CR-65224

ONE-DIMENSIONAL REACTING GAS

NONEQUILIBRIUM PERFORMANCE PROGRAM

INTERIM ANALYSIS REPORT

5435-6004-RU000

17 SEPTEMBER 1965

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER

Under Contract No. NAS9-4358

TRW SYSTEMS

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Prepared for

National Aeronautics and Space Administration
Manned Spacecraft Center

Under Contract No. NAS9-4358

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CONTENTS

NOMENCLATURE

a	Nozzle area, also reaction rate parameter
A	Diabatic heat addition term linking fluid dynamic and relaxation processes
b	Reaction rate parameter
B	Energy exchange term linking fluid dynamic and relaxation processes
c	Species mass fraction
c_F	Thrust coefficient
C_P	Heat capacity
C^*	Characteristic exhaust velocity
f	Derivative
F	Free energy
h	Enthalpy, also integration increment
H	Total enthalpy
ΔH_F	Heat of formation
I_{sp}	Specific impulse
k	Variable increment, also reaction rate parameter
K	Equilibrium constant
m	Reaction rate ratio
M	Mach number, also third body reaction term
n	Reaction rate parameter, also summation or iteration index
N_P	Pressure expansion coefficient
N_T	Temperature expansion coefficient
P	Pressure
r^*	Nozzle throat radius

R	Gas constant
R^*	Nozzle wall radius of curvature at throat
S	Entropy, also summation term
T	Temperature
V	Velocity
x	Axial distance
y	Dependent variable
α_i	Partial derivative, $\partial f_i/\partial x$
$\beta_{i,j}$	Partial derivative, $\partial f_i/\partial y_j$
γ	Gamma
δ_i	Incremental error
$\delta_{i,j}$	Kronecker delta
ϵ	Area ratio
ρ	Density
θ	Nozzle cone angle

Subscripts:

c	Refers to chamber conditions
i	Refers to ith species or equation
j	Refers to jth reaction or variable
o	Refers to reference conditions

Superscripts:

C	Refers to corrected increment
P	Refers to predicted increment
*	Refers to throat conditions

1. INTRODUCTION

This report contains a complete engineering description of the first computer program being developed by TRW Systems Group for NASA (MSC) under Contract NAS9-4358, Development of Six (6) Computer Programs for Analytical Prediction of Delivered Specific Surpulse.

The objective of this contract is to develop a family of six computer programs to calculate inviscid, one-dimensional, and axisymmetric non-equilibrium nozzle flow fields. Assuming that equilibrium conditions exist in the combustion chamber, these programs will calculate the non-equilibrium nozzle expansion of propellant exhaust mixtures containing the six elements: carbon, hydrogen, oxygen, nitrogen, fluorine, chlorine, and one metal element, either aluminum, beryllium, boron or lithium. These computer programs will account for the nonequilibrium effects of finite rate chemical reactions between gaseous combustion products and velocity and thermal lags between gaseous and condensed combustion products.

The computer program described in this report calculates the inviscid one-dimensional nonequilibrium nozzle expansion of propellant exhaust mixtures containing the six elements: carbon, hydrogen, oxygen, nitrogen, fluorine, and chlorine. The computer program considers the 18 significant gaseous species present in the exhaust mixtures of propellants containing these elements and the 39 chemical reactions (12 dissociation-recombination reactions and 27 binary exchange reactions) which can occur between the exhaust products. The computer program is designed for engineering use and is specified and programmed in a straightforward manner to facilitate its use as a development tool. In order to reduce the computation time per case to a minimum, the program utilizes a second order implicit integration method. This integration method has been demonstrated to reduce the computation time per case several orders of magnitude when directly compared with the computation times required utilizing standard explicit integration methods such as fourth order Runge-Kutta or Adams-Moulton methods.

Section 2 contains a derivation of the equations governing the inviscid, one-dimensional flow of a chemically reacting gas mixture in the form in which they are integrated in the computer program.

Section 3 contains a brief discussion of the use of both implicit and explicit integration methods to integrate relaxation equations, and a complete derivation of the second order implicit integration method used in the computer program.

Section 4 contains a detailed engineering description of all the calculations performed in the computer program.

At the completion and delivery of this computer program to NASA (MSC), an updated version of this document describing the engineering analyses, a similar document describing the programming and program logic, and a user's manual describing the use of the program will be delivered to NASA (MSC) to complete the program documentation.

2. CONSERVATION EQUATIONS

The conservation equations governing the inviscid one-dimensional flow of reacting gas mixtures have been given by Hirshfelder, Curtiss and Byrd,[1] Penner[2] and others. The basic assumptions made in deriving these conservation equations are:

- There are no mass or energy losses from the system.
- The gas is inviscid.
- Each component of the gas is a perfect gas.
- The internal degrees of freedom (translational, rotational and vibrational) of each component of the gas are in equilibrium.

The conservation equations are presented here in the form used in the present analysis.

For each component of the gas the continuity equation is

$$\frac{d}{dx}(\rho_i V a) = \omega_i r^* a \tag{2-1}$$

where the axial coordinate (x) has been normalized with the throat radius. Summing over all components of the mixture, the overall continuity equation is obtained

$$\frac{d}{dx}(\rho V a) = 0 \tag{2-2}$$

By use of the above equation, Equation (2-1) can be rewritten as

$$\frac{dc_i}{dx} = \frac{\omega_i r^*}{\rho V} \tag{2-3}$$

The momentum equation is

$$\rho V \frac{dV}{dx} + \frac{dP}{dx} = 0 \tag{2-4}$$

The energy equation is

$$h + \frac{1}{2} V^2 = H_c \tag{2-5}$$

where

$$h = \sum_{i=1}^{n} c_i h_i \tag{2-5a}$$

and

$$h_i = \int_0^T C_{pi} dT + h_{io} \tag{2-5b}$$

For each component of the gas, the equation of state is

$$P_i = \rho_i R_i T \tag{2-6}$$

Summing over all components of the mixture, the overall equation of state is obtained

$$P = \rho R T \tag{2-7}$$

where

$$R = \sum_{i=1}^{n} c_i R_i \tag{2-7a}$$

Since the expansion through a nozzle can be specified either by the expansion process or by the nozzle geometry, two forms of the above equations are of interest.

If the expansion process is specified and the pressure is known as a function of distance through the nozzle, the above equations become

$$\frac{dc_i}{dx} = \frac{\omega_i r^*}{\rho V} \tag{2-8}$$

$$\frac{dV}{dx} = -\frac{1}{\rho V}\frac{dP}{dx} \qquad (2\text{-}9)$$

$$\frac{d\rho}{dx} = \left[\frac{1}{\gamma P}\frac{dP}{dx} - A\right]\rho \qquad (2\text{-}10)$$

$$\frac{dT}{dx} = \left[\frac{\gamma - 1}{\gamma}\frac{1}{P}\frac{dP}{dx} - B\right]T \qquad (2\text{-}11)$$

while if the nozzle geometry is specified, the above equations become

$$\frac{dc_i}{dx} = \frac{\omega_i r^*}{\rho V} \qquad (2\text{-}12)$$

$$\frac{dV}{dx} = \left[\frac{1}{a}\frac{da}{dx} - A\right]\frac{V}{M^2 - 1} \qquad (2\text{-}13)$$

$$\frac{d\rho}{dx} = \left\{\left[\frac{1}{a}\frac{da}{dx} - A\right]\frac{M^2}{M^2 - 1} - A\right\}\rho \qquad (2\text{-}14)$$

$$\frac{dT}{dx} = -\left\{\left[\frac{1}{a}\frac{da}{dx} - A\right]\frac{M^2}{M^2 - 1} - B\right\}T \qquad (2\text{-}15)$$

$$\frac{dP}{dx} = -\left[\frac{1}{a}\frac{da}{dx} - A\right]\frac{\gamma M^2}{M^2 - 1}P \qquad (2\text{-}16)$$

where

$$A = \frac{r^*}{PV}\left[\sum_{i=1}^{n}\omega_i R_i T + \frac{\gamma - 1}{\gamma}\sum_{i=1}^{n}\omega_i h_i\right] \qquad (2\text{-}17a)$$

$$B = \frac{r^*}{PV}\sum_{i=1}^{n}\omega_i R_i T \qquad (2\text{-}17b)$$

$$M = \frac{V}{\sqrt{\gamma R T}} \qquad (2\text{-}17c)$$

$$\gamma = \frac{C_p}{C_p - R} \qquad (2\text{-}17d)$$

and

$$C_p = \sum_{i=1}^{n} c_i C_{pi}. \qquad (2\text{-}17e)$$

The first set of equations is completely specified at the sonic point while the second set of equations is singular. Thus, if the expansion through the nozzle is specified by the pressure distribution, the equations governing the expansion can be directly integrated through the sonic point without mathematical difficulty. The expansion from the chamber through the sonic point is specified by the pressure distribution in the present program in order to eliminate numerical difficulties at the sonic point. In the expansion section downstream of the sonic point, however, the area variation is specified and the second set of equations is integrated through the supersonic expansion section.

In specifying the nozzle pressure distribution from the chamber through the sonic point, rather than the known area distribution, a question naturally arises regarding how accurately the calculation represents the flow through a specified nozzle geometry. It has been shown by Bray[3] and others that the pressure distribution through a nozzle is essentially identical with the equilibrium pressure distribution up to the freeze point which generally occurs downstream of the throat (or sonic point). Thus, the difference in the expansion and predicted performance caused by utilizing the equilibrium pressure distribution rather than the nozzle geometry to specify the expansion from the chamber to the sonic point is negligible. If a case does arise in which the equilibrium pressure distribution is not an adequate representation of the expansion, the pressure distribution can be iterated to obtain the correct pressure distribution. Experience has shown that this is rarely if ever required, however.

Assuming that equilibrium conditions exist in the combustion chamber, the present program has been written to calculate the non-equilibrium nozzle expansion of propellant exhaust mixtures containing the six elements: carbon, hydrogen, oxygen, nitrogen, fluorine and chorine.

Gold[4] has established that the 18 species and 39 chemical reactions (12 dissociation-recombination reactions and 27 binary exchange reactions) given in Tables 2-1 and 2-2 need to be considered in calculating the non-equilibrium nozzle expansions of propellant exhaust mixtures containing the above six elements. Considering these species and chemical reactions, the net species production rates (ω_i) for each species considered by the program are:

For CO_2,

$$\omega_1 = -44.011\,\rho^2 \left[X_1 + X_{13} + X_{14} - X_{18} - X_{21}\right] \tag{2-18}$$

For H_2O,

$$\omega_2 = -18.016\,\rho^2 \left[X_2 + X_{15} + X_{16} + X_{17} - X_{31}\right] \tag{2-19}$$

For CO,

$$\omega_3 = 28.011\,\rho^2 \left[X_1 - X_3 + X_{13} + X_{14} - 2X_{18} - X_{19} - X_{20} - X_{21} - X_{22}\right] \tag{2-20}$$

For Cl_2,

$$\omega_4 = -70.914\,\rho^2 \left[X_4 - X_{23} - X_{24}\right] \tag{2-21}$$

For F_2,

$$\omega_5 = -38.000\,\rho^2 \left[X_5 - X_{27} - X_{29}\right] \tag{2-22}$$

For HCl,

$$\omega_6 = -36.465\,\rho^2 \left[X_6 - X_{15} + X_{23} + 2X_{24} + X_{25} - X_{26} - X_{32}\right] \tag{2-23}$$

Table 2-1. Chemical Species Considered in the Program

Species Number	Chemical Species
1	CO_2
2	H_2O
3	CO
4	Cl_2
5	F_2
6	HCl
7	HF
8	H_2
9	N_2
10	NO
11	OH
12	O_2
13	C
14	Cl
15	F
16	H
17	N
18	O

