excess of the activation energy E_{a_m} and the factor B_m represents a multitude of phenomena associated with the probability of success of a single collision (e.g. collision orientation).

When kinetically-controlled reactions approach equilibrium, difficulty is often encountered in the treatment of the relevant conservational equations. To understand the nature of this difficulty, and thus the means of avoiding it, it is instructive to consider the simple time dependent character of the H-O system previously described. Recalling that α_i represents the moles of "element" i in a unit mass, and that r_i represents the rate of production of moles of "element" i per unit volume, it follows that

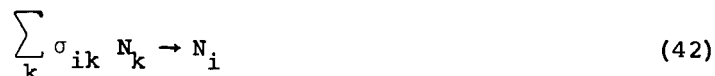
$$\frac{d\alpha_i}{dt} = \frac{r_i RT}{P\eta} \quad (39)$$

At this point it is necessary to introduce a new concept. From the base species, a subset of N_{bb} base-base species can be obtained much as if all specified kinetic reactions were permitted to equilibrate. For this example, O and H will be selected for this honor and the "formation reaction" for the remaining base species written as



* As in the equilibrium relation, it is convenient to consider the partial pressures of condensed species as one atmosphere as a device to include heterogeneous reactions in the same framework as homogeneous reactions.

These reactions will equilibrate if the kinetic reaction (Eq. (30)) and the reaction of either Eq. (28) or Eq. (29) have infinite rates.* More generally, Eqs. (40) and (41) can be written as



where the index k represents the base-base subset of base species. It can be shown that

$$\sum_i \sigma_{ik} r_i = 0 \quad (43)$$

which implies that atoms and/or certain combinations of atoms cannot be created or destroyed by chemical reactions in this system. Since there are two base-base species, two of the Eqs. (39) can be replaced by

$$\sum_i \sigma_{ik} \frac{d\alpha_i}{dt} = \frac{RT}{P\eta} \sum_i \sigma_{ik} r_i = 0 \quad (44)$$

Defining

$$\tilde{\alpha}_k \equiv \sum_i \sigma_{ik} \alpha_i \quad (45)$$

it follows that

$$\frac{d\tilde{\alpha}_k}{dt} = 0 \quad (46)$$

For each base species i which is also a base-base species k , an equation of the form of Eq. (46) will replace the corresponding one of the form of Eq. (39). The other Eqs. (39) are maintained unaltered in the system of equations and still contain the kinetic expressions. These will be referred to as the reactive mass balance equations. In the general case, a given reaction, m , will affect more than one of these equations introducing a term of the form

*The number of base-base species can still exceed the number of atomic elements in the system if insufficient kinetic paths have been specified to permit full system equilibrium.

$$\left\{ \left[\sum_j (\mu_{jm}^P - \mu_{jm}^R) \nu_{ji} \right] k_{F_m} \exp \sum_j \mu_{jm}^R \ell_n p_j \right\} \times \left\{ 1 - \exp \left[\sum_j (\mu_{jm}^P - \mu_{jm}^R) \ell_n p_j - \ell_n K_{P_m} \right] \right\} \quad (48)$$

If the first term in braces approaches infinity, the balancing of the overall reactive mass balance equation will reduce to setting the second term in braces equal to unity, or equivalently,

$$\sum_j (\mu_{jm}^P - \mu_{jm}^R) \ell_n p_j - \ell_n K_{P_m} = 0 \quad (49)$$

which is simply the appropriate equilibrium relation. If this reduction for reaction m occurs in more than one mass balance equation, a net loss of non-redundant relations can occur.* To avoid this, it is important that the reactive mass balance equations be combined in such a manner that the production terms from each near-equilibrated reaction is entered into only one equation. The means of establishing this combination of the reactive mass balance equations is based on the selection of controlling reactions equal in number to the number of reactive mass balances. (This number equals the difference between the number of base species and the number of base-base species.) In turn the selection of the controlling reactions is based on the array Q_{im} where

$$Q_{im} = \left[\sum_j (\mu_{jm}^P - \mu_{jm}^R) \nu_{ji} \right] k_{F_m} \exp \sum_j \mu_{jm}^R \ell_n p_j \quad (50)$$

The performance of a conventional pivotal Gaussian reduction on this rectangular array results in the selection of certain of the Q_{im} as pivotal terms. It is the column numbers, m , of these terms which are considered as the indices of the controlling reactions, one having been selected for each reactive mass balance, i . The combination of the reactive mass balance equations such as to eliminate terms consequent to the controlling reactions from all but one equation thus becomes a relatively straight-forward manipulation following the same steps as the original Gaussian reduction. This manipulation is carried forward independently for both the mass balances and the kinetic relations, before the two sets are combined, in order to avoid the loss of important significant figures. In actual practice, this manipulation is performed in conjunction with the transformation indicated by Eq. (44) and is effected by an augmented σ_{ki} transformation matrix.

* Such a loss is only a result of the limited significant figures retained in the calculational process since differences in the other terms in the equation could still be used if unlimited significant figures existed.

2.3 MASS BALANCE RELATIONS

In the preceding sections the equilibrium and nonequilibrium relations have been developed for a fairly general chemical state. These relations are in themselves insufficient until other relations, in particular the mass balance relations, are imposed. In the case of kinetic control, the time dependence of the system must be equated to flow rates and other rate dependent parameters entering the mass balances. Likewise, in diffusional systems the local state is determined by mass-balance relations associated with mass-transfer processes. In the following subsections the mass balance relations appropriate to various systems will be presented.

2.3.1 Expansion of Isolated Systems

In the expansion of a fixed mass, closed, adiabatic system it is usually appropriate to trace its state history as a function of static pressure. If the process is reversible, the entropy is constant and the local state is not a function of the time history (process path) of the expansion. Such systems satisfy the simple mass balance constraint

$$\alpha_i = \text{constant} \quad (51)$$

This equation implies either total equilibrium or a mixed equilibrium-frozen chemical process. If, however, finite reaction rates are important, the path ceases to be reversible, entropy rises, and the time history of the expansion must be considered. If the pressure is a known function of time, the expansion can be treated as

$$\text{state} = f(\alpha_i, s, P) \quad (52)$$

where the state includes such terms as $d\alpha_i/dt$ and ds/dt . The rate of change of the "elemental" composition is obtained from Eqs. (33) and (35), whereas the rate of increase in entropy (see, e.g., Ref. 6, Eq. (3.32)) is obtained from

$$\frac{ds}{dt} = \sum_m \frac{A_m}{T} \left(\bar{R}_m \frac{RT}{P} \right) \quad (53)$$

where A_m (the "affinity") is defined as

$$A_m = RT \left[\ln K_{P_m} - \sum_j (\mu_{jm}^P - \mu_{jm}^R) \ln p_j \right] \quad (54)$$

Thus

$$\frac{ds}{dt} = R \sum_m \left[\ln K_{P_m} - \sum_j (\mu_{jm}^P - \mu_{jm}^R) \ln p_j \right] \bar{R}_m \frac{RT}{P_m} \quad (55)$$

This derivative is well behaved, even as equilibrium is approached, and may be evaluated explicitly if desired. The α_i derivatives, however, must be treated implicitly if any hope for near equilibrium solutions is to be maintained. Once a particular formulation is adopted, the techniques suggested in the nonequilibrium presentation (Section 2.2) can be introduced in order to assure consistent solution validity. Because of the simplicity of the mass-balance relation for this process, it is practical to include the kinetic mass balances directly with the iterative solution of the chemical state. This state calculation includes the relations previously presented together with the entropy constraint, namely

$$\sum p_j S_j = P_m s \quad (56)$$

where the entropy of a perfect gas species j is related to the standard state entropy (at one atmosphere pressure) by

$$S_j = S_j^0 - R \ln p_j \quad (57)$$

and S_j^0 is a function of temperature only. For condensed species the simplifying assumption presented previously leads to $S_j = S_j^0$. In all standard conservation equations, the partial pressure, p_j , assumes the general definition of the number of moles of species j for P gas-phase moles.