Table 2-2. Chemical Reaction Considered in the Program

Reaction Number	Chemical Reaction	Reaction Number	Chemical Reaction
1	$CO_2 + M \rightleftharpoons CO + O + M$	21	$CO + NO \rightleftharpoons CO_2 + N$
2	$H_2O + M \rightleftharpoons OH + H + M$	22	$CO + O \rightleftharpoons C + O_2$
3	$CO + M \rightleftharpoons C + O + M$	23	$HCl + Cl \rightleftharpoons H + Cl_2$
4	$Cl_2 + M \rightleftharpoons 2Cl + M$	24	$HCl + HCl \rightleftharpoons H_2 + Cl_2$
5	$F_2 + M \rightleftharpoons 2F + M$	25	$HCl + O \rightleftharpoons OH + Cl$
6	$HCl + M \rightleftharpoons H + Cl + M$	26	$HF + Cl \rightleftharpoons HCl + F$
7	$HF + M \rightleftharpoons H + F + M$	27	$HF + F \rightleftharpoons H + F_2$
8	$H_2 + M \rightleftharpoons 2H + M$	28	$HF + H \rightleftharpoons H_2 + F$
9	$N_2 + M \rightleftharpoons 2N + M$	29	$HF + HF \rightleftharpoons H_2 + F_2$
10	$NO + M \rightleftharpoons N + O + M$	30	$HF + O \rightleftharpoons OH + F$
11	$OH + M \rightleftharpoons O + H + M$	31	$HF + OH \rightleftharpoons H_2O + F$
12	$O_2 + M \rightleftharpoons 2O + M$	32	$H_2 + Cl \rightleftharpoons HCl + H$
13	$CO_2 + H \rightleftharpoons CO + OH$	33	$H_2 + O \rightleftharpoons OH + H$
14	$CO_2 + O \rightleftharpoons CO + O_2$	34	$H_2 + O_2 \rightleftharpoons 2OH$
15	$H_2O + Cl \rightleftharpoons OH + HCl$	35	$N_2 + O \rightleftharpoons NO + N$
16	$H_2O + H \rightleftharpoons OH + H_2$	36	$N_2 + O_2 \rightleftharpoons 2NO$
17	$H_2O + O \rightleftharpoons 2OH$	37	$NO + H \rightleftharpoons N + OH$
18	$CO + CO \rightleftharpoons CO_2 + C$	38	$NO + O \rightleftharpoons N + O_2$
19	$CO + H \rightleftharpoons C + OH$	39	$O_2 + H \rightleftharpoons OH + O$
20	$CO + N \rightleftharpoons C + NO$		

For HF,

$$\omega_7 = -20.008\ \rho^2 \left[X_7 + X_{26} + X_{27} + X_{28} + 2X_{29} + X_{30} + X_{31}\right] \quad (2\text{-}24)$$

For H_2,

$$\omega_8 = -2.016\ \rho^2 \left[X_8 - X_{16} - X_{24} - X_{28} - X_{29} + X_{32} + X_{33} + X_{34}\right] \quad (2\text{-}25)$$

For N_2,

$$\omega_9 = -28.016\ \rho^2 \left[X_9 + X_{35} + X_{36}\right] \quad (2\text{-}26)$$

For NO,

$$\omega_{10} = -30,008\ \rho^2 \left[X_{10} - X_{20} + X_{21} - X_{35} - 2X_{36} + X_{37} + X_{38}\right] \quad (2\text{-}27)$$

For OH,

$$\omega_{11} = 17.008\ \rho^2 \left[X_2 - X_{11} + X_{13} + X_{15} + X_{16} + 2X_{17} + X_{19} + X_{25} + X_{30} - X_{31} + X_{33} + 2X_{34} + X_{37} + X_{39}\right] \quad (2\text{-}28)$$

For O_2,

$$\omega_{12} = -32.000\ \rho^2 \left[X_{12} - X_{14} - X_{22} + X_{34} + X_{36} - X_{38} + X_{39}\right] \quad (2\text{-}29)$$

For C,

$$\omega_{13} = 12.011\,\rho^2 \left[X_3 + X_{18} + X_{19} + X_{20} + X_{22}\right] \tag{2-30}$$

For Cl,

$$\omega_{14} = 35.457\,\rho^2 \left[2X_4 + X_6 - X_{15} - X_{23} + X_{25} - X_{26} - X_{32}\right] \tag{2-31}$$

For F,

$$\omega_{15} = 19.000\,\rho^2 \left[2X_5 + X_7 + X_{26} - X_{27} + X_{28} + X_{30} + X_{31}\right] \tag{2-32}$$

For H,

$$\omega_{16} = 1.008\,\rho^2 \left[X_2 + X_6 + X_7 + 2X_8 + X_{11} - X_{13} - X_{16} - X_{19} + X_{23} + X_{27} - X_{28} + X_{32} + X_{33} - X_{37} - X_{39}\right] \tag{2-33}$$

For N,

$$\omega_{17} = 14.008\,\rho^2 \left[2X_9 + X_{10} - X_{20} + X_{21} + X_{35} + X_{37} + X_{38}\right] \tag{2-34}$$

For O,

$$\omega_{18} = 16.000\,\rho^2 \left[X_1 + X_3 + X_{10} + X_{11} + 2X_{12} - X_{14} - X_{17} - X_{22} - X_{25} - X_{30} - X_{33} - X_{35} - X_{38} + X_{39}\right] \tag{2-35}$$

where the net production rate for each reaction (X_j) considered by the program is:

Reaction 1, $CO_2 + M \rightleftharpoons CO + O + M$

$$X_1 = \left[K_1 c_1 - \rho c_3 c_{18}\right] M_1 k_1 \qquad (2\text{-}36)$$

Reaction 2, $H_2O + M \rightleftharpoons OH + H + M$

$$X_2 = \left[K_2 c_2 - \rho c_{11} c_{16}\right] M_2 k_2 \qquad (2\text{-}37)$$

Reaction 3, $CO + M \rightleftharpoons C + O + M$

$$X_3 = \left[K_3 c_3 - \rho c_{12} c_{18}\right] M_3 k_3 \qquad (2\text{-}38)$$

Reaction 4, $Cl_2 + M \rightleftharpoons 2Cl + M$

$$X_4 = \left[K_4 c_4 - \rho c_{14}^2\right] M_4 k_4 \qquad (2\text{-}39)$$

Reaction 5, $F_2 + M \rightleftharpoons 2F + M$

$$X_5 = \left[K_5 c_5 - \rho c_{15}^2\right] M_5 k_5 \qquad (2\text{-}40)$$

Reaction 6, $HCl + M \rightleftharpoons H + Cl + M$

$$X_6 = \left[K_6 c_6 - \rho c_{14} c_{16}\right] M_6 k_6 \qquad (2\text{-}41)$$

Reaction 7, $HF + M \rightleftharpoons H + F + M$

$$X_7 = \left[K_7 c_7 - \rho c_{15} c_{16}\right] M_7 k_7 \qquad (2\text{-}42)$$

Reaction 8, $H_2 + M \rightleftharpoons 2H + M$

$$X_8 = \left[K_2 c_8 - \rho c_{16}^2\right] M_8 k_8 \qquad (2\text{-}43)$$

Reaction 9, $N_2 + M \rightleftharpoons 2N + M$

$$X_9 = \left[K_9 c_9 - \rho c_{17}^2\right] M_9 k_9 \tag{2-44}$$

Reaction 10, $NO + M \rightleftharpoons N + O + M$

$$X_{10} = \left[K_9 c_{10} - \rho c_{17} c_{18}\right] M_{10} k_{10} \tag{2-45}$$

Reaction 11, $OH + M \rightleftharpoons O + H + M$

$$X_{11} = \left[K_{11} c_{11} - \rho c_{16} c_{18}\right] M_{11} k_{11} \tag{2-46}$$

Reaction 12, $O_2 + M \rightleftharpoons 2O + M$

$$X_{12} = \left[K_{12} c_{12} - \rho c_{18}^2\right] M_{12} k_{12} \tag{2-47}$$

Reaction 13, $CO_2 + H \rightleftharpoons CO + OH$

$$X_{13} = \left[K_{13} c_1 c_{16} - c_3 c_{11}\right] k_{13} \tag{2-48}$$

Reaction 14, $CO_2 + O \rightleftharpoons CO + O_2$

$$X_{14} = \left[K_{14} c_1 c_{18} - c_3 c_{12}\right] k_{14} \tag{2-49}$$

Reaction 15, $H_2O + Cl \rightleftharpoons HCl + OH$

$$X_{15} = \left[K_{15} c_2 c_{14} - c_6 c_{11}\right] k_{15} \tag{2-50}$$

Reaction 16, $H_2O + H \rightleftharpoons H_2 + OH$

$$X_{16} = \left[K_{16} c_2 c_{16} - c_8 c_{11}\right] k_{16} \tag{2-51}$$

Reaction 17, $H_2O + O \rightleftharpoons 2OH$

$$X_{17} = \left[K_{17} c_2 c_{18} - c_{11}^2\right] k_{17} \tag{2-52}$$

Reaction 18, $2CO \rightleftharpoons CO_2 + C$

$$X_{18} = \left[K_{18}c_3^2 - c_1c_{13}\right]k_{18} \tag{2-53}$$

Reaction 19, $CO + H \rightleftharpoons OH + C$

$$X_{19} = \left[K_{19}c_3c_{16} - c_{11}c_{13}\right]k_{19} \tag{2-54}$$

Reaction 20, $CO + N \rightleftharpoons NO + C$

$$X_{20} = \left[K_{20}c_3c_{17} - c_{10}c_{13}\right]k_{20} \tag{2-55}$$

Reaction 21, $CO + NO \rightleftharpoons CO_2 + N$

$$X_{21} = \left[K_{21}c_3c_{10} - c_1c_{17}\right]k_{21} \tag{2-56}$$

Reaction 22, $CO + O \rightleftharpoons O_2 + C$

$$X_{22} = \left[K_{22}c_3c_{18} - c_{12}c_{13}\right]k_{22} \tag{2-57}$$

Reaction 23, $HCl + Cl \rightleftharpoons Cl_2 + H$

$$X_{23} = \left[K_{23}c_6c_{14} - c_4c_{16}\right]k_{23} \tag{2-58}$$

Reaction 24, $2HCl \rightleftharpoons Cl_2 + H_2$

$$X_{24} = \left[K_{24}c_6^2 - c_4c_8\right]k_{24} \tag{2-59}$$

Reaction 25, $HCl + O \rightleftharpoons OH + Cl$

$$X_{25} = \left[K_{25}c_6c_{18} - c_{11}c_{14}\right]k_{25} \tag{2-60}$$

Reaction 26, $HF + Cl \rightleftharpoons HCl + F$

$$X_{26} = \left[K_{26}c_7c_{14} - c_6c_{15}\right]k_{26} \tag{2-61}$$

Reaction 27, $HF + F \rightleftharpoons F_2 + H$

$$X_{27} = \left[K_{27}c_7c_{15} - c_5c_{16}\right]k_{27} \tag{2-62}$$

Reaction 28, $HF + H \rightleftharpoons H_2 + F$

$$X_{28} = \left[K_{28}c_7c_{16} - c_8c_{15}\right]k_{28} \tag{2-63}$$

Reaction 29, $2HF \rightleftharpoons F_2 + H_2$

$$X_{29} = \left[K_{29}c_7^2 - c_5c_8\right]k_{29} \tag{2-64}$$

Reaction 30, $HF + O \rightleftharpoons OH + F$

$$X_{30} = \left[K_{30}c_7c_{18} - c_{11}c_{15}\right]k_{30} \tag{2-65}$$

Reaction 31, $HF + OH \rightleftharpoons H_2O + F$

$$X_{31} = \left[K_{31}c_7c_{11} - c_2c_{15}\right]k_{31} \tag{2-66}$$

Reaction 32, $H_2 + Cl \rightleftharpoons HCl + H$

$$X_{32} = \left[K_{32}c_8c_{14} - c_6c_{16}\right]k_{32} \tag{2-67}$$

Reaction 33, $H_2 + O \rightleftharpoons OH + H$

$$X_{33} = \left[K_{33}c_8c_{18} - c_{11}c_{16}\right]k_{33} \tag{2-68}$$

Reaction 34, $H_2 + O_2 \rightleftharpoons 2OH$

$$X_{34} = \left[K_{34}c_8c_{12} - c_{11}^2\right]k_{34} \tag{2-69}$$

Reaction 35, $N_2 + O \rightleftharpoons NO + N$

$$X_{35} = \left[K_{35}c_9c_{18} - c_{10}c_{17}\right]k_{35} \tag{2-70}$$

Reaction 36, $N_2 + O_2 \rightleftharpoons 2NO$

$$X_{36} = \left[K_{36}c_9c_{12} - c_{10}^2\right]k_{36} \tag{2-71}$$

Reaction 37, $NO + H \rightleftharpoons OH + N$

$$X_{37} = \left[K_{37}c_{10}c_{16} - c_{11}c_{17}\right]k_{37} \tag{2-72}$$

Reaction 38, $NO + O \rightleftharpoons O_2 + N$

$$X_{38} = \left[K_{38}c_{10}c_{18} - c_{12}c_{17}\right]k_{38} \tag{2-73}$$

Reaction 39, $O_2 + H \rightleftharpoons OH + O$

$$X_{39} = \left[K_{39}c_{12}c_{16} - c_{11}c_{18}\right]k_{39} \tag{2-74}$$

The dissociation-recombination reactions have a distinct reaction rate associated with each third body. Benson and Fueno[5] have shown that the temperature dependence of recombination rates is approximately T^{-1} independent of the third body. Thus the rates associated with each third body can be considered by calculating the third body term (M_j) as

$$M_j = \sum_{i=1}^{18} m_{j,i}c_i \tag{2-75}$$

where $m_{j,i}$ is the ratio of the recombination rate associated with the ith species (third body) and the recombination rate (k_j) associated with the reference species (third body) in the calculation.

In summary, assuming that equilibrium conditions exist in the chamber, the program calculates the nonequilibrium expansion of propellant exhaust mixtures containing the six elements: carbon, hydrogen, oxygen, nitrogen, fluorine and chlorine. The 18 species and 39 chemical reactions (12 dissociation-recombination reactions and 27 binary exchange reactions) given in Tables 2-1 and 2-2 are considered in the nonequilibruim expansion calculation. The expansion process from the chamber through the throat is specified by the pressure distribution through the nozzle and the set of equations

$$\frac{dc_i}{dx} = \frac{\omega_i r^*}{\rho V} \quad , \quad i = 1, 2, \cdots, 18. \tag{2-8}$$

$$\frac{dV}{dx} = - \frac{1}{\rho V} \frac{dP}{dx} \tag{2-9}$$

$$\frac{d\rho}{dx} = \left[\frac{1}{\gamma P} \frac{dP}{dx} - A \right] \rho \tag{2-10}$$

$$\frac{dT}{dx} = \left[\frac{\gamma - 1}{\gamma} \frac{1}{P} \frac{dP}{dx} - B \right] T \tag{2-11}$$

are integrated from the chamber through the sonic point. In the expansion section downstream of the sonic point, the area variation is specified and the set of equations

$$\frac{dc_i}{dx} = \frac{\omega_i r^*}{\rho V} \quad , \quad i = 1, 2, \cdots, 18. \tag{2-12}$$

$$\frac{dV}{dx} = \left[\frac{1}{a} \frac{da}{dx} - A \right] \frac{V}{M^2 - 1} \tag{2-13}$$

$$\frac{d\rho}{dx} = - \left\{ \left[\frac{1}{a} \frac{da}{dx} - A \right] \frac{M^2}{M^2 - 1} - A \right\} \rho \tag{2-14}$$

$$\frac{dT}{dx} = - \left\{ \left[\frac{1}{a} \frac{da}{dx} - A \right] \frac{M^2}{M^2 - 1} - B \right\} T \tag{2-15}$$

$$\frac{dP}{dx} = - \left\{ \left[\frac{1}{a} \frac{da}{dx} - A \right] \frac{\gamma M^2}{M^2 - 1} \right\} P \tag{2-16}$$

are integrated to the nozzle exit.

The above equations are all of the form

$$\frac{dy_i}{dx} = f_i(x, y, \cdots, y_n) \quad , \quad i = 1, 2, \cdots, n \tag{2-76}$$

The numerical method used in the program to integrate these equations is described in detail in Section 3. All calculations performed in the program are described in Section 4.

3. NUMERICAL INTEGRATION METHOD

It has been shown by Tyson[6] that in the numerical integration of relaxation equations in near equilibrium flow regions (such as the chamber and nozzle inlet in rocket engines), explicit integration methods are unstable unless the integration step size is of the order of the characteristic relaxation distance of the relaxation equations. Since the characteristic relaxation distance is orders of magnitude smaller than the characteristic physical dimensions of the system of interest (such as the nozzle throat diameter and length) in near equilibrium flow regions, the use of explicit methods to integrate relaxation equations in these regions results in excessively long computation times. Implicit integration methods were shown to be inherently stable in integrating relaxation equations in all flow situations (whether near equilibrium or frozen) and can thus be used to integrate with step sizes of the order of the physical dimensions of the system of interest throughout the integration reducing the computation time per case several orders of magnitude. Since it has been demonstrated that there are significant advantages in using implicit rather than explicit integration methods for integrating relaxation equations, a second order implicit integration method has been chosen for use in TRW/NASA One-Dimensional Nonequilibrium Performance Programs.

3.1 STABILITY CONSIDERATIONS

The numerical considerations leading to the above conclusions can be illustrated by considering the simple relaxation equation

$$\frac{dy}{dx} = - \frac{y - y_e}{\tau} \tag{3-1}$$

which represents the relaxation toward equilibrium of chemical reactions, gas particle lags, etc. In this equation, y_e is the equilibrium condition and τ is the characteristic relaxation distance of the equation. In the equilibrium limit, τ is very small compared to the physical dimensions of the system of interest while in the frozen limit, τ, is very large compared to the physical dimensions of the system of interest. The mathematical behavior of solutions to the above equation can be found by considering the simple case where τ is constant and

$$y_e = y_{eo} + a(x - x_o) \tag{3-2}$$

which is equivalent to terminating the Taylor series for y_e after the first term. The exact solution of Equation (3-1) for this case can be shown to be

$$y(x_o + h) = y(x_o) + \left[y_{eo} - y(x_o) - a\tau\right]\left[1 - e^{-h/\tau}\right] + ah \tag{3-3}$$

where $y(x_o)$ is the initial value of y and h is the integration step.

It is seen that the solution consists of two parts, a term which varies slowly with x and a term which exponentially decays with a relaxation length of τ, the characteristic relaxation length of Equation (3-1). Thus after a few relaxation lengths

$$y(x) \simeq y_{eo} + ah, \qquad h \gg \tau \tag{3-4}$$

which is independent of $y(x_o)$ the initial condition. Since explicit integration methods construct the solution of Equation (3-1) as a Taylor series about the initial condition $y(x_o)$, the above example indicates that explicit integration methods should be limited to step sizes of the order of a few relaxation lengths.

That this is indeed the case can be shown by explicitly integrating Equation (3-1) using Euler's method. The explicit finite difference form of Equation (3-1) is then

$$\frac{y(x_o + h) - y(x_o)}{h} = -\frac{y(x_o) - y_{eo}}{\tau} \tag{3-5}$$

which yields the truncated Taylor series

$$y(x_o + h) = y(x_o)\left(1 - \frac{h}{\tau}\right) + y_{eo}\frac{h}{\tau} \tag{3-6}$$

when solved for $y(x_o + h)$. After n integration steps, it is found that

$$y(x_o + nh) = y(x_o)\left[1 - \frac{h}{\tau}\right]^n + \sum_{i=1}^{n}\left[y_{eo} + (i - 1)\,ah\right]\left[1 - \frac{h}{\tau}\right]^{-n-i}\frac{h}{\tau} \quad (3\text{-}7)$$

Examination of this equation shows that the dependence on the initial condition $y(x_o)$ will decay only if $|1 - h/\tau| < 1$, otherwise $y(x_o + nh)$ will oscillate with rapidly increasing amplitude. Hence the calculation will be stable only if $h/\tau < 2$. Similar results are obtained for other explicit integration methods. (The stable step size for Runge-Kutta integrations is $h/\tau < 5.6$.) Thus the stable step size for explicit integration of relaxation equations is of the order of the relaxation distance which explains the large computation times associated with explicit integration of relaxation equations in near equilibrium flow regions. As shown below, the use of implicit integration methods allows the integration of relaxation equations on a step size which is independent of the relaxation length.

Implicitly integrating Equation (3-1) using Euler's method, the finite difference form of Equation (3-1) is

$$\frac{y(x_o + h) - y(x_o)}{h} = -\frac{y(x_o + h) - y_{eo} - ah}{\tau} \quad (3\text{-}8)$$

which yields

$$y(x_o + h) = \frac{y(x_o) + (y_{eo} + ah)\frac{h}{\tau}}{1 + \frac{h}{\tau}} \quad (3\text{-}9)$$

when solved for $y(x_o + h)$. After n integration steps it is found that

$$y(x_o + nh) = \frac{y(x_o)}{\left[1 + \frac{h}{\tau}\right]^n} + \sum_{i=1}^{n}\frac{y_{eo} + iah}{\left[1 + \frac{h}{\tau}\right]^{n+1-i}}\frac{h}{\tau} \quad (3\text{-}10)$$

Examination of this equation shows that the dependence on the initial condition $y(x_o)$ always decays, regardless of the step size. Hence the implicit calculation will always be stable. As an extreme example, consider one integration step, $h = x - x_o$. From Equation (3-9), it is seen that

$$y(x) \simeq y_{eo} + ah \quad , \quad h \gg \tau \quad (3\text{-}11)$$

when the step size is large compared to the relaxation length and

$$y(x) = y(x_o)\left(1 - \frac{h}{\tau}\right) + y_{eo}\frac{h}{\tau} + \cdots, \quad h_o << \tau \qquad (3\text{-}12)$$

when the step size is small compared to the relaxation length.

It is seen that in the equilibrium limit (τ small, h/τ large) the exact solution and the implicit integration of the relaxation equation go to the same limit which is independent of the relaxation distance and depends only on the rate of change of the equilibrium condition. In the frozen case (τ large and h/τ small) the implicit and explicit methods are essentially the same (terminated Taylor series). Thus, implicit numerical integration methods can be used to integrate relaxation equations using step sizes of the order of the physical dimensions of the system of interest in all flow situations whether near equilibrium or near frozen. For a complete discussion of the numerical integration of relaxation equations, the reader is referred to Reference (6).

In choosing a numerical integration method, the primary items of concern are the stability, accuracy and simplicity of the method. As shown by Tyson[(1)] and discussed above, implicit methods are to be preferred for numerically integrating relaxation equations due to their inherent stability. Having chosen the basic integration method for stability reasons, the order of the integration method is determined by accuracy and simplicity considerations. In general, the higher the order of the integration method, the more complex the method becomes requiring more information in the form of past values or past derivatives of the function being integrated. Second order methods (accurate to h^2 with error of order h^3) have the advantage of simplicity and flexibility since they do not require past values of the function or its derivatives while retaining sufficient accuracy to allow the use of reasonably economical step sizes. It is also desired to use this numerical integration method in characteristic mesh calculations which are inherently limited to second order accuracy. For these reasons, a second order implicit numerical integration method derived below was chosen for use in the TRW/NASA One-Dimensional Nonequilibrium Performance Programs. A complete derivation of this numerical integration method is given in the following section.

3.2 DERIVATION OF NUMERICAL INTEGRATION METHOD

Consider the coupled set of first order simultaneous differential equations.

$$\frac{dy_i}{dx} = f_i\,(x, y_i, \cdots, y_N) \quad , \quad i = 1, 2, \cdots, N \tag{3-13}$$

It will be assumed that the equations are not singular and that a solution exists which may be developed as a Taylor series about the forward point

$$k_i = \left.\frac{dy_i}{dx}\right|_{x_n+h} h - \left.\frac{d^2y_i}{dx^2}\right|_{x_n+h} \frac{h^2}{2} + \left.\frac{d^3y_i}{dx^3}\right|_{x_n+h} \frac{h^3}{6} - \left.\frac{d^4y_i}{dx^4}\right|_{x_n+h} \frac{h^4}{24} + \cdots \tag{3-14}$$

where k_i is the increment in y_i and h is sufficiently small. The first two coefficients of the Taylor series may be calculated as

$$\frac{dy_i}{dx} = f_i(x, y_1, \cdots, y_n) \tag{3-15}$$

$$\frac{d^2y_i}{dx^2} = \alpha_i + \sum_{j=1}^{N} \beta_{i,j} f_j \tag{3-16}$$

where

$$f_i = f_i(x, y, \cdots, y_N) \tag{3-17a}$$

$$\alpha_i = \frac{\partial f_i}{\partial x} \tag{3-17b}$$

$$\beta_{i,j} = \frac{\partial f_i}{\partial y_j} \tag{3-17c}$$

These coefficients must be evaluated implicitly by iteration since they are functions of the unknowns, $y_i(x_n+h)$. Expanding them as a Taylor series about the point x_n it is found that as a first approximately

$$\left.\frac{dy_i}{dx}\right|_{x_n+h}^{(P)} = f_{i,n} + a_{i,n}h + \sum_{j=1}^{N} \beta_{i,j,n} k_j^{(P)} + 0(h^2) \tag{3-18}$$

$$\left.\frac{d^2y_i}{dx^2}\right|_{x_n+h}^{(P)} = a_{i,n} + \sum_{j=1}^{N} \beta_{i,j,n} \left[f_{j,n} + a_{j,n}h + \sum_{\ell=1}^{N} \beta_{j,\ell} k_\ell^{(P)}\right] + 0(h) \tag{3-19}$$

where the subscript n refers to the functions f_i, a_i and $\beta_{i,j}$ evaluated at the point x_n and $k_i^{(P)}$ is the predicted value of the increment k_i. Substituting the predicted derivatives into Equation (3-14) yields the predictor equation

$$k_i^{(P)} = f_{i,n}h + a_{i,n}\frac{h^2}{2} + \sum_{j=1}^{N} \beta_{i,j,n}\left(hk_j^{(P)} - f_{j,n}\frac{h^2}{2} - a_{j,n}\frac{h^3}{2}\right.$$

$$\left. - \sum_{\ell=1}^{N} \beta_{j,\ell,n} k_\ell^{(P)} \frac{h^2}{2}\right) + \left.\frac{d^3y_i}{dx^3}\right|_{x_n+h} \frac{h^3}{6} + E(h^3) + \cdots \tag{3-20}$$

where the error term $E(h^3)$ of order h^3 has been introduced through the use of the predicted derivatives at the forward point [Equations (3-18) and (3-19)]. Neglecting the third order error and derivative terms and solving the set of N linear nonhomogeneous algebraic equations

$$\left(1 - \beta_{i,i,n}h + \beta_{i,i,n}^2\frac{h^2}{2}\right)k_i^{(P)} - \sum_{j=1}^{N}(1 - \delta_{ij})\beta_{i,j,n}\left(1 - \sum_{i=1}^{N}\beta_{i,j,n}\frac{h}{2}\right)k_j^{(P)}$$

$$= \left(1 - \beta_{i,i,n}\frac{h}{2}\right)(f_{i,n} + a_{i,n}h)\,h - \sum_{j=1}^{N}(1 - \delta_{ij})\beta_{i,j,n}(f_{j,n} + a_{i,n}h)\frac{h^2}{2} \tag{3-21}$$

where δ_{ij} is the Kronecker delta thus yields a second order implicit solution of the above coupled set of first order simultaneous differential equations.