2.3.2 State Calculations for Open Systems

The evaluation of the state in a general open system involving diffusive and convective mass and energy fluxes is most generally performed as a subordinate solution. For example, in the boundary-layer solutions of current interest, state solutions are required at several interacting locations. Thus, in Ref. 7 (Part III of the present series of reports) state solutions are required based on assigned "elemental" mass fractions (or α_i), enthalpy and pressure, i.e.

$$\text{state} = f(\alpha_i, h, P) \quad (58)$$

This solution provides to the boundary-layer solution the detailed state including thermodynamic, transport and radiative properties as well as the production rates $d\alpha_i/dt$. The last term must be included with the general mass-balance relations of the boundary-layer program.

The specific relations used to achieve the state solution are the equilibrium equations (Eq. (16)), the mass balance relations (Eq. (25)), the pressure constraint (Eq. (19)) and an enthalpy constraint

$$\sum_j p_j H_j = P h \quad (59)$$

which involve no greater complexity than the conventional isolated system equilibrium solution. The coupling between this solution and the boundary-layer solution requires not only the evaluation of the production rates, $d\alpha_i/dt$ but also the rate of change of these rates with respect to the independent parameters on the right-hand-side of Eq. (58). The rates are determined with Eqs. (35) and the derivatives by use of relations to be developed in section 3 of this report.

Again, the problem of stability threatens when equilibrium approaches. However, by following the approach previously presented, the kinetic terms can be treated separately while all other terms of the mass-balance equations are being collected. These equations can then be rearranged and combined with the kinetic relations in such a way that controlling reactions again affect only one equation at each location. Because of the overall implicit character of the boundary-layer solution, this procedure will, on convergence, yield valid stable solutions. It has been found, however, that the introduction of equilibrium type relations into the set of boundary-layer equations can destroy the linearity of the system. Therefore the approach of equilibrium by the kinetic equations included in the boundary-layer mass balances will probably delay convergence and necessitate the inclusion of certain iterations constraints.

2.3.3 Surface State Solutions

A more complex set of mass-balance relations are introduced when surface state solutions are sought. Coupling between boundary layer, internal conduction, and surface mechanical removal solutions may be involved in these relations. In effect, all the other mass-balance solutions become subordinate to this solution. Two types of boundary-layer representations are considered in this section. One is the transfer-coefficient correlation of mass transfer using the Z^* -potential developed in Ref. 5 and also in Appendix B of Ref. 8. In Ref. 7 the fluxes at the wall are expressed using an influence coefficient approach. Mathematically these approaches reduce to

$$j_i = \rho_e u_e C_M (\bar{Z}_i^* - \bar{Z}_{i_e}^*) \quad (60)$$

and

$$j_i = j_i^o + \frac{\partial j_i}{\partial h}(h - h^o) + \frac{\partial j_i}{\partial (\rho v)_w} \left[(\rho v)_w - (\rho v)_w^o \right] + \sum_k \frac{\partial j_i}{\partial \tilde{K}_k} (\tilde{K}_k - \tilde{K}_k^o) \quad (61)$$

respectively. The nomenclature is as given in those references and the list of symbols of this document. The diffusional mass flux j_i of "element" i is coupled with the surface mass-balance equation

$$\dot{m}_c \tilde{K}_{c_i} + \dot{m}_g \tilde{K}_{g_i} - \sum_l \dot{m}_{r_l} \tilde{K}_{l_i} - (\rho v)_w \tilde{K}_i - j_i = 0 \quad (62)$$

This equation includes fluxes due to the pyrolysis gas generation rate, \dot{m}_g , the char consumption rate, \dot{m}_c , the surface mechanical removal rates of species l due to various mechanisms, \dot{m}_{r_l} , the bulk gas-phase convective flux, $(\rho v)_w$, each times their respective fraction of "element" i , and the diffusive flux, j_i , of "element" i . An overall mass balance can also be written by summing Eq. (62) over all i and noting the $\sum j_i = 0$, namely,

$$\dot{m}_c + \dot{m}_g - \sum_l \dot{m}_{r_l} - (\rho v)_w = 0 \quad (63)$$

Because of the different treatment used with Eqs. (60) and (61), they will be developed individually, but generalized in a consistent format.

2.3.3.1 Surface Transfer Coefficients

In many boundary-layer analyses, the net diffusional flux of mass, heat and/or momentum to or from the wall are the only results of practical concern. Because of this, transfer coefficients have become extremely effective tools of analysis when it is possible to develop good correlations by which their values can be adequately estimated. Using the transfer potentials developed in Ref. 5 and Appendix B of Ref. 8, a directly coupled equilibrium surface thermochemistry routine has been developed. Combining Eqs. (60) and (62) and rearranging yields

$$\frac{1}{\tilde{m}_i} \left[\tilde{Z}_{i_e}^* + \frac{\dot{m}_c}{\rho_e u_e C_M} \tilde{K}_{c_i} + \frac{\dot{m}_g}{\rho_e u_e C_M} \tilde{K}_{g_i} \right] = \alpha_{Z_i} =$$

$$\frac{1}{\tilde{m}_i} \left[\tilde{Z}_i^* + \frac{(\rho v)_w}{\rho_e u_e C_M} \tilde{K}_i + \sum_l \frac{\dot{m}_{r_l}}{\rho_e u_e C_M} \tilde{K}_{l_i} \right] \quad (64)$$

where the l subscript refers to the possible condensed species in the system. The mass fraction of "element: i in the species l , \tilde{K}_{li} , can be expressed as

$$\tilde{K}_{li} = v_{li} \frac{m_i}{m_l} \quad (65)$$

Similarly, the gas phase mass fraction of "element" i can be expressed in terms of the partial pressures of the gaseous species, j , namely,

$$\tilde{K}_i = \frac{1}{Pm_g} \sum_j v_{ji} P_j m_i \quad (66)$$

where m_g is the mean molecular weight of the gases adjacent to the wall, that is,

$$Pm_g = \sum_j P_j m_j \quad (67)$$

where the summation over j is for gaseous species only. Recall that the v_{ji} are the stoichiometric coefficients in the formation of species j from "element" i or the atoms of "element" i in a molecule of species j .

It is convenient to define the term p_l for condensed species in a special fashion for this open system mass balance, namely

$$p_l = \frac{\dot{m}_r P m_g}{\rho_e u_e C_M m_l} \quad (68)$$

Combining Eqs. (63), (65), (66) and (68) with Eq. (64) yields

$$\alpha_{Z_i} = \frac{\tilde{Z}_i^*}{m_i} + \frac{1}{Pm_g} \left(\frac{\dot{m}_g + \dot{m}_c}{\rho_e u_e C_M} - \frac{\sum p_l m_l}{Pm_g} \right) \sum_j v_{ji} P_j + \frac{\sum p_l v_{li}}{Pm_g} \quad (69)$$

From Ref. 5, the definition of \tilde{Z}_i^* is found to be

$$\tilde{Z}_i^* = \frac{m_i}{P\mu_2} \sum_j P_j \frac{v_{ji}}{F_j} \quad (70)$$

where F_j^* is equal to F_j raised to some power, usually $2/3$ for boundary layer applications. The diffusion factor F_j is described in detail in Ref. 5 and in Ref. 9. Also

$$P\mu_2 \equiv \sum_j P_j \frac{m_j}{F_j^*} \quad (71)$$

Combining this result with Eq. (69) yields, after introducing a normalizing parameter \bar{F} ($\equiv m_g/\mu_2$)

$$Pm_g^{\alpha} Z_i = \left(\frac{\dot{m}_g + \dot{m}_c}{\rho_e u_e C_M} - \frac{\sum_l m_l P_l}{Pm_g} \right) \sum_j P_j v_{ji} + \sum_l P_l v_{li} + \sum_j P_j \frac{v_{ji}}{F_j^*/\bar{F}} \quad (72)$$

From Eqs. (67) and (71), \bar{F} is defined by

$$\bar{F} \equiv \frac{m_g}{\mu_2} = \frac{\sum_j P_j m_j}{\sum_j P_j m_j / F_j^*} \quad (73)$$

One of the more elusive aspects of surface-state solutions is the adequate specification of the mechanical-chemical surface constraint. The present formulation is based on the following set of constraints for condensed-phase species.

$$P_l = 0 \quad \text{if} \quad T < T_{F_l} \quad (74)$$

and

$$\sum_i v_{li} \ln p_i \leq \ln K_{P_l} \quad (75)$$

with the equality applying to one species with $T_{F_l} \geq T$. The first equation implies that a particular condensed species cannot leave the surface until the surface temperature is at or above that species fail or flow temperature, T_{F_l} . The second relation states that all present condensed species are in equilibrium with the base species. The inequality applies to non-present condensed species and prohibits a super-saturated vapor state. This is equivalent to saying that at 100°C

$$P_{H_2O} \leq 1 \text{ atm.}$$

(76)

The requirement that one species be at or below its fail temperature establishes the structural limitation of the surface. A typical result might show a surface at 2500°K with the equilibrium holding for SiC* and SiO₂*, but if SiO₂* has been assigned a fail temperature of, say, 2300°K, P_{SiO_2} and thus \dot{m}_{SiO_2} will be positive indicating liquid removal of SiO₂*. The SiC*, with a fail temperature greater than 2500°K, represents the surface constraining species.

2.3.3.2 Boundary Layer Coupled Surface State

In order to couple the boundary-layer solution to the surface state equation, several approaches are feasible. Because of the nonlinearity of surface-state solutions, there are significant advantages to isolating this solution from the more linearly behaving transfer equations of the boundary-layer. The chemical-state routines expect and can accept quite nonlinear systems of equations. The boundary-layer aspects of the surface-state calculations are thus reduced to influence coefficients, similar in form to the transfer coefficients discussed in the previous subsection, which are introduced into the surface state equations. This linear reduction of the boundary-layer equation is discussed in Ref. 7. With this approach in mind, the second surface diffusional flux equation (Eq. (61)) can be introduced into Eq. (62) yielding, after some rearrangement

$$\begin{aligned} & \frac{1}{\dot{m}_i} \left[\dot{m}_c \tilde{K}_{c_i} + \dot{m}_g \tilde{K}_{g_i} + \frac{\partial j_i}{\partial (\rho v)_w} (\rho v)_w^o + \frac{\partial j_i}{\partial h} h^o + \sum_k \frac{\partial j_i}{\partial \tilde{K}_k} \tilde{K}_k^o - j_i^o \right] \\ & \equiv \bar{\alpha}_i = \frac{1}{\dot{m}_i} \left[\frac{\partial j_i}{\partial (\rho v)_w} (\rho v)_w + \frac{\partial j_i}{\partial h} h + \sum_k \frac{\partial j_i}{\partial \tilde{K}_k} \tilde{K}_k + (\rho v)_w \tilde{K}_i + \sum_l \dot{m}_r \tilde{K}_{l_i} \right] \quad (77) \end{aligned}$$

where the partial derivatives and prior values (^o) of the variables are developed by the boundary-layer solution procedure.

Making use of Eqs. (63), (65) and (66) and introducing the following definitions

$$p_\ell = \dot{m}_{r_\ell} \frac{P m_g}{m_\ell} \quad (78)$$

$$\gamma_{f_i} \equiv \frac{1}{m_i} \frac{\partial j_i}{\partial (\rho v)_w} \quad \gamma_{h_i} \equiv \frac{1}{m_i} \frac{\partial j_i}{\partial (\rho v)_w} \quad \gamma_{K_{ki}} \equiv \frac{m_k}{m_i} \frac{\partial j_i}{\partial \tilde{K}_k} \quad (79-81)$$

yields

$$\begin{aligned} P m_g \bar{\alpha}_i &= \left(\dot{m}_g + \dot{m}_c - \frac{m_\ell p_\ell}{P m_g} \right) \left(P m_g \gamma_{f_i} + \sum_j p_j v_{ji} \right) \\ &+ \sum_j \left(p_j \sum_k \gamma_{K_{ki}} v_{jk} \right) + \gamma_{h_i} \sum p_j H_j + \sum v_{\ell i} p_\ell \end{aligned} \quad (82)$$

Introducing a new coefficient

$$\lambda_{ji} = \sum_k \gamma_{K_{ki}} v_{jk} \quad (83)$$

reduces Eq. (82) to

$$\begin{aligned} P m_g \bar{\alpha}_i &= \left(\dot{m}_g + \dot{m}_c - \frac{\sum p_\ell m_\ell}{P m_g} \right) \left(P m_g \gamma_{f_i} + \sum_j p_j v_{ji} \right) \\ &+ \sum_j p_j \lambda_{ji} + \sum p_\ell v_{\ell i} + \gamma_{h_i} \sum p_j H_j \end{aligned} \quad (84)$$

This equation is similar to Eq. (72) and can be reduced to that equation if

$$\dot{m}_g + \dot{m}_c \quad \text{is replaced by} \quad \frac{\dot{m}_g + \dot{m}_c}{\rho_e u_e C_M} \quad (85)$$

$$\gamma_h \quad \text{and} \quad \gamma_f \quad \text{are replaced by} \quad 0 \quad (86)$$

$$\lambda_{ji} \quad \text{is replaced by} \quad \frac{v_{ji} \bar{F}}{F_j} \quad (87)$$

The inclusion of heterogeneous kinetics in these equations is accomplished by adding the production rate of "element" i per unit surface area to the left side of Eq. (72) or (84). The subsequent treatment of this term is quite similar to that previously presented for homogeneous kinetics. Thus with the k_{F_m} of Eq. (38) defined in terms of stoichiometric moles per unit of time and surface area, the production term to be appended to the left of the final Eq. (84) is $P\mathcal{M}r_i$ with r_i defined according to Eq. (35). The same term should be added to Eq. (72) but the k_{F_m} are then normalized by $\rho_e u_e C_M$. As in the preceding kinetic problems, a set of controlling reactions is determined and the mass balance equations are rearranged so that each of these reactions appears in only one of these equations, at which juncture the kinetic terms are introduced into the mass-balance equations.

2.4 OBLIQUE SHOCK RELATIONS AND SUMMARY OF STATE RELATIONS

Certain constraints in addition to mass and equilibrium balances have been mentioned in the preceding paragraphs. It is well to summarize these briefly and to introduce one additional set of constraints, namely those associated with flow across a shock wave. Up to this point, total pressure has always been an independently assigned variable, thus

$$\sum_j p_j = P \quad (88)$$

is an obvious constraint on the partial pressures. Other state constraints have also been mentioned. In addition to temperature specification they are

$$\sum_{j,l} p_j H_j = hP\mathcal{M} \quad (89)$$

and

$$\sum_{j,l} p_j S_j = \sum_{j,l} p_j (S_j^0 - R \ln p_j) = sP\mathcal{M} \quad (90)$$

for specified enthalpy, h , and entropy, s , both defined per unit mass.