By using the predicted increments $k_i^{(P)}$ and iterating once, the error term $E(h^3)$ may be eliminated and the absolute error in the integration estimated. The corrected estimates for the first two terms in the Taylor series expansion are

$$\left.\frac{dy_i}{dx}\right|_{x_n+h}^{(C)} = f_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1}\left[k_j^{(C)} - k_j^{(P)}\right] + 0(h^6) \qquad (3\text{-}22)$$

$$\left.\frac{d^2y_i}{dx^2}\right|_{x_n+h}^{(C)} = a_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1}\left\{f_{j,n+1} + \sum_{\ell=1}^{N} \beta_{j,\ell,n+1}\left[k_\ell^{(C)} - k_\ell^{(P)}\right]\right\} + 0(h^3)$$

(3-23)

where the subscript n+1 refers to the functions f_i, x_i and $\beta_{i,j}$ evaluated at the point x_n+h using the predicted increments $k_i^{(P)}$ and $k_i^{(C)}$ is the corrected value of the increment k_i. Substituting the corrected derivatives into Equation (3-14) yields the corrector equation

$$k_i^{(C)} = f_{i,n+1}\, h - a_{i,n+1}\frac{h^2}{2} + \sum_{j=1}^{N} \beta_{i,j,n+1}\left\{h\left[k_j^{(C)} - k_j^{(P)}\right] - f_{j,n+1}\frac{h^2}{2}\right.$$

$$\left. - \sum_{\ell=1}^{N} \beta_{j,\ell,n+1}\left[k_\ell^{(C)} - k_\ell^{(P)}\right]\frac{h^2}{2}\right\} + \left.\frac{d^3y_i}{dx^3}\right|_{x_n+h}\frac{h^3}{6} + \cdots \qquad (3\text{-}24)$$

The error term $E(h^3)$ is eliminated in the Taylor series expansion through use of the corrected derivatives. Thus, solving the set of N linear non-homogeneous algebraic equations

$$\left(1 - \beta_{i,i,n+1} h - \beta_{i,i,n+1}^2 \frac{h^2}{2}\right) k_i^{(C)} - \sum_{j=1}^{N} (1-\delta_{ij}) \beta_{i,j,n+1} \left(1 - \sum_{i=1}^{N} \beta_{i,j,n+1} \frac{h}{2}\right) k_j^{(C)} h$$

$$= \left(1 - \beta_{i,i,n+1} \frac{h}{2}\right) f_{i,n+1}\, h - \sum_{j=1}^{N} (1-\delta_{ij}) \beta_{i,j,n+1}\, f_{j,n+1} \frac{h^2}{2} - \alpha_{i,n+1} \frac{h^2}{2}$$

$$- \sum_{j=1}^{N} \beta_{i,j,n+1} \left(1 - \sum_{i=1}^{N} \beta_{i,j,n+1} \frac{h}{2}\right) k_j^{(P)} h \qquad (3\text{-}25)$$

yields a corrected second order solution of the above coupled set of first order simultaneous differential equations.

The error associated with the integration is

$$k_i - k_i^{(C)} = \left.\frac{d^3 y_i}{dx^3}\right|_{x_n+h} \frac{h^3}{6} + \cdots \qquad (3\text{-}26)$$

which can be written as

$$k_i - k_i^{(C)} = \frac{1}{h}\left[\left.\frac{d^2 y_i}{dx^2}\right|_{x_n+h} - \left.\frac{d^2 y_i}{dx^2}\right|_{x_n}\right] \frac{h^3}{6} + \cdots$$

$$= \left[\alpha_{i,n} + \sum_{j=1}^{N} \beta_{i,j,n} f_{j,n} - \left(\alpha_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1} f_{j,n+1}\right)\right] \frac{h^2}{6} + \cdots \qquad (3\text{-}27)$$

to order h^3. Thus, if it is desired to control the absolute fractional integration error

$$\left|\frac{k_i - k_i^{(C)}}{k_i^{(C)}}\right|$$

to within δ_i, then the integration step size must satisfy the criteria

$$h \leq \left[\left| \frac{6\delta_i k_i^{(C)}}{a_{i,n} + \sum_{j=1}^{N} \beta_{i,j,n} f_{j,n} - \left(a_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1} f_{j,n+1} \right)} \right| \right]^{1/2} \tag{3-28}$$

In summary, solution of the predictor-corrector equations

$$\left(1 - \beta_{i,i,n} h + \beta_{i,i,n}^2 \frac{h^2}{2}\right) k_i^{(P)} - \sum_{j=1}^{N} (1 - \delta_{ij}) \beta_{i,j,n} \left(1 - \sum_{i=1}^{N} \beta_{i,j,n} \frac{h}{2}\right) k_j^{(P)}$$

$$= \left(1 - \beta_{i,i,n} \frac{h}{2}\right) (f_{i,n} + a_{i,n} h) h - \sum_{j=1}^{N} (1 - \delta_{ij}) \beta_{i,j,n} (f_{j,n} + a_{i,n} h) \frac{h^2}{2} \tag{3-29}$$

$$\left(1 - \beta_{i,i,n+1} h + \beta_{i,i,n+1}^2 \frac{h^2}{2}\right) k_i^{(C)} - \sum_{j=1}^{N} (1 - \delta_{ij}) \beta_{i,j,n+1} \left(1 - \sum_{i=1}^{N} \beta_{i,j,n+1} \frac{h}{2}\right) k_j^{(C)} h$$

$$= \left(1 - \beta_{i,i,n+1} \frac{h}{2}\right) f_{i,n+1} h - \sum_{j=1}^{N} (1 - \delta_{ij}) \beta_{i,j,n+1} f_{j,n+1} \frac{h^2}{2} - a_{i,n+1} \frac{h^2}{2}$$

$$- \sum_{j=1}^{N} \beta_{i,j,n+1} \left(1 - \sum_{i=1}^{N} \beta_{i,j,n+1} \frac{h}{2}\right) k_j^{(P)} h \tag{3-30}$$

yields a second order implicit solution of the coupled set of first order simultaneous differential equations

$$\frac{dy_i}{dx} = f_i(x, y_1, \cdots, y_N) \quad , \quad i = 1, 2, \cdots, N \tag{3-31}$$

with a fractional incremental error of

$$\delta_i = \frac{1}{k_i^{(C)}} \left[a_{i,n} + \sum_{j=1}^{N} \beta_{i,j,n} f_{j,n} - \left(a_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1} f_{j,n+1} \right) \right] \frac{h^2}{6} \tag{3-32}$$

Inversion of the error equation allows the determination of maximum allowable step size

$$h \leq \left[\frac{6\delta_i k_i^{(C)}}{\alpha_{i,n} + \sum_{j=1}^{N} \beta_{i,j,n} f_{j,n} - \left(\alpha_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1} f_{j,n+1} \right)} \right]^{1/2} \qquad (3\text{-}33)$$

which will maintain the incremental error per step within specified limits.

4. PROGRAM SUBROUTINES

The program internally calculates in engineering units (lbm, ft, sec, ^{o}R) where the poundal has been chosen as the unit of force in order to eliminate conversion constants in the calculations.

The engineering nomenclature used in deriving the conservation equations (described in Section 2) and the integration method (described in Section 3) has been retained in specifying the program subroutines so that all calculations performed in the program can be readily related to the equations being solved. The program has been organized into seven subroutines to separate logically independent calculations in order to facilitate programming and program checkout. The logical and calculational functions are summarized below:

- The Input Subroutine (described in Section 4.1) processes the input data, converts the data to the proper units, stores the converted data and calculates those quantities required during the nozzle integrations.

- The Derivative Evaluation Subroutine (described in Section 4.2) calculates the derivatives and partial derivatives of the chemical relaxation equations and the fluid dynamic equations which are used in the Integration Subroutine.

- The Integration Subroutine (described in Section 4.3) integrates the chemical relaxation equations and the fluid dynamic equations using the second order implicit integration method derived in Section 3.

- The Species Thermal Function Subroutine (described in Section 4.4) calculates the required species thermal functions from the input thermodynamic data.

- The Equilibrium Function Subroutine (described in Section 4.5) calculates the required equilibrium function for the dissociation-recombination reactions.

- The Gas Thermal Function Subroutine (described in Section 4.6) calculates the required gas mixture thermal properties.

- The Output Subroutine (described in Section 4.7) processes the output data, converts the data to the proper units and calculates the required output quantities.

A detailed description of the calculations performed in these subroutines is given in the following sections.

4.1 INPUT SUBROUTINE

This subroutine processes the input data, converts the data to the proper units, stores the converted data and calculates those quantities required during the nozzle integration. There calculations are performed in the following order:

- The species gas constants are calculated
- The species thermal functions are input, converted from chemists' units to the units in which the program computes, and stored
- The temperature derivatives of the species thermal functions are calculated and stored
- The heat of reaction for each of the recombination reactions is calculated
- The reaction rates are input, converted from chemists' units to the units in which the program computes, and stored
- The case data are input and those quantities required during the nozzle integration are calculated

The calculations performed by this subroutine are described in the following sections.

4.1.1 Species Gas Constant Calculation

The species gas constants are calculated from the following relationships:

$R_1 = 1129.74$ $R_{10} = 1656.92$

$R_2 = 2759.82$ $R_{11} = 2923.39$

$R_3 = 1775.05$ $R_{12} = 1553.78$

$R_4 = 701.15$ $R_{13} = 4139.62$

$R_5 = 1308.45$ $R_{14} = 1402.29$

$R_6 = 1363.53$ $R_{15} = 2616.89$

$R_7 = 2485.06$ $R_{16} = 49326.4$

$R_8 = 24663.2$ $R_{17} = 3549.47$

$R_9 = 1774.74$ $R_{18} = 3107.56$

4.1.2 Species Thermal Functions Input and Conversion

The species thermal functions tabulated at 100°K temperature increments between 100°K and 5000°K in the JANAF thermochemical tables are input and converted to a set of tables in the required units which include the enthalpy of formation. Using the JANAF nomenclature, the converted tables are calculated from

$$F_i = \frac{1}{1.98726}\left[-\frac{F^o - H^o_{298}}{T} + \frac{1000\left(H^o - H^o_{298}\right)_c}{T}\right]_i \quad , \quad i = 1, 2, \cdots, 18$$

$$h_i = 905.770R_i\left[H^o - H^o_{298} - \left(H^o - H^o_{298}\right)_o + \Delta H^o_F\right]_i \quad , \quad i = 1, 2, \cdots, 18$$

$$C_{pi} = \frac{R_i}{1.98726}\, C^o_p\Big|_i \quad , \quad i = i, 2, \cdots, 18$$

and stored as functions of temperature at 180°R temperature increments between 180°R and 9000°R.