In the case of an oblique shock wave, none of the above constraints apply. Instead, conservation of energy, mass and momentum are required. Using the subscripts, 1 and 2, to denote conditions upstream and downstream of the shock, respectively, with θ as the angle between the flow vector and a normal to the shock wave, these equations are

energy

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{u_2^2}{2} \quad (91)$$

mass

$$\rho_1 u_1 \cos \theta_1 = \rho_2 u_2 \cos \theta_2 \quad (92)$$

normal momentum

$$P_1 + \rho_1 u_1 \cos \theta_1 u_1 \cos \theta_1 = P_2 + \rho_2 u_2 \cos \theta_2 u_2 \cos \theta_2 \quad (93)$$

tangential momentum

$$\rho_1 u_1 \cos \theta_1 u_1 \sin \theta_1 = \rho_2 u_2 \cos \theta_2 u_2 \sin \theta_2 \quad (94)$$

Combining Eqs. (92) and (94) yields

$$u_1 \sin \theta_1 = u_2 \sin \theta_2 \quad (95)$$

that is, the tangential component of velocity is preserved across the shock. Eqs. (92) and (93) combine to yield

$$P_1 + \frac{(\rho_1 u_1 \cos \theta_1)^2}{\rho_1} = P_2 + \frac{(\rho_1 u_1 \cos \theta_1)^2}{\rho_2} \quad (96)$$

Now

$$u_2^2 = (u_2 \sin \theta_2)^2 + (u_2 \cos \theta_2)^2 \quad (97)$$

which with Eqs. (92) and (95) becomes

$$u_2^2 = (u_1 \sin \theta_1)^2 + \left(\frac{\rho_1 u_1 \cos \theta_1}{\rho_2} \right)^2 \quad (98)$$

With this, relation (96) becomes

$$h_1 + \frac{u_1^2}{2} = h_2 + \frac{1}{2} (u_1 \sin \theta_1)^2 + \frac{1}{2} (\rho_1 u_1 \cos \theta_1)^2 \frac{1}{\rho_2^2} \quad (99)$$

Presuming knowledge of the upstream conditions, Eqs. (96) and (99) contain as unknowns only h_2 , ρ_2 and P_2 . These two equations can be further reduced to

$$\sum_j p_j + (\rho_1 u_1 \cos \theta_1)^2 \frac{RT}{P\mathcal{M}} = P_1 + \frac{(\rho_1 u_1 \cos \theta_1)^2}{\rho_1} \quad (100)$$

$$\sum_j p_j H_j + \frac{1}{2} (\rho_1 u_1 \cos \theta_1)^2 \frac{(RT)^2}{P\mathcal{M}} = P\mathcal{M} \left[h_1 + \frac{(u_1 \cos \theta_1)^2}{2} \right] \quad (101)$$

where the non-subscripted variables are downstream of the shock. The first of this pair of equations replaces the more conventional pressure constraint and the latter the enthalpy constraint.

2.5 SUMMARY

In this section an attempt has been made to formalize the basic relations so as to simplify the generation of an orderly solution. Unfortunately dealing with nonlinear equations such as these is never straightforward and is subject to many pitfalls. In the next section, the procedures as adopted in the current solution technique are described.

SECTION 3 SOLUTION PROCEDURES

3.1 INTRODUCTION

The solution to a set of simultaneous nonlinear algebraic equations can be either trivially simple or agonizingly difficult, depending on the linearity of the system and the depth of coupling existing between the equations. None of the problems formulated in the last section fall into the first class and some fall into the latter. The basic formulation adopted is relatively conventional, and will be described first, followed by some discussion of the pitfalls that can be encountered and devices adopted to circumvent them.

3.2 BASIC FORMULATION

The most direct method of solving a set of nonlinear algebraic equations is the Newton-Raphson procedure. Its application is straightforward in concept but in reality many choices occur during the formulation of a specific problem, choices which can affect the success or failure of a specific solution. The method itself is the extension of Newton's iterative method to

multi-dimensional problems. Errors are evaluated for each of the equations based on a set of trial values for the unknown independent variables. The rates of change of these errors with respect to these independent variables are analytically determined, also based on the trial values. The differential relation

$$dE_1 = \frac{\partial E_1}{\partial V_1} dV_1 + \frac{\partial E_1}{\partial V_2} dV_2 + \dots \quad (102)$$

will apply for each error and the set of independent variables V_1, V_2, \dots . Considering this as a set of simultaneous equations in dV_1, dV_2, \dots , solution is readily obtained as

$$dV_1 = \frac{\partial V_1}{\partial E_1} dE_1 + \frac{\partial V_2}{\partial E_2} dE_2 + \dots \quad (103)$$

where the partial derivatives are the elements of the inverse of the matrix of the partial derivative coefficients of Eq. (102). Presuming these derivatives to be constants, the necessary corrections to each independent variable could be obtained as, for example

$$\Delta V_1 = \frac{\partial V_1}{\partial E_1} \Delta E_1 + \frac{\partial V_2}{\partial E_2} \Delta E_2 + \dots \quad (104)$$

where the $\Delta E_1, \Delta E_2, \dots$ are simply $-E_1, -E_2, \dots$ if the errors are to be driven to zero.

It should be noted that if some function of V is substituted for V in the above equation

$$\Delta f(V_1) = \frac{df(V_1)}{dV_1} \left\{ \frac{\partial V_1}{\partial E_1} \Delta E_1 + \frac{\partial V_2}{\partial E_2} \Delta E_2 + \dots \right\} \quad (105)$$

implying simply that in the formulation of the derivatives no commitment is made with regard to the optimum means of expressing the corrections of the independent variables, for example, in terms of $\ln p_j$ or simply p_j . In the formulation followed here, $\ln p_j, p_j, \ln T$, and $\ln(PM)$ are taken as the set of independent variables, but corrections are often in terms of $p_j, 1/T$ and PM . In some systems this choice yields linear mass balance equations which if once satisfied will never deviate.

In Table I the relations developed in the preceding section are summarized. In addition to the relations, given as error equations, the derivatives of the errors with respect to each of the set of independent variables are given. It should be apparent that many arbitrary choices go into the relations for these derivatives. As an example of this arbitrariness, consider the closed system mass balance and the derivative with respect to $\ln(P^M)$. In the table $\alpha_i P^M$ is given but the actual program permits either that term or the summation of $v_{ji} p_j$ over all j and l . At convergence these terms are identical, but during the convergence process different paths are followed by the two expressions. Cases have been encountered where convergence was unsuccessful with the first expression and successful with the latter.

3.3 SOLUTION CONVERGENCE

In general the convergence of the set of equations appropriate to a particular problem will depend on a number of factors in addition to the formulation of the derivatives. Correction coordinates, initial estimates, and correction restraints are all major factors. The following subsections will explore these factors in some detail.

3.3.1 Correction Coordinates

It has already been mentioned that the choice of coordinates can demonstrably effect the convergence of a system. Obviously a coordinate system that most nearly linearizes the relations between errors and independent variables is to be sought. Thus we note that with the closed system mass balance relation, the error expression is linearly dependent on P^M , p_j , and p_l , thus making them prime candidates as the independent correction variables. Likewise, the gas-phase equilibrium equation with error expressed as shown is linear in $1/T$ and $\ln p_j$, creating a bit of conflict between the two expressions for p_j .

Another specific example involves sets of species which are significant in only one mass balance, in particular ions which may be consequential in only the charge neutrality balance. For singly charged or ionized species, it can be shown that both charge balances and equilibrium can be expressed linearly in terms of the product $p_I p_j$ where I denotes the base species associated with charge neutrality (usually the electron) and j represents all charged species. The mass balance (i.e., charge neutrality balance) is simply multiplied by p_I . The equilibrium relations (Eq. (16)) are written as

$$E_j^I = p_I p_j - \frac{1}{K_{p_j}} \prod_{\substack{i \\ i \neq I}} p_i^{v_{ji}} p_I^{v_{jI}+1} \quad (106)$$

where the product is for all the neutral base species. For singly charged species with the electron as I, v_{jI} is either +1 or -1 and the linearity of $p_I p_j$ is obtained. (Note that p_I^2 is included in $p_I p_j$.) This represents a considerable departure from the previous evaluation of equilibrium errors, this error equation being related to the previous one (Table I) by

$$E_j' = -p_I p_j \left[\exp(E_j) - 1 \right] \quad (107)$$

The purpose of this discussion has been to establish the flexibility of the Newton-Raphson procedure with regard to dependent and independent variable specifications and the advantages that can be achieved by seeking a nearly linear dependence of the errors on the independent variables.

3.3.2 Correction Restraints

In this highly nonlinear application of the Newton-Raphson technique a variety of constraints with regard to independent variable corrections are necessary. These constraints all manifest themselves in a damping factor which limits the extent which the solution is advanced down the correction vector.

This factor is determined by use of the following limiting relation,

$$(\ln \bar{p}_j)_{hi} \leq \frac{4 + 4(\ln \bar{p}_j)_{lo}}{3 - (\ln \bar{p}_j)_{lo}} \quad (108)$$

that is, if a predicted increase in \bar{p}_j from a value $\bar{p}_{j_{lo}}$ yields a value of $\bar{p}_{j_{hi}}$ exceeding that indicated by the right hand side of Eq. (108), a damping factor will be applied such as to achieve the equality. For the case of decreasing \bar{p}_j this equation can be manipulated to

$$(\ln \bar{p}_j)_{lo} \geq \frac{-4 + 3(\ln \bar{p}_j)_{hi}}{4 + (\ln \bar{p}_j)_{hi}} \quad (109)$$

with the same implications. The following table demonstrates the nature of the equality in these relations.

$\ln \bar{p}_j$	lo	$-\infty$	-13	-5	-3	-2.33	-2	-1	0
	hi	-4	-3	-2	-1.33*	-1	-.6	0	1.33

The term, \bar{p}_j , is the partial pressure of species i normalized by its relative contribution to the mass balance equation wherein it is most significant. Specifically,

$$\bar{p}_j = p_j \left[\frac{\chi_{j,k}}{(\chi_{j,k})_{\max \text{ over all } j}} \right]_{\max \text{ over all } k} \quad (110)$$

where $\chi_{j,k}$ is the sum of all terms involving p_j in mass balance k . For gas phase species whose initial value of \bar{p}_j is less than the appropriate starred entry in the above table a logarithmic partial pressure correction is applied. Otherwise linear corrections are employed. After evaluating all corrections the minimum damping factor is determined, and is subsequently applied uniformly to all corrections.

3.3.3 Initial Guesses

It is obvious that a good first guess can save time in any iterative solution. In the present formulation these guesses are generally based on previous solutions and only the initial stagnation or shock solution does not have the benefit of prior solution. This solution is readily obtained from practically any first guess, since the stagnation state is usually at relatively elevated temperatures and has a fixed "elemental" composition. In the subroutine version of the chemical-state program used in conjunction with the boundary-layer procedure, first guesses are generally based on solutions at the same boundary-layer transverse location stored during prior iterations in the boundary-layer program or from solutions at the preceding axial station.

Because of the introduction of new species by the wall material it is necessary to initialize their compositions when the corresponding elements appear in the state solutions. Likewise if a species disappears, e.g., as the edge of the boundary layer is approached or because the sequence of boundary layer iterations results in the termination of surface mass addition, it

is necessary to zero the species in a fashion that will not result in a singular solution for the rest of the equations.

It is apparent that bookkeeping becomes a major factor in the state programs if efficient and stable repetitive utilization is to be made of the routines. This bookkeeping establishes optimum first guesses, determines which atomic elements are present, and zeros or initializes the appropriate molecular species.

3.4 SOLUTION MECHANICS

Up to this point the more basic aspects of the solution procedure have been presented. The actual mechanics also need to be described. The computational procedure is composed of eight major parts, the bookkeeping, the input and data organization, the evaluation of temperature-dependent thermodynamic properties, the evaluation of errors and the derivatives of the errors with respect to the independent variables, evaluation and integration of kinetic terms into the arrays of errors and derivatives, the inversion of the reduced form of the resultant matrix, the evaluation of corrections as limited by the constraints, and the determination of properties and property derivatives (after final convergence).

These eight parts are represented by eight routines in the Aerotherm Chemical Equilibrium (ACE) program. Each of these will be briefly described in the following paragraphs.

EQUIL

This routine is the main routine of the ACE program (or subprogram in conjunction with the CABLE program). It controls the majority of the bookkeeping, develops the constant terms of the mass balances, outputs the solution, controls the main iteration, and exercises certain limited solution constraints.

INPUT

This routine controls the reading of element and species data, the selection and setting-up of base species, the evaluation of the v_{ji} array, flagging of condensed species, and the setting-up of the very first guesses.

THERM

The evaluation of such temperature-dependent thermodynamic properties as enthalpy, entropy, specific heat and free energy are determined for each species by this routine.

MATER

For the specific option being considered, this routine evaluates all errors and error derivatives according to the relations given in Table I. It also prepares a matrix of coefficients based on a reduced set of independent variables. This is accomplished by substituting the expression for $\ln p_j$ obtained from the equilibrium relations (Eq. (16)) into the mass balance relations. This simple algebraic substitution produces a very significant reduction in the order of the coefficient array. Thus in the mass balance equations

$$\frac{\partial E_i}{\partial \ln p_j} d \ln p_j \quad (111)$$

is replaced by

$$\frac{\partial E_i}{\partial \ln p_j} \left[\sum_i v_{ji} d \ln p_i + \frac{\Delta H_j}{RT} d \ln T - dE_j \right] \quad (112)$$

The variables in the reduced array become $\ln p_i$, $\ln T$, $\ln P^M$ and p_ℓ . This procedure is essentially the same as that described in Refs. 3 and 4.

KINET

This routine determines reaction rates; ascertains the controlling reactions, on the basis of which it forms the σ_{ik} transformation matrix; prepared the reduced correction coefficients for the kinetic terms; and combines them with the previously determined coefficients.

RERAY

This general purpose inversion routine inverts the reduced coefficient and multiplies the result times the set of errors yielding an unconstrained set of corrections for the reduced set of independent variables.

CRECT

The unconstrained corrections for the remaining independent variables are calculated by this routine. For species which are important in mass balances the logarithmic corrections are changed to linear corrections, i.e.

$$\Delta p_j = \frac{1}{p_j} \Delta \ln p_j \quad (113)$$

in order to emphasize the linearity of the mass balance equations; all corrections are checked with regard to the constraints of Eqs. (108) or (109) and the minimum multiplier is determined, and corrections are appropriately reduced and added to the previous trial balance.

PROPS

This routine evaluates transport properties according to equations of Ref. 1 as well as the derivatives appropriate to the boundary-layer solution (see Section 4).

These brief descriptions serve to give an overview of the routines involved in the state calculations. The program has been extremely successful on a wide range of problems and convergence has usually been quite satisfactory.