4.1.3 Species Thermal Function Temperature Derivative Calculation

At each temperature between 180°R and 9000°R, the species thermal function temperature derivatives are calculated from

$$\frac{dC_{pi}}{dT}\Big|_{180} = \frac{1}{360}\left[4C_{pi}\Big|_{360} - 3C_{pi}\Big|_{180} - C_{pi}\Big|_{480}\right]$$

$$\frac{d^2C_p}{dT^2}\Big|_{180} = \frac{1}{64800}\left[C_{pi}\Big|_{540} - 2C_{pi}\Big|_{360} + C_{pi}\Big|_{180}\right]$$

$$\frac{dC_{pi}}{dT}\Big|_T = \frac{1}{360}\left[C_{pi}\Big|_{T+180} - C_{pi}\Big|_{T-180}\right] \quad , \quad 360 \le T \le 8820$$

$$\frac{d^2C_{pi}}{dT^2}\Big|_T = \frac{1}{64800}\left[C_{pi}\Big|_{T+180} - 2C_{pi}\Big|_T + C_{pi}\Big|_{T-180}\right] \quad , \quad 360 \le T \le 8820$$

$$\left.\frac{dC_{pi}}{dT}\right|_{9000} = \frac{1}{360}\left[3C_{pi}\Big|_{9000} - 4C_{pi}\Big|_{8820} + C_{pi}\Big|_{8640}\right]$$

$$\left.\frac{d^2C_{pi}}{dT^2}\right|_{9000} = \frac{1}{64800}\left[C_{pi}\Big|_{9000} - 2C_{pi}\Big|_{8820} + C_{pi}\Big|_{8640}\right]$$

$$\left.\frac{dh_i}{dT}\right|_{T} = C_{pi}\Big|_{T}$$

$$\left.\frac{d^2h_i}{dT^2}\right|_{T} = \left.\frac{dC_{pi}}{dT}\right|_{T}$$

$$\left.\frac{dF_i}{dT}\right|_{T} = \left.\frac{F_i - h_i}{T}\right|_{T}$$

$$\left.\frac{d^2F_i}{dT^2}\right|_{T} = -\left.\frac{C_{pi}}{T}\right|_{T}$$

and stored with the species thermal functions.

4.1.4 Heat of Reaction Calculation

The heat of reaction for each of the recombination reactions is calculated from the following relationships:

$$\Delta H_1 = 905.770\left[\Delta H^o_{F,3} + \Delta H^o_{F,18} - \Delta H^o_{F,1}\right]$$

$$\Delta H_2 = 905.770\left[\Delta H^o_{F,11} + \Delta H^o_{F,16} - \Delta H^o_{F,2}\right]$$

$$\Delta H_3 = 905.770\left[\Delta H^o_{F,13} + \Delta H^o_{F,18} - \Delta H^o_{F,3}\right]$$

$$\Delta H_4 = 905.770 \left[2\Delta H^o_{F,14} - \Delta H^o_{F,4} \right]$$

$$\Delta H_5 = 905.770 \left[2\Delta H^o_{F,15} - \Delta H^o_{F,5} \right]$$

$$\Delta H_6 = 905.770 \left[\Delta H^o_{F,14} + \Delta H^o_{F,15} - \Delta H^o_{F,6} \right]$$

$$\Delta H_7 = 905.770 \left[\Delta H^o_{F,15} + \Delta H^o_{F,16} - \Delta H^o_{F,7} \right]$$

$$\Delta H_8 = 905.770 \left[2\Delta H^o_{F,16} - \Delta H^o_{F,8} \right]$$

$$\Delta H_9 = 905.770 \left[2\Delta H^o_{F,17} - \Delta H^o_{F,9} \right]$$

$$\Delta H_{10} = 905.770 \left[\Delta H^o_{F,17} + \Delta H^o_{F,18} - \Delta H^o_{F,10} \right]$$

$$\Delta H_{11} = 905.770 \left[\Delta H^o_{F,16} + \Delta H^o_{F,18} - \Delta H^o_{F,11} \right]$$

$$\Delta H_{12} = 905.770 \left[2\Delta H^o_{F,18} - \Delta H^o_{F,12} \right]$$

4.1.5 Reaction Rate Input and Conversion

The reaction rate parameters a_j, n_j and b_j are input and converted to the required units. (Since the reaction rate parameter n_j is a dimensionless temperature exponent, it does not require conversion.) The converted reaction rate parameters are calculated from the following relationships:

$$b_j = 905.770\, b_j' \quad , \quad j = 1, 2, \cdots, 39$$

$$a_1 = 0.59305 \cdot 10^{-6} (1.8)^{n_1}\, a_1'$$

$$a_2 = 0.15503 \cdot 10^{-4} (1.8)^{n_2}\, a_2'$$

$$a_3 = 0.13830 \cdot 10^{-5} (1.8)^{n_3}\, a_3'$$

$$a_4 = 0.21140 \cdot 10^{-6} (1.8)^{n_4}\, a_4'$$

$$a_5 = 0.73626 \cdot 10^{-6} (1.8)^{n_5}\, a_5'$$

$$a_6 = 0.74366 \cdot 10^{-5} (1.8)^{n_6}\, a_6'$$

$$a_7 = 0.13878 \cdot 10^{-4} (1.8)^{n_7}\, a_7'$$

$$a_8 = 0.26158 \cdot 10^{-3} (1.8)^{n_8}\, a_8'$$

$$a_9 = 0.13545 \cdot 10^{-5} (1.8)^{n_9}\, a_9'$$

$$a_{10} = 0.11859 \cdot 10^{-5} (1.8)^{n_{10}}\, a_{10}'$$

$$a_{11} = 0.16480 \cdot 10^{-4} (1.8)^{n_{11}}\, a_{11}'$$

$$a_{12} = 0.10382 \cdot 10^{-5} (1.8)^{n_{12}}\, a_{12}'$$

$$a_{13} = 0.55790 \cdot 10^{-6} (1.8)^{n_{13}}\, a_{13}'$$

$$a_{14} = 0.29652 \cdot 10^{-6} (1.8)^{n_{14}}\, a_{14}'$$

$$a_{15} = 0.42856 \cdot 10^{-6}(1.8)^{n_{15}} a'_{15}$$

$$a_{16} = 0.77517 \cdot 10^{-5}(1.8)^{n_{16}} a'_{16}$$

$$a_{17} = 0.91882 \cdot 10^{-6}(1.8)^{n_{17}} a'_{17}$$

$$a_{18} = 0.50280 \cdot 10^{-6}(1.8)^{n_{18}} a'_{18}$$

$$a_{19} = 0.13011 \cdot 10^{-5}(1.8)^{n_{19}} a'_{19}$$

$$a_{20} = 0.73743 \cdot 10^{-6}(1.8)^{n_{20}} a'_{20}$$

$$a_{21} = 0.43112 \cdot 10^{-6}(1.8)^{n_{21}} a'_{21}$$

$$a_{22} = 0.69153 \cdot 10^{-6}(1.8)^{n_{22}} a'_{22}$$

$$a_{23} = 0.37183 \cdot 10^{-5}(1.8)^{n_{23}} a'_{23}$$

$$a_{24} = 0.18592 \cdot 10^{-5}(1.8)^{n_{24}} a'_{24}$$

$$a_{25} = 0.44074 \cdot 10^{-6}(1.8)^{n_{25}} a'_{25}$$

$$a_{26} = 0.38363 \cdot 10^{-6}(1.8)^{n_{26}} a'_{26}$$

$$a_{27} = 0.69389 \cdot 10^{-5}(1.8)^{n_{27}} a'_{27}$$

$$a_{28} = 0.69389 \cdot 10^{-5}(1.8)^{n_{28}} a'_{28}$$

$$a_{29} = 0.34695 \cdot 10^{-5}(1.8)^{n_{29}} a'_{29}$$

$$a_{30} = 0.82249 \cdot 10^{-6}(1.8)^{n_{30}} a'_{30}$$

$$a_{31} = 0.77647 \cdot 10^{-6}(1.8)^{n_{31}} a'_{31}$$

$$a_{32} = 0.72310 \cdot 10^{-5}(1.8)^{n_{32}} a'_{32}$$

$$a_{33} = 0.15503 \cdot 10^{-4}(1.8)^{n_{33}} a'_{33}$$

$$a_{34} = 0.91882 \cdot 10^{-6}(1.8)^{n_{34}} a'_{34}$$

$$a_{35} = 0.63230 \cdot 10^{-6}(1.8)^{n_{35}} a'_{35}$$

$$a_{36} = 0.29516 \cdot 10^{-6}(1.8)^{n_{36}} a'_{36}$$

$$a_{37} = 0.11156 \cdot 10^{-5}(1.8)^{n_{37}} a'_{37}$$

$$a_{38} = 0.59294 \cdot 10^{-6}(1.8)^{n_{38}} a'_{38}$$

$$a_{39} = 0.97671 \cdot 10^{-6}(1.8)^{n_{39}} a'_{39}$$

The reaction rate parameters $m_{i,j}$ are input and converted to the required units. The converted reaction rate parameters are calculated from the following relationships:

$$m_{j,1} = \frac{m'_{j,1}}{44.011} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,2} = \frac{m'_{j,2}}{18.016} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,3} = \frac{m'_{j,3}}{28.011} \quad . \quad j = 1, 2, \cdots, 18$$

$$m_{j,4} = \frac{m'_{j,4}}{70.914} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,5} = \frac{m'_{j,5}}{38.000} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,6} = \frac{m'_{j,6}}{36.465} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,7} = \frac{m'_{j,7}}{20.008} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,8} = \frac{m'_{j,8}}{2.016} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,9} = \frac{m'_{j,9}}{28.016} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,10} = \frac{m'_{j,10}}{30.008} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,11} = \frac{m'_{j,11}}{17.008} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,12} = \frac{m'_{j,12}}{32.000} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,13} = \frac{m'_{j,13}}{12.011} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,14} = \frac{m'_{j,14}}{35.457} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,15} = \frac{m'_{j,15}}{19.000} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,16} = \frac{m'_{j,16}}{1.008} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,17} = \frac{m'_{j,17}}{14.008} \quad , \quad j = 1, 2, \cdots, 18$$

$$m_{j,18} = \frac{m'_{j,18}}{16.000} \quad , \quad j = 1, 2, \cdots, 18$$

4.1.6 Case Data Input and Conversion

The case data are input and the chamber pressure, the initial pressure and the nozzle throat radius are converted to the required units. The converted quantities are calculated from

$$P_c = 4633.056\, P'_c$$

$$P = 4633.056\, P'$$

$$r^* = \frac{r^{*\prime}}{12}$$

If the initial species concentrations are input as mole fractions, the required mass fractions are calculated

$$c_i = \frac{1}{R_i} \frac{c'_{i,m}}{\bar{c}} \quad , \quad i = 1, 2, \cdots, 18$$

where

$$\bar{c} = \sum_{i=1}^{18} \frac{c'_{i,m}}{R_i}$$

The case data are output to supply a permanent case record with the nozzle integration results.

4.2 DERIVATIVE EVALUATION SUBROUTINE

Given the flow properties at a point, this subroutine calculates the derivatives (f_i) and partial derivatives (α_i and $\beta_{i,j}$) of the chemical relaxations equations and the fluid dynamic equations. These calculations are performed in the following order:

- The species free energy, enthalpy, heat capacity and the heat capacity temperature derivative are calculated using the Species Thermal Function Subroutine (described in Section 4.4).
- The dissociation-recombination reaction equilibrium constants and their temperature derivatives are calculated using the Equilibrium Function Subroutine (described in Section 4.5).
- The mixture gas constant, heat capacity, gamma and the partial derivatives of gamma are calculated using the Gas Thermal Function Subroutine (described in Section 4.).
- The contribution of the individual reactions to the net species production rate (X_j) and its partial derivatives are calculated.
- The derivatives (f_i) and partial derivatives (α_i and $\beta_{i,j}$) of the chemical relaxation equations are calculated.
- In the subsonic and transonic nozzle inlet and throat, the pressure and its derivatives are calculated from the pressure table by quadratic interpolation.
- In the supersonic nozzle expansion cone, the nozzle area and Mach number and their derivatives are calculated.
- The diabatic heat addition terms coupling the chemical relaxation equations and the fluid dynamic equations are calculated.
- The derivatives (f_i) and partial derivatives (α_i and $\beta_{i,j}$) of the fluid dynamic equations are calculated.

A detailed description of these calculations is given in the following sections.