SECTION 4 THERMODYNAMIC PROPERTY EVALUATION

Once solution is obtained for a given set of input parameters it is still necessary to evaluate a variety of properties which are state dependent. Some of these require simple summations and no particular discussion is required. Others involve either first or second derivatives of the state with respect to certain input variables. It is these properties with which the present section is primarily concerned. One of the incidental advantages of the Newton-Raphson procedure over other direct search or optimization (gradient) methods is that most of the information necessary for derivative determination is already compiled when solution is achieved.

Consider the closed system, assigned-enthalpy-pressure option. The reduced set of independent variables used in the formulation are $\ln p_i$, p_ℓ , $\ln(PM)$, and $\ln T$. In the program assignment, the independent variables are h , P , and α_i , the last term being the gram-atoms of "element" i in a gram of system. The equations which implicitly describe this system were summarized in Table I. The problem reduces to a set of equations

$$f_i(x_i, y_\ell) = 0 \quad (114)$$

where the x_i might be considered as the reduced set of variables $\ln p_i$, p_ℓ , $\ln(PM)$, and $\ln T$, and the y_ℓ are h , P and α_i . The goal is to achieve derivatives of the form $(\partial x/\partial y)$ at constant all other y , for example $(\partial T/\partial h)_{P, \alpha_i}$. The general procedure for doing this is described in Appendix A. The appendix actually considers both first and second derivatives, although

in practice only the first derivatives have been calculated. For the first derivatives

$$\left(\frac{\partial x_i}{\partial y_\ell}\right)_{y_\ell, \ell' \neq \ell} = - \left| \left(\frac{\partial f_k}{\partial x_i}\right)_{x_i', y_\ell} \right|^{-1} \left| \left(\frac{\partial f_k}{\partial y_\ell}\right)_{x_i', y_\ell} \right| \quad (115)$$

The matrix which must be inverted is identical with the error-coefficient array previously developed. The last vector term in the above equation is readily evaluated based on the error equations. Considering the error equations of Table I, the following table indicates the important derivatives for the assigned enthalpy, pressure and elemental composition problem.

Derivative with respect to Equation	P	h	α_k
Enthalpy	0	$-P\mathcal{M}$	0
Pressure	-1	0	0
Conservation	0	0	$-P\mathcal{M}$
Equilibrium	0	0	0

It should be noted that the reduction of independent variables that occurs when the equilibrium equations are substituted into the remaining equations does not affect these derivatives because P, h, and α_k do not appear in the equilibrium relations. Also the $P\mathcal{M}$ product is taken as a single independent variable (of the x-set) and thus does not enter into the partial derivative terms tabulated above. For the given example, derivatives of $\ln T$, $\ln P\mathcal{M}$, $\ln p_i$, and p_ℓ are determined with respect to h, P, and α_k . The derivatives of $\ln p_j$ are obtained by applying

$$d \ln p_j = \sum_i v_{ji} d \ln p_i + \frac{\Delta H_j}{RT} d \ln T \quad (116)$$

Derivatives of composition-dependent properties can then be obtained by conventional procedures. It is perhaps worth noting the relation between some

of the more conventional thermodynamic properties and the base set of variables. Specifically

$$C_p = \frac{1}{T} \left(\frac{\partial \ln T}{\partial h} \right)_{P, \alpha_k}^{-1} \quad (117)$$

$$\left(\frac{\partial \ln \mathcal{M}}{\partial \ln P} \right)_{T, \alpha_k} = P \left[\left(\frac{\partial \ln P \mathcal{M}}{\partial P} \right)_{h, \alpha_k} - \left(\frac{\partial \ln P \mathcal{M}}{\partial h} \right)_{P, \alpha_k} \left(\frac{\partial \ln T}{\partial h} \right)_{P, \alpha_k}^{-1} \left(\frac{\partial \ln T}{\partial P} \right)_{h, \alpha_k} \right] - 1 \quad (118)$$

$$\left(\frac{\partial \ln \mathcal{M}}{\partial \ln T} \right)_{P, \alpha_k} = \left(\frac{\partial \ln P \mathcal{M}}{\partial h} \right)_{P, \alpha_k} \left(\frac{\partial \ln T}{\partial h} \right)_{P, \alpha_k}^{-1} \quad (119)$$

$$\gamma = \left(\frac{\partial \ln p}{\partial \ln \rho} \right)_S = \left\{ 1 + \left(\frac{\partial \ln \mathcal{M}}{\partial \ln P} \right)_{T, \alpha_k} - \frac{R}{\mathcal{M} C_p} \left[1 - \left(\frac{\partial \ln \mathcal{M}}{\partial \ln T} \right)_{P, \alpha_k} \right]^2 \right\}^{-1} \quad (120)$$

are useful relations. A convenient reference to other thermodynamic derivatives is listed under "Thermodynamic Formulas" in more recent editions of the Handbook of Chemistry and Physics.

Similar relations to those given above can readily be generated for solutions at assigned entropy and pressure. For other cases it is often simplest to formulate the enthalpy, pressure, composition derivative array after obtaining solution based on a different set of constraints. This array is then used as indicated in the example above.

SECTION 5

SUMMARY AND CURRENT STATUS

In the preceding sections a general chemical state procedure has been developed and mathematically applied to a number of open and closed thermodynamic systems. An effort has been made to provide a relatively general approach to the problems associated with such solutions and to indicate, via examples in some cases, means of circumventing them. A very brief discussion of the mechanics of the solution served to introduce the program and subprograms involved in the computer analysis. Some of these routines are quite general in their present formulation, others directed toward specific systems.

Currently all equilibrium aspects of the program are fully operational for general chemical systems. This includes the various closed and open system options, the shock wave relations, the surface coupled boundary layer mass balances, the bookkeeping involved with treating appearing and disappearing atomic elements, and the property and property derivative calculations. The KINET routine currently treats only the heterogeneous reactions associated with graphite oxidation and reduction. The generalization of this routine following the detailed approach presented in this report is a major recommendation of this report.

The report has discussed in rather general fashion the treatment of general chemical systems. The ultimate program which should evolve from this study will be a General Nonequilibrium Ablation Thermochemistry (GNAT) program designed for treating the problems associated with equilibrium and nonequilibrium at and above ablating surfaces.

TABLE I

SUMMARY OF EQUATIONS AND RELEVANT INFLUENCE COEFFICIENTS*

1. Gas Phase Equilibrium: for all non-base gas phase species

$$\text{ERROR} = -\ln K_{p_j} + Y_j - \sum_i \nu_{j,i} Y_i \textcircled{1}$$

Derivatives with respect to:

$$\ln p_j: \delta_{jj'} (= 1.0 \text{ if } j = j'; = 0 \text{ if } j \neq j')$$

$$\left\{ \begin{array}{l} Y_i: -\nu_{j,i} \\ \text{or} \\ P_i: 0 \end{array} \right\} \textcircled{2}$$

$$P_\ell: 0$$

$$\ln P\%: 0$$

$$\ln T: \frac{-H_{j'} + \sum \nu_{j',i} H_i}{RT}$$

2. Condensed Species Equilibrium: for all present non-base condensed species
- $\textcircled{3}$

$$\text{ERROR} = -\ln K_{P_\ell} - \sum_i \nu_{\ell,i} Y_i \textcircled{1}$$

Derivatives with respect to

$$\ln p_j: 0$$

$$\left\{ \begin{array}{l} Y_i: -\nu_{\ell,i} \\ \text{or} \\ P_i: 0 \end{array} \right\} \textcircled{2}$$

$$P_\ell: 0$$

$$\ln P\%: 0$$

$$\ln T: \frac{-H_{\ell'} + \sum \nu_{\ell',i} H_i}{RT}$$

* Notes in circles and indexing conventions are at the conclusion of the table.

TABLE I (continued)

3. Surface Equilibrium: for the condensed species with the smallest algebraic error having a fail temperature equal to or greater than system temperature

$$\text{ERROR} = -\ln K_{P_{l^*}} - \sum_i v_{l^*i} y_i \quad \text{if } l^* \text{ is non-base} \quad \textcircled{1}$$

$$\text{ERROR} = -Y_{l^*} \quad \text{if } l^* \text{ is base species}$$

Derivatives with respect to:

$$\ln p_j: 0$$

$$\left\{ \begin{array}{l} y_i: -v_{l^*i} \\ \text{or} \\ p_i: 0 \end{array} \right\} \quad \textcircled{2}$$

$$p_l: 0$$

$$\ln P^M: 0$$

$$\ln T: \frac{H_{l^*} + \sum_i v_{l^*i} H_i}{RT} \quad \text{if } l^* \text{ is non-base}$$

$$\ln T: 0 \quad \text{if } l^* \text{ is base species}$$

This constraint is deleted if the chosen species is a present condensed species, i.e., if the system temperature equals the species fail temperature.

4. Closed System Enthalpy:

$$\text{ERROR} = -P^M h + \sum_{j,i,l} p_j H_i$$

Derivatives with respect to

$$\ln p_j: p_j H_i$$

$$\left\{ \begin{array}{l} y_i: p_i H_i \\ \text{or} \\ p_i: H_i \end{array} \right\} \quad \textcircled{3}$$

$$p_l: H_l$$

$$\ln P^M: -P^M h$$

$$\ln T: \sum_{i,j,l} C_{p_i} p_i$$

TABLE I (continued)

5. Closed System Entropy:

$$\text{ERROR} = -P\mathcal{M}S + \sum_{j,i,\ell} p_j S_j$$

Derivative with respect to

$$\ln p_j: p_j (S_j - R)$$

$$\left\{ \begin{array}{l} y_i: p_i (S_i - R) \\ \text{or} \\ p_i: S_i \end{array} \right\} \textcircled{2}$$

$$p_\ell: S_\ell$$

$$\ln (P\mathcal{M}): -P\mathcal{M}s$$

$$\ln T: \sum_{i,j,\ell} p_i C_{p_i}$$

6. Pressure:

$$\text{ERROR} = -P + \sum_{j,i_g} p_j$$

Derivatives with respect to

$$\ln p_j: p_j$$

$$\left\{ \begin{array}{l} y_i: p_i \\ \text{or} \\ p_i: 0 \end{array} \right\} \textcircled{2}$$

$$p_\ell: 0$$

$$\ln (P\mathcal{M}): 0$$

$$\ln T: 0$$

TABLE I (continued)

7. Oblique Shock Momentum:

$$\text{ERROR} = -P_1 - \frac{(\rho_1 u_1 \cos \theta_1)^2}{\rho_1} + \sum_{j, i_g} p_j + (\rho_1 u_1 \cos \theta_1)^2 \frac{RT}{P\mathcal{M}}$$

Derivatives with respect to

$$\ln p_j: p_j$$

$$\left\{ \begin{array}{l} y_i: p_i \\ \text{or} \\ p_i: 0 \end{array} \right\} \textcircled{2}$$

$$p_\ell: 0$$

$$\ln P\mathcal{M}: -(\rho_1 u_1 \cos \theta_1)^2 \frac{RT}{P\mathcal{M}}$$

$$\ln T: (\rho_1 u_1 \cos \theta_1)^2 \frac{RT}{P\mathcal{M}}$$

8. Oblique Shock Energy:

$$\text{ERROR} = -P\mathcal{M} \left[h_1 + \frac{(u_1 \cos \theta_1)^2}{2} \right] + \sum_{j, i, \ell} p_j H_j + \frac{1}{2} (\rho_1 u_1 \cos \theta_1)^2 \frac{(RT)^2}{P\mathcal{M}}$$

Derivatives with respect to

$$\ln p_j: p_j H_j$$

$$\left\{ \begin{array}{l} y_i: p_i H_i \\ \text{or} \\ p_i: H_i \end{array} \right\} \textcircled{2}$$

$$p_\ell: H_\ell$$

$$\ln (P\mathcal{M}): -P\mathcal{M} \left[h_1 + \frac{(u_1 \cos \theta_1)^2}{2} \right] - \frac{1}{2} (\rho_1 u_1 \cos \theta_1)^2 \frac{(RT)^2}{P\mathcal{M}}$$

$$\ln T: (\rho_1 u_1 \cos \theta_1)^2 \frac{(RT)^2}{P\mathcal{M}} + T \sum_{i, j, \ell} C_{P_i} p_i$$

TABLE I (continued)

9. Closed System Mass Balance:

$$\text{ERROR} = -P\mathcal{M}\alpha_i + \sum_{j,i,\ell} v_{ji,P_j}$$

Derivatives with respect to

$$\begin{aligned} \ln P_j: & v_{ji,P_j} & P_\ell: & v_{\ell i} \\ \left\{ \begin{array}{l} Y_i: \delta_{ii,P_i} \\ \text{or} \\ P_i: \delta_{ii} \end{array} \right\} & \textcircled{2} & \ln (P\mathcal{M}): & -P\mathcal{M}\alpha_i \\ & & \ln T: & 0 \end{aligned}$$

10. Surface Mass Balance Coupled to Boundary Layer:

$$\begin{aligned} \text{ERROR} &= -P\mathcal{M}_g \bar{\alpha}_i + (\rho v) (P\mathcal{M}_g \gamma_{f_i} + \sum_j P_j v_{ji} + P_{i_g}) \\ &+ \sum_{j,i_g} P_j \lambda_{ji} + \sum_\ell P_\ell v_{\ell i} + P_{i_c} + \gamma_{h_i} \sum_{j,i_g} P_j H_j \\ (\rho v) &= \dot{m}_g + \dot{m}_c - \sum_{\ell,i_c} P_\ell \mathcal{M}_\ell / P\mathcal{M}_g \end{aligned}$$

Derivatives with respect to

$$\begin{aligned} \ln P_j: & [(\rho v) v_{ji} + \lambda_{ji} + \gamma_{h_i} H_j] P_j \\ \left\{ \begin{array}{l} Y_i: [(\rho v) \delta_{ii} + \lambda_{ii} + \gamma_{h_i} H_i] P_i \\ \text{or} \\ P_i: 1 - (\mathcal{M}_i / P\mathcal{M}_g) \left(P\mathcal{M}_g \gamma_{f_i} + \sum_{j,i_g} P_j v_{ji} \right) \end{array} \right\} & \textcircled{2} \\ P_\ell: & v_{\ell i} - (\mathcal{M}_\ell / P\mathcal{M}_g) \left(P\mathcal{M}_g \gamma_{f_i} + \sum_{j,i_g} P_j v_{ji} \right) \end{aligned}$$

$$\begin{aligned} \ln (P\mathcal{M}_g): & [-\bar{\alpha}_i + (\dot{m}_g + \dot{m}_c) \gamma_{f_i}] P\mathcal{M}_g + \frac{\sum P_\ell \mathcal{M}_\ell}{P\mathcal{M}_g} \left(\sum_{j,i} P_j v_{ji} \right) \\ \ln T: & \gamma_{h_i} T \sum_{j,i_g} P_j H_j \end{aligned}$$

TABLE I (continued)