4.2.1 Calculation of X_j and Its Partial Derivatives

For the reactions of interest, X_j and its derivatives are calculated from the following relationships:

Reaction 1, $CO_2 + M \rightleftharpoons CO + O + M$

$$k_1 = a_1 T^{-n_1} e^{-b_1/T}$$

$$M_1 = \sum_{i=1}^{18} m_{1,i} c_i$$

$$X_1 = \left[K_1 c_1 - \rho c_3 c_{18}\right] M_1 k_1$$

$$\frac{\partial X_1}{\partial c_j} = \frac{X_1}{M_1} m_{1,j} + \delta_{1,j} K_1 M_1 k_1 - \delta_{3,j} \rho c_{18} M_1 k_1$$

$$- \delta_{18,j} \rho c_3 M_1 k_1 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_1}{\partial \rho} = -c_3 c_{18} M_1 k_1$$

$$\frac{\partial X_1}{\partial T} = c_1 M_1 k_1 \frac{dK_1}{dT} - \left[n_1 + \frac{b_1}{T}\right] \frac{X_1}{T}$$

Reaction 2, $H_2O + M \rightleftharpoons OH + H + M$

$$k_2 = a_2 T^{-n_2} e^{-b_2/T}$$

$$M_2 = \sum_{i=1}^{18} m_{2,i} c_i$$

$$X_2 = \left[K_2 c_2 - \rho c_{11} c_{16}\right] M_2 k_2$$

$$\frac{\partial X_{2,j}}{\partial c_j} = \frac{X_2}{M_2} m_{2,j} + \delta_{2,j} K_2 M_2 k_2 - \delta_{11,j} \rho c_{16} M_2 k_2$$

$$- \delta_{16,j} \rho c_{11} M_2 k_2 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_2}{\partial \rho} = -c_{11} c_{16} M_2 k_2$$

$$\frac{\partial X_2}{\partial T} = c_2 M_2 k_2 \frac{dK_2}{dT} - \left[n_2 + \frac{b_2}{T}\right] \frac{X_2}{T}$$

Reaction 3, $CO + M \rightleftarrows C + O + M$

$$k_3 = a_3 T^{-n_3} e^{-b_3/T}$$

$$M_3 = \sum_{i=1}^{18} m_{3,i} c_i$$

$$X_3 = \left[K_3 c_3 - \rho c_{13} c_{18}\right] M_3 k_3$$

$$\frac{\partial X_3}{\partial c_j} = \frac{X_3}{M_3} m_{3,j} + \delta_{3,j} K_3 M_3 k_3 - \delta_{13,j} \rho c_{18} M_3 k_3$$

$$-\delta_{18,j} \rho c_{13} M_3 k_3 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_3}{\partial \rho} = -c_{13} c_{18} M_3 k_3$$

$$\frac{\partial X_3}{\partial T} = c_3 M_3 k_3 \frac{dK_3}{dT} - \left[n_3 + \frac{b_3}{T}\right] \frac{X_3}{T}$$

Reaction 4, $Cl_2 + M \rightleftarrows 2Cl + M$

$$k_4 = a_4 T^{-n_4} e^{-b_4/T}$$

$$M_4 = \sum_{i=1}^{18} m_{4,i} c_i$$

$$X_4 = \left[K_4 c_4 - \rho c_{14}^2\right] M_4 k_4$$

$$\frac{\partial X_4}{\partial c_j} = \frac{X_4}{M_4} m_{4,j} + \delta_{4,j} K_4 M_4 k_4 - 2\delta_{14,j} \rho c_{14} M_4 k_4 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_4}{\partial \rho} = -c_{14}^2 M_4 k_4$$

$$\frac{\partial X_4}{\partial T} = c_4 M_4 k_4 \frac{dK_4}{dT} - \left[n_4 + \frac{b_4}{T}\right] \frac{X_4}{T}$$

Reaction 5, $F_2 + M \rightleftharpoons 2F + M$

$$k_5 = a_5 T^{-n_5} e^{-b_5/T}$$

$$M_5 = \sum_{i=1}^{18} m_{5,i} c_i$$

$$X_5 = \left[K_5 c_5 - \rho c_{15}^2\right] M_5 k_5$$

$$\frac{\partial X_5}{\partial c_j} = \frac{X_5}{M_5} m_{5,j} + \delta_{5,j} K_5 M_5 k_5 - 2\delta_{15,j} \rho c_{15} M_5 k_5 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_5}{\partial \rho} = -c_{15}^2 M_5 k_5$$

$$\frac{\partial X_5}{\partial T} = c_5 M_5 k_5 \frac{dK_5}{dT} - \left[n_5 + \frac{b_5}{T}\right] \frac{X_5}{T}$$

Reaction 6, $HCl + M \rightleftharpoons H + Cl + M$

$$k_6 = a_6 T^{-n_6} e^{-b_6/T}$$

$$M_6 = \sum_{i=1}^{18} m_{6,i} c_i$$

$$X_6 = \left[K_6 c_6 - \rho c_{14} c_{16}\right] M_6 k_6$$

$$\frac{\partial X_6}{\partial c_j} = \frac{X_6}{M_6} m_{6,j} + \delta_{6,j} K_6 M_6 k_6 - \delta_{14,j} \rho c_{16} M_6 k_6$$

$$- \delta_{16,j} \rho c_{14} M_6 k_6 \quad , \quad j = 1, 2, \ldots, 18$$

$$\frac{\partial X_6}{\partial \rho} = -c_{12}c_{16}M_6k_6$$

$$\frac{\partial X_6}{\partial T} = c_6M_6k_6\frac{dK_6}{dT} - \left[n_6 + \frac{b_6}{T}\right]\frac{X_6}{T}$$

Reaction 7, $HF + M \rightleftharpoons H + F + M$

$$k_7 = a_7T^{-n_7}e^{-b_7/T}$$

$$M_7 = \sum_{i=1}^{18} m_{7,i}c_i$$

$$X_7 = \left[K_7c_7 - \rho c_{15}c_{16}\right]M_7k_7$$

$$\frac{\partial X_7}{\partial c_j} = \frac{X_7}{M_7}m_{7,j} + \delta_{7,j}K_7M_7k_7 - \delta_{15,j}\rho c_{16}M_7k_7 - \delta_{16,j}\rho c_{15}M_7k_7$$

$$\frac{\partial X_7}{\partial \rho} = -c_{15}c_{16}M_7k_7$$

$$\frac{\partial X_7}{\partial T} = c_7M_7k_7\frac{dK_7}{dT} - \left[n_7 + \frac{b_7}{T}\right]\frac{X_7}{T}$$

Reaction 8, $H_2 + M \rightleftharpoons 2H + M$

$$k_8 = a_8T^{-n_8}e^{-b_8/T}$$

$$M_8 = \sum_{i=1}^{18} m_{8,i}c_i$$

$$X_8 = \left[K_8c_8 - \rho c_{16}^2\right]M_8k_8$$

$$\frac{\partial X_8}{\partial c_j} = \frac{X_8}{M_8}m_{8,j} + \delta_{8,j}K_8M_8k_8 - 2\delta_{16,j}\rho c_{16}M_8k_8 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_8}{\partial \rho} = -c_{16}^2 M_8 k_8$$

$$\frac{\partial X_8}{\partial T} = c_8 M_8 k_8 \frac{dK_8}{dT} - \left[n_8 + \frac{b_8}{T}\right] \frac{X_8}{T}$$

Reaction 9, $N_2 + M \rightleftharpoons 2N + M$

$$k_9 = a_9 T^{-n_9} e^{-b_9/T}$$

$$M_9 = \sum_{i=1}^{18} m_{9,i} c_i$$

$$X_9 = \left[K_9 c_9 - \rho c_{17}^2\right] M_9 k_9$$

$$\frac{\partial X_9}{\partial c_j} = \frac{X_9}{M_9} m_{i,j} + \delta_{9,j} K_9 M_9 k_9 - 2\delta_{17,j} \rho c_{17} M_9 k_9 \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_9}{\partial \rho} = -c_{17}^2 M_9 k_9$$

$$\frac{\partial X_9}{\partial T} = c_9 M_9 k_9 \frac{dK_9}{dT} - \left[n_9 + \frac{b_9}{T}\right] \frac{X_9}{T}$$

Reaction 10, $NO + M \rightleftharpoons N + O + M$

$$k_{10} = a_{10} T^{-n_{10}} e^{-b_{10}/T}$$

$$M_{10} = \sum_{i=1}^{N} m_{10,i} c_i$$

$$X_{10} = \left[K_{10} c_{10} - \rho c_{17} c_{18}\right] M_{10} k_{10}$$

$$\frac{\partial X_{10}}{\partial c_j} = \frac{X_{10}}{M_{10}} m_{10,j} + \left[\delta_{10,j} K_{10} M_{10} k_{10}\right] - \delta_{17,j} \rho c_{18} M_{10} k_{10}$$

$$- \delta_{18,j} \rho c_{17} M_{10} k_{10} \quad , \quad j = 1, 2, \ldots, 18$$

$$\frac{\partial X_{10}}{\partial \rho} = -c_{17}c_{18}M_{10}k_{10}$$

$$\frac{\partial X_{10}}{\partial T} = c_{10}M_{10}k_{10}\frac{dK_{10}}{dT} - \left[n_{10} + \frac{b_{10}}{T}\right]\frac{X_{10}}{T}$$

Reaction 11, $OH + M \rightleftarrows O + H + M$

$$k_{11} = a_{11}T^{-n_{11}}e^{-b_{11}/T}$$

$$M_{11} = \sum_{i=1}^{18} m_{11,i}c_i$$

$$X_{11} = \left[K_{11}c_{11} - \rho c_{16}c_{18}\right]M_{11}k_{11}$$

$$\frac{\partial X_{11}}{\partial c_j} = \frac{X_{11}}{M_{11}}m_{11,j} + \delta_{11,j}K_{11}M_{11}k_{11} - \delta_{16,j}\rho c_{18}M_{11}k_{11}$$

$$- \delta_{18,j}\rho c_{16}M_{11}k_{11} \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial X_{11}}{\partial \rho} = -c_{16}c_{18}M_{11}k_{11}$$

$$\frac{\partial X_{11}}{\partial T} = c_{11}M_{11}k_{11}\frac{dK_{11}}{dT} - \left[n_{11} + \frac{b_{11}}{T}\right]\frac{X_{11}}{T}$$

Reaction 12, $O_2 + M \rightleftarrows 2O + M$

$$k_{12} = a_{12}T^{-n_{12}}e^{-b_{12}/T}$$

$$M_{12} = \sum_{i=1}^{18} m_{12,i}c_i$$

$$X_{12} = \left[K_{12}c_{12} - \rho c_{18}^2\right]M_{12}k_{12}$$

$$\frac{\partial X_{12}}{\partial c_j} = \frac{X_{12}}{M_{12}} m_{12,j} + \delta_{12,j} K_{12} M_{12} k_{12} - 2\delta_{18,j} \rho c_{18} M_{12} k_{12} ,$$

$$j = 1, 2, \cdots, 18$$

$$\frac{\partial X_{12}}{\partial \rho} = -c_{18}^2 M_{12} k_{12}$$

$$\frac{\partial X_{12}}{\partial T} = c_{12} M_{12} k_{12} \frac{dK_{12}}{dT} - \left[n_{12} + \frac{b_{12}}{T} \right] \frac{X_{12}}{T}$$

Reaction 13, $CO_2 + H \rightleftharpoons CO + OH$

$$K_{13} = \frac{K_1}{K_{11}}$$

$$k_{13} = a_{13} T^{-n_{13}} e^{-b_{13}/T}$$

$$X_{13} = \left[K_{13} c_1 c_{16} - c_3 c_{11} \right] k_{13}$$

$$\frac{\partial X_{13}}{\partial c_1} = K_{13} c_{16} k_{13}$$

$$\frac{\partial X_{13}}{\partial c_3} = -c_{11} k_{13}$$

$$\frac{\partial X_{13}}{\partial c_{11}} = -c_3 k_{13}$$

$$\frac{\partial X_{13}}{\partial c_{16}} = K_{13} c_1 k_{13}$$

$$\frac{\partial X_{13}}{\partial T} = \left[\frac{1}{K_1} \frac{dK_1}{dT} - \frac{1}{K_{11}} \frac{dK_{11}}{dT} \right] K_{13} c_1 c_{16} k_{13} - \left[n_{13} + \frac{b_{13}}{T} \right] \frac{X_{13}}{T}$$

Reaction 14, $CO_2 + O \rightleftharpoons CO + O_2$

$$K_{14} = \frac{K_1}{K_{12}}$$

$$k_{14} = a_{14}T^{-n_{14}} e^{-b_{14}/T}$$

$$X_{14} = \left[K_{14}c_1c_{18} - c_3c_{12}\right]k_{14}$$

$$\frac{\partial X_{14}}{\partial c_1} = K_{14}c_{18}k_{14}$$

$$\frac{\partial X_{14}}{\partial c_3} = -c_{12}k_{14}$$

$$\frac{\partial X_{14}}{\partial c_{12}} = -c_3k_{14}$$

$$\frac{\partial X_{14}}{\partial c_{18}} = K_{14}c_1k_{14}$$

$$\frac{\partial X_{14}}{\partial T} = \left[\frac{1}{K_1}\frac{dK_1}{dT} - \frac{1}{K_{12}}\frac{dK_{12}}{dT}\right]K_{14}c_1c_{18}k_{14} - \left[n_{14} + \frac{b_{14}}{T}\right]\frac{X_{14}}{T}$$

Reaction 15, $H_2O + Cl \rightleftharpoons HCl + OH$

$$K_{15} = \frac{K_2}{K_6}$$

$$k_{15} = a_{15}T^{-n_{15}} e^{-b_{15}/T}$$

$$X_{15} = \left[K_{15}c_2c_{14} - c_6c_{11}\right]k_{15}$$

$$\frac{\partial X_{15}}{\partial c_2} = K_{15}c_{14}k_{15}$$

$$\frac{\partial X_{15}}{\partial c_6} = -c_{11}k_{15}$$

$$\frac{\partial X_{15}}{\partial c_{11}} = -c_6 k_{15}$$

$$\frac{\partial X_{15}}{\partial c_{14}} = K_{15} c_2 k_{15}$$

$$\frac{\partial X_{15}}{\partial T} = \left[\frac{1}{K_2}\frac{dK_2}{dT} - \frac{1}{K_6}\frac{dK_6}{dT}\right] K_{15} c_2 c_{14} k_{15} - \left[n_{15} + \frac{b_{15}}{T}\right]\frac{X_{15}}{T}$$

Reaction 16, $H_2O + H \rightleftharpoons H_2 + OH$

$$K_{16} = \frac{K_2}{K_8}$$

$$k_{16} = a_{16} T^{-n_{16}} e^{-b_{16}/T}$$

$$X_{16} = \left[K_{16} c_2 c_{16} - c_8 c_{11}\right] k_{16}$$

$$\frac{\partial X_{16}}{\partial c_2} = K_{16} c_{16} k_{16}$$

$$\frac{\partial X_{16}}{\partial c_8} = -c_{11} k_{16}$$

$$\frac{\partial X_{16}}{\partial c_{11}} = -c_8 k_{16}$$

$$\frac{\partial X_{16}}{\partial c_{16}} = K_{16} c_2 k_{16}$$

$$\frac{\partial X_{16}}{\partial T} = \left[\frac{1}{K_2}\frac{dK_2}{dT} - \frac{1}{K_8}\frac{dK_8}{dT}\right] K_{16} c_2 c_{16} k_{16} - \left[n_{16} + \frac{b_{16}}{T}\right]\frac{X_{16}}{T}$$

Reaction 17, $H_2O + O \rightleftharpoons 2OH$

$$K_{17} = \frac{K_2}{K_{11}}$$

$$k_{17} = a_{17}T^{-n_{17}} e^{-b_{17}/T}$$

$$X_{17} = \left[K_{17}c_2c_{18} - c_{11}^2\right] k_{17}$$

$$\frac{\partial K_{17}}{\partial c_2} = K_{17}c_{18}k_{17}$$

$$\frac{\partial X_{17}}{\partial c_{11}} = -2c_{11}k_{17}$$

$$\frac{\partial X_{17}}{\partial c_{18}} = K_{17}c_2k_{17}$$

$$\frac{\partial X_{17}}{\partial T} = \left[\frac{1}{K_2}\frac{dK_2}{dT} - \frac{1}{K_{11}}\frac{dK_{11}}{dT}\right]K_{17}c_2c_{18}k_{17} - \left[n_{17} + \frac{b_{17}}{T}\right]\frac{X_{17}}{T}$$

Reaction 18, $2CO \rightleftharpoons CO_2 + C$

$$K_{18} = \frac{K_2}{K_1}$$

$$k_{19} = a_{18}T^{-n_{18}} e^{-b_{18}/T}$$

$$X_{18} = \left[K_{18}c_3^2 - c_1c_{13}\right] k_{18}$$

$$\frac{\partial X_{18}}{\partial c_1} = -c_{13}k_{18}$$

$$\frac{\partial X_{18}}{\partial c_3} = 2K_{18}c_3$$

$$\frac{\partial X_{18}}{\partial c_{13}} = -c_1 k_{18}$$

$$\frac{\partial X_{18}}{\partial T} = \left[\frac{1}{K_3}\frac{dK_3}{dT} - \frac{1}{K_1}\frac{dK_1}{dT}\right] K_{18} c_3^2 k_{18} - \left[n_{18} + \frac{b_{18}}{T}\right] \frac{X_{18}}{T}$$

Reaction 19, $CO + H \rightleftarrows OH + C$

$$K_{19} = \frac{K_3}{K_{11}}$$

$$k_{19} = a_{19} T^{-n_{19}} e^{-b_{19}/T}$$

$$X_{19} = \left[K_{19} c_3 c_{16} - c_{11} c_{13}\right] k_{19}$$

$$\frac{\partial X_{19}}{\partial c_3} = K_{19} c_{16} k_{19}$$

$$\frac{\partial X_{19}}{\partial c_{11}} = -c_{13} k_{19}$$

$$\frac{\partial X_{19}}{\partial c_{13}} = -c_{11} k_{19}$$

$$\frac{\partial X_{19}}{\partial c_{16}} = K_{19} c_3 k_{19}$$

$$\frac{\partial X_{19}}{\partial T} = \left[\frac{1}{K_3}\frac{dK_3}{dT} - \frac{1}{K_{11}}\frac{dK_{11}}{dT}\right] K_{19} c_3 c_{16} k_{19} - \left[n_{19} + \frac{b_{19}}{T}\right] \frac{X_{19}}{T}$$

Reaction 20, $CO + N \rightleftarrows NO + C$

$$K_{20} = \frac{K_3}{K_{10}}$$

$$k_{20} = a_{20} T^{-n_{20}} e^{-b_{20}/T}$$

$$X_{20} = \left[K_{20}c_3c_{17} - c_{10}c_{13}\right]k_{20}$$

$$\frac{\partial X_{20}}{\partial c_3} = K_{20}c_{17}$$

$$\frac{\partial X_{20}}{\partial c_{10}} = -c_{13}k_{20}$$

$$\frac{\partial X_{20}}{\partial c_{13}} = -c_{10}k_{20}$$

$$\frac{\partial X_{20}}{\partial c_{17}} = K_{20}c_3$$

$$\frac{\partial X_{20}}{\partial T} = \left[\frac{1}{K_3}\frac{dK_3}{dT} - \frac{1}{K_{10}}\frac{dK_{10}}{dT}\right]K_{20}c_3c_{17}k_{20} - \left[n_{20} + \frac{b_{20}}{T}\right]\frac{X_{20}}{T}$$

Reaction 21, $CO + NO \rightleftharpoons CO_2 + N$

$$K_{21} = \frac{K_{10}}{K_1}$$

$$k_{21} = a_{21}T^{-n_{21}}e^{-b_{21}/T}$$

$$X_{21} = \left[K_{21}c_3c_{10} - c_1c_{17}\right]k_{21}$$

$$\frac{\partial X_{21}}{\partial c_1} = -c_{17}k_{21}$$

$$\frac{\partial X_{21}}{\partial c_3} = K_{21}c_{10}k_{21}$$

$$\frac{\partial X_{21}}{\partial c_{10}} = K_{21}c_3k_{21}$$

$$\frac{\partial X_{21}}{\partial c_{17}} = -c_1k_{21}$$

$$\frac{\partial X_{21}}{\partial T} = \left[\frac{1}{K_{10}}\frac{dK_{10}}{dT} - \frac{1}{K_1}\frac{dK_1}{dT}\right] K_{21}c_3c_{10}k_{21} - \left[n_{21} + \frac{b_{21}}{T}\right]\frac{X_{21}}{T}$$

Reaction 22, $CO + O \rightleftharpoons O_2 + C$

$$K_{22} = \frac{K_3}{K_{12}}$$

$$k_{22} = a_{22}T^{-n_{22}} e^{-b_{22}/T}$$

$$X_{22} = \left[K_{22}c_3c_{18} - c_{12}c_{13}\right]k_{22}$$

$$\frac{\partial X_{22}}{\partial c_3} = K_{22}c_{18}k_{22}$$

$$\frac{\partial X_{22}}{\partial c_{12}} = -c_{13}k_{22}$$

$$\frac{\partial X_{22}}{\partial c_{13}} = -c_{12}k_{22}$$

$$\frac{\partial X_{22}}{\partial c_{18}} = K_{22}c_3k_{22}$$

$$\frac{\partial X_{22}}{\partial T} = \left[\frac{1}{K_3}\frac{dK_3}{dT} - \frac{1}{K_{12}}\frac{dK_{12}}{dT}\right] K_{22}c_3c_{18}k_{22} - \left[n_{22} + \frac{b_{22}}{T}\right]\frac{X_{22}}{T}$$

Reaction 23, $HCl + Cl \rightleftharpoons Cl_2 + H$

$$K_{23} = \frac{K_6}{K_4}$$

$$k_{23} = a_{23}T^{-n_{23}} e^{-b_{23}/T}$$

$$X_{23} = \left[K_{23}c_6c_{14} - c_4c_{16}\right]k_{23}$$

$$\frac{\partial X_{23}}{\partial c_4} = -c_{16}k_{23}$$

$$\frac{\partial X_{23}}{\partial c_6} = K_{23}c_{14}k_{23}$$

$$\frac{\partial X_{23}}{\partial c_{14}} = K_{23}c_6k_{23}$$

$$\frac{\partial X_{23}}{\partial c_{16}} = -c_4k_{23}$$

$$\frac{\partial X_{23}}{\partial T} = \left[\frac{1}{K_6}\frac{dK_6}{dT} - \frac{1}{K_4}\frac{dK_4}{dT}\right]K_{23}c_6c_{14}k_{23} - \left[n_{23} + \frac{b_{23}}{T}\right]\frac{X_{23}}{T}$$

Reaction 24, $2HCl \rightleftharpoons Cl_2 + H_2$

$$K_{24} = \frac{K_6^2}{K_4K_8}$$

$$k_{24} = a_{24}T^{-n_{24}}e^{-b_{24}/T}$$

$$X_{24} = \left[K_{24}c_6^2 - c_4c_8\right]k_{24}$$

$$\frac{\partial X_{24}}{\partial c_4} = -c_8k_{24}$$

$$\frac{\partial X_{24}}{\partial c_6} = 2K_{24}c_6k_{24}$$

$$\frac{\partial X_{24}}{\partial c_8} = -c_4k_{24}$$

$$\frac{\partial X_{24}}{\partial T} = \left[\frac{2}{K_6}\frac{dK_6}{dT} - \frac{1}{K_4}\frac{dK_4}{dT} - \frac{1}{K_8}\frac{dK_8}{dT}\right]K_{24}c_6^2k_{24} - \left[n_{24} + \frac{b_{24}}{T}\right]\frac{X_{24}}{T}$$

Reaction 25, $HCl + O \rightleftharpoons OH + Cl$

$$K_{25} = \frac{K_6}{K_{11}}$$

$$k_{25} = a_{25} T^{-n_{25}} e^{-b_{25}/T}$$

$$X_{25} = \left[K_{25} c_6 c_{18} - c_{11} c_{14}\right] k_{25}$$

$$\frac{\partial X_{25}}{\partial c_6} = K_{25} c_{18} k_{25}$$

$$\frac{\partial X_{25}}{\partial c_{11}} = c_{14} k_{25}$$

$$\frac{\partial X_{25}}{\partial c_{14}} = -c_{11} k_{25}$$

$$\frac{\partial X_{25}}{\partial c_{18}} = K_{25} c_6 k_{25}$$

$$\frac{\partial X_{25}}{\partial T} = \left[\frac{1}{K_6}\frac{dK_6}{dT} - \frac{1}{K_{11}}\frac{dK_{11}}{dT}\right] K_{25} c_6 c_{13} k_{25} - \left[n_{25} + \frac{b_{25}}{T}\right]\frac{X_{25}}{T}$$

Reaction 26, $HF + Cl \rightleftharpoons HCl + F$

$$K_{26} = \frac{K_7}{K_6}$$

$$k_{26} = a_{26} T^{-n_{26}} e^{-b_{26}/T}$$

$$X_{26} = \left[K_{26} c_7 c_{14} - c_6 c_{15}\right] k_{26}$$

$$\frac{\partial X_{26}}{\partial c_6} = -c_{15} k_{26}$$

$$\frac{\partial X_{26}}{\partial c_7} = K_{26} c_{14} k_{26}$$

$$\frac{\partial X_{26}}{\partial c_{14}} = K_{26} c_7 k_{26}$$

$$\frac{\partial X_{26}}{\partial c_{15}} = -c_6 k_{26}$$

$$\frac{\partial X_{26}}{\partial T} = \left[\frac{1}{K_7}\frac{dK_7}{dT} - \frac{1}{K_6}\frac{dK_6}{dT}\right] K_{26} c_7 c_{14} k_{26} - \left[n_{26} + \frac{b_{26}}{T}\right]\frac{X_{26}}{T}$$

Reaction 27, $HF + F \rightleftharpoons F_2 + H$

$$K_{27} = \frac{K_7}{K_5}$$

$$k_{27} = a_{27} T^{-n_{27}} e^{-b_{27}/T}$$

$$X_{27} = \left[K_{27} c_7 c_{15} - c_5 c_{16}\right] k_{27}$$

$$\frac{\partial X_{27}}{\partial c_5} = -c_{16} k_{27}$$

$$\frac{\partial X_{27}}{\partial c_7} = K_{27} c_{15} k_{27}$$

$$\frac{\partial X_{27}}{\partial c_{15}} = K_{27} c_7 k_{27}$$

$$\frac{\partial X_{27}}{\partial c_{16}} = -c_5 k_{27}$$

$$\frac{\partial X_{27}}{\partial T} = \left[\frac{1}{K_7}\frac{dK_7}{dT} - \frac{1}{K_5}\frac{dK_5}{dT}\right] - \left[n_{27} + \frac{b_{27}}{T}\right]\frac{X_{27}}{T}$$

Reaction 28, $HF + H \rightleftharpoons H_2 + F$

$$K_{28} = \frac{K_7}{K_8}$$

$$k_{28} = a_{28}T^{-n_{28}} e^{-b_{28}/T}$$

$$X_{28} = \left[K_{28}c_7c_{16} - c_8c_{15}\right]k_{28}$$

$$\frac{\partial K_{28}}{\partial c_7} = K_{28}c_{16}k_{28}$$

$$\frac{\partial X_{28}}{\partial c_8} = -c_{15}k_{28}$$

$$\frac{\partial X_{28}}{\partial c_{15}} = -c_8k_{28}$$

$$\frac{\partial X_{28}}{\partial c_{16}} = K_{28}c_7k_{28}$$

$$\frac{\partial X_{28}}{\partial T} = \left[\frac{1}{K_7}\frac{dK_7}{dT} - \frac{1}{K_8}\frac{dK_8}{dT}\right]K_{28}c_7c_{16}k_{28} - \left[n_{28} + \frac{b_{28}}{T}\right]\frac{X_{28}}{T}$$

Reaction 29, $2HF \rightleftharpoons F_2 + H_2$

$$K_{29} = \frac{K_7^2}{K_5K_8}$$

$$k_{29} = a_{29}T^{-n_{29}} e^{-b_{29}/T}$$

$$X_{29} = \left[K_{29}c_7^2 - c_5c_8\right]k_{29}$$

$$\frac{\partial X_{29}}{\partial c_5} = -c_8k_{29}$$

$$\frac{\partial X_{29}}{\partial c_7} = 2K_{29}c_7k_{29}$$

$$\frac{\partial X_{29}}{\partial c_8} = -c_5k_{29}$$

$$\frac{\partial X_{29}}{\partial T} = \left[\frac{2}{K_7}\frac{dK_7}{dT} - \frac{1}{K_5}\frac{dK_5}{dT} - \frac{1}{K_8}\frac{dK_8}{dT}\right]K_{29}c_7^2k_{29} - \left[n_{29} + \frac{b_{29}}{T}\right]\frac{X_{29}}{T}$$

Reaction 30, $HF + O \rightleftharpoons OH + F$

$$K_{30} = \frac{K_7}{K_4}$$

$$k_{30} = a_{30}T^{-n_{30}}e^{-b_{30}/T}$$

$$X_{30} = \left[K_{30}c_7c_{18} - c_{11}c_{15}\right]k_{30}$$

$$\frac{\partial X_{30}}{\partial c_7} = K_{30}c_{18}k_{30}$$

$$\frac{\partial X_{30}}{\partial c_{11}} = -c_{15}k_{30}$$

$$\frac{\partial X_{30}}{\partial c_{15}} = -c_{11}k_{30}$$

$$\frac{\partial X_{30}}{\partial c_{18}} = K_{30}c_7k_{30}$$

$$\frac{\partial X_{30}}{\partial T} = \left[\frac{1}{K_7}\frac{dK_7}{dT} - \frac{1}{K_{11}}\frac{dK_{11}}{dT}\right]K_{30}c_7c_{18}k_{30} - \left[n_{30} + \frac{b_{30}}{T}\right]\frac{X_{30}}{T}$$

Reaction 31, $HF + OH \rightleftharpoons H_2O + F$

$$K_{31} = \frac{K_7}{K_2}$$

$$k_{31} = a_{31}T^{-n_{31}} e^{-b_{31}/T}$$

$$X_{31} = \left[K_{31}c_7c_{11} - c_2c_{15}\right]k_{31}$$

$$\frac{\partial X_{31}}{\partial c_2} = -c_{15}k_{31}$$

$$\frac{\partial X_{31}}{\partial c_7} = K_{31}c_{11}k_{31}$$

$$\frac{\partial X_{31}}{\partial c_{11}} = K_{31}c_7k_{31}$$

$$\frac{\partial X_{31}}{\partial c_{15}} = -c_2k_{31}$$

$$\frac{\partial X_{31}}{\partial T} = \left[\frac{1}{K_7}\frac{dK_7}{dT} - \frac{1}{K_2}\frac{dK_2}{dT}\right]K_{31}c_7c_{11}k_{31} - \left[n_{31} + \frac{b_{31}}{T}\right]\frac{X_{31}}{T}$$

Reaction 32, $H_2 + Cl \rightleftharpoons HCl + H$

$$K_{32} = \frac{K_8}{K_6}$$

$$k_{32} = a_{32}T^{-n_{32}} e^{-b_{32}/T}$$

$$X_{32} = \left[K_{32}c_8c_{14} - c_6c_{16}\right]k_{32}$$

$$\frac{\partial X_{32}}{\partial c_6} = -c_{16}k_{32}$$

$$\frac{\partial X_{32}}{\partial c_8} = K_{32}c_{14}k_{32}$$

$$\frac{\partial X_{32}}{\partial c_{14}} = K_{32}c_8k_{32}$$

$$\frac{\partial X_{32}}{\partial c_{16}} = -c_6 k_{32}$$

$$\frac{\partial X_{32}}{\partial T} = \left[\frac{1}{K_8}\frac{dK_8}{dT} - \frac{1}{K_6}\frac{dK_6}{dT}\right] K_{32} c_8 c_{14} k_{32} - \left[n_{32} + \frac{b_{32}}{T}\right]\frac{X_{32}}{T}$$

Reaction 33, $H_2 + O \rightleftharpoons OH + H$

$$K_{33} = \frac{K_8}{K_{11}}$$

$$k_{33} = a_{33} T^{-n_{33}} e^{-b_{33}/T}$$

$$X_{33} = \left[K_{33} c_8 c_{18} - c_{11} c_{16}\right] k_{33}$$

$$\frac{\partial X_{33}}{\partial c_8} = K_{33} c_{18} k_{33}$$

$$\frac{\partial X_{33}}{\partial c_{11}} = -c_{16} k_{33}$$

$$\frac{\partial X_{32}}{\partial c_{16}} = -c_{11} k_{33}$$

$$\frac{\partial X_{32}}{\partial c_{18}} = K_{33} c_8 k_{33}$$

$$\frac{\partial X_{32}}{\partial T} = \left[\frac{1}{K_8}\frac{dK_8}{dT} - \frac{1}{K_{11}}\frac{dK_{11}}{dT}\right] K_{33} c_8 c_{18} k_{33} - \left[n_{33} + \frac{b_{33}}{T}\right]\frac{X_{33}}{T}$$

Reaction 34, $H_2 + O_2 \rightleftharpoons 2OH$

$$K_{34} = \frac{K_8 K_{12}}{K_{11}^2}$$

$$k_{34} = a_{34} T^{-n_{34}} e^{-b_{34}/T}$$

$$X_{34} = \left[K_{34}c_8c_{12} - c_{11}^2\right]k_{34}$$

$$\frac{\partial X_{34}}{\partial c_8} = K_{34}c_{12}k_{34}$$

$$\frac{2X_{34}}{\partial c_{11}} = -2c_{11}k_{34}$$

$$\frac{\partial X_{34}}{\partial c_{12}} = K_{34}c_8k_{34}$$

$$\frac{\partial X_{34}}{\partial T} = \left[\frac{1}{K_8}\frac{dK_8}{dT} + \frac{1}{K_{12}}\frac{dK_{12}}{dT} - \frac{2}{K_{11}}\frac{dK_{11}}{dT}\right]K_{34}c_8c_{12}k_{34} - \left[n_{34} + \frac{b_{34}}{T}\right]\frac{X_{34}}{T}$$

Reaction 35, $N_2 + O \rightleftharpoons NO + N$

$$K_{35} = \frac{K_9}{K_{10}}$$

$$k_{35} = a_{35}T^{-n_{35}}e^{-b_{35}/T}$$

$$X_{35} = \left[K_{35}c_9c_{18} - c_{10}c_{17}\right]k_{35}$$

$$\frac{\partial X_{35}}{\partial c_9} = K_{35}c_{18}k_{35}$$

$$\frac{\partial X_{35}}{\partial c_{10}} = -c_{17}k_{35}$$

$$\frac{\partial X_{35}}{\partial c_{17}} = -c_{10}k_{35}$$

$$\frac{\partial X_{35}}{\partial c_{18}} = K_{35}c_9k_{35}$$

$$\frac{\partial X_{35}}{\partial T} = \left[\frac{1}{K_9}\frac{dK_9}{dT} - \frac{1}{K_{10}}\frac{dK_{10}}{dT}\right]K_{35}c_9c_{18}k_{35} - \left[n_{35} + \frac{b_{35}}{T}\right]\frac{X_{35}}{T}$$

Reaction 36, $N_2 + O_2 \rightleftharpoons 2NO$

$$K_{36} = \frac{K_9 K_{12}}{K_{10}^2}$$

$$k_{36} = a_{36} T^{-n_{36}} e^{-b_{36}/T}$$

$$X_{36} = \left[K_{36} c_9 c_{12} - c_{10}^2\right] k_{36}$$

$$\frac{\partial X_{36}}{\partial c_9} = K_{36} c_{12} k_{36}$$

$$\frac{\partial X_{36}}{\partial c_{10}} = -2c_{10} k_{36}$$

$$\frac{\partial X_{36}}{\partial c_{12}} = K_{36} c_9 k_{36}$$

$$\frac{\partial X_{36}}{\partial T} = \left[\frac{1}{K_9}\frac{dK_9}{dT} + \frac{1}{K_{12}}\frac{dK_{12}}{dT} - \frac{2}{K_{10}}\frac{dK_{10}}{\partial T}\right] K_{36} c_9 c_{12} k_{36} - \left[n_{36} + \frac{b_{36}}{T}\right]\frac{X_{36}}{T}$$

Reaction 37, $NO + H \rightleftharpoons OH + N$

$$K_{37} = \frac{K_{10}}{K_{11}}$$

$$k_{37} = a_{37} T^{-n_{37}} e^{-b_{37}/T}$$

$$X_{37} = \left[K_{37} c_{10} c_{16} - c_{11} c_{17}\right] k_{37}$$

$$\frac{\partial X_{37}}{\partial c_{10}} = K_{37} c_{16} k_{37}$$

$$\frac{\partial X_{37}}{\partial c_{11}} = -c_{17} k_{37}$$

$$\frac{\partial X_{37}}{\partial c_{16}} = K_{37} c_{10} k_{37}$$

$$\frac{\partial X_{37}}{\partial c_{17}} = -c_{11}k_{37}$$

$$\frac{\partial X_{37}}{\partial T} = \left[\frac{1}{K_{10}} \frac{dK_{10}}{dT} - \frac{1}{K_{11}} \frac{dK_{11}}{dT}\right] K_{37}c_{10}c_{16}k_{37} - \left[n_{37} + \frac{b_{37}}{T}\right] \frac{X_{37}}{T}$$

Reaction 38, $NO + O