11. Surface Mass Balance Coupled to Convective Coefficients:

$$\begin{aligned} \text{ERROR} &= -P m_g^a z_{i'} + (\rho v) \sum_{j,i_g} P_j v_{ji'} + \sum_l P_l v_{li'} + P_{i'} c \\ &+ \sum_{j,i_g} P_j \frac{v_{ji'}}{F_j^*/\bar{F}} \\ \bar{F} &= \frac{\sum_{j,i_g} P_j m_j}{\sum_{j,i_g} P_j m_j / F_j^*} \\ (\rho v) &= \frac{\dot{m}_g + \dot{m}_c}{\rho_e^u e^c M} - \frac{\sum_{l,i_c} m_l P_l}{\sum_{j,i_g} P_j m_j} \end{aligned}$$

Derivatives with respect to

$$\begin{aligned} \ln p_j: & \left((\rho v) + \frac{\bar{F}}{F_j^*} \right) v_{ji', P_j} + \left[\sum_{j', i_g} v_{j', i'} \frac{P_{j'}}{F_{j'}^* \bar{F}} (1 - \bar{F}/F_{j'}^*) \right. \\ & \left. + \sum_{j', i_g} P_{j'} v_{j'i'} \frac{\sum_{l, i_c} m_l P_l}{\sum_{j, i_g} P_j m_j} \right] \frac{m_j P_j}{\sum_{j, i_g} P_j m_j} \\ \left. \begin{aligned} y_i: & \left((\rho v) + \frac{\bar{F}}{F_j^*} \right) \delta_{ii', P_i} + \left[\sum_{j', i_g} v_{j', i'} \frac{P_{j'}}{F_{j'}^* \bar{F}} (1 - \bar{F}/F_{j'}^*) \right. \\ & \left. + \sum_{j', i_g} P_{j'} v_{j'i'} \frac{\sum_{l, i_c} m_l P_l}{\sum_{j, i_g} P_j m_j} \right] \frac{m_i P_i}{\sum_{j, i_g} P_j m_j} \\ \text{or} & \\ P_i: & \delta_{ii'} - \frac{m_i}{P m_g} \sum_{j, i_g} P_j v_{ji'} \end{aligned} \right\} \textcircled{2} \end{aligned}$$

TABLE I (concluded)

$$P_l: \quad v_{li'} - \frac{m_l}{\sum_{j, i_g} p_j m_j} \sum_{j, i_g} p_j v_{ji'}$$

$$\ln (P m_g): \quad -P m_g \alpha_{Z_i}$$

$$\ln T: \quad 0$$

INDICES

i, i'	base species or "elements"
j, j'	gas phase non-base species
l, l'	condensed non-base species
i_c	included for condensed base species only
i_g	included for gas phase base species only
\sum_{j, i_g}	implies successive summation over all gas phase species

NOTES

- The variable y_i can have the following specifications
 - = $\ln p_i$, for gas phase base species
 - = 0, for present condensed base species or base species representing a non-present element (in this case p_i becomes the system variable in place of y_i)
 - < 0, for non-present condensed base species
 - variable, for non-present base species representing a present element.
 In all but the second instance y_i is a necessary but unknown variable of the system of equations.
- The variable p_i is used in lieu of y_i if the base species, i , is a present condensed species or represents a non-present element.
- Note the $v_{l^*i} = \delta_{l^*i}$ if l^* is a base species, likewise, $v_{ii'} = \delta_{ii'}$.

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APPENDIX A

DETERMINATION OF A SET OF FIRST AND SECOND DERIVATIVES
IMPLICITLY DEFINED BY A SET OF NONLINEAR ALGEBRAIC EQUATIONS

A set of K nonlinear algebraic equations in K variables x_i and j parameters y_j , can be expressed generally as

$$f_k(x_i, y_j) = 0 \quad 1 \leq k \leq K, \quad 1 \leq i \leq K \quad (1)$$

For any set of values for the parameters, y_j , the x_i are implicitly defined by the Eqs. (1). In many instances it is also desirable to obtain the effect of changes in the parameters y_j on the variables x_i , that is $\partial x_i / \partial y_j$. In the present case $\partial x_i / \partial y_j \partial y_j$, are also sought.

By differentiating Eq. (1) considering all x_i and y_j independent, the following partial derivatives can readily be obtained

$$f_{k x_i}, \quad f_{k y_j}, \quad f_{k x_i x_i}, \quad f_{k y_j y_j}, \quad f_{k x_i y_j}$$

The total differential of Eq. (1) is

$$df_k = f_{k x_i} dx_i + f_{k y_j} dy_j = 0 \quad (2)$$

where the repeated index implies summation. Dividing Eq. (2) by dy_j , holding all other y_j constant, but allowing the x_i to vary in accord with the Eqs. (1), yields

$$\frac{\partial f_k}{\partial y_j} = f_{k x_i} \frac{\partial x_i}{\partial y_j} + f_{k y_j} = 0 \quad (3)$$

where a convention has been adopted whereby $\partial f_k / \partial y_j$, implies $(\partial f_k / \partial y_j)_{y_j}$, $j \neq j'$ but with x_i varying to satisfy Eqs. (1) and $f_{k y_j}$, implies $(\partial f_k / \partial y_j)_{y_i x_i}$, $j \neq j'$. This set of K linear (in $\partial x_i / \partial y_j$) algebraic equations can be solved to yield

$$\frac{\partial x_i}{\partial y_j} = - \left| f_{k x_i} \right|^{-1} f_{k y_j} \quad (4)$$

which represents the desired result for first derivatives . Taking the differential of Eq. (3) yields

$$d\left(\frac{\partial f_k}{\partial y_{j'}}\right) = f_{k_{x_i x_i}} \frac{\partial x_i}{\partial y_{j'}} dx_i + f_{k_{x_i y_{j'}}} \frac{\partial x_i}{\partial y_{j'}} dy_{j'} + f_{k_{x_i}} d\left(\frac{\partial x_i}{\partial y_{j'}}\right) + f_{k_{y_{j'} y_{j'}}} dy_{j'} + f_{k_{y_{j'} x_i}} dx_i = 0 \quad (5)$$

If this relation is divided by dy_{j^*} at constant all other y_j but with x_i varying in accord with the Eqs. (1), there results

$$\frac{\partial^2 f_k}{\partial y_{j^*} \partial y_{j'}} = f_{k_{x_i x_i}} \frac{\partial x_i}{\partial y_{j'}} \frac{\partial x_i}{\partial y_{j^*}} + f_{k_{x_i y_{j^*}}} \frac{\partial x_i}{\partial y_{j'}} + f_{k_{x_i}} \frac{\partial^2 x_i}{\partial y_{j'} \partial y_{j^*}} + f_{k_{y_{j^*} y_{j'}}} + f_{k_{y_{j^*} x_i}} \frac{\partial x_i}{\partial y_{j^*}} = 0 \quad (6)$$

Solving for $\partial^2 x_i / \partial y_{j'} \partial y_{j^*}$ yields

$$\frac{\partial^2 x_i}{\partial y_{j'} \partial y_{j^*}} = - \left| f_{k_{x_i x_i}} \right|^{-1} \left\{ \left(f_{k_{x_i x_i}} \frac{\partial x_i}{\partial y_{j'}} + f_{k_{y_{j'} x_i}} \right) \frac{\partial x_i}{\partial y_{j^*}} + f_{k_{x_i y_{j^*}}} \frac{\partial x_i}{\partial y_{j'}} + f_{k_{y_{j'} y_{j^*}}} \right\} \quad (7)$$

which represents the desired result for second derivatives. Note that the first term in the brace involves a triple sum (over k, i and i') and thus the time required to generate a single term is proportional to K^3 . To generate all terms in the three-dimensional array of second derivatives requires a time proportional to K^4 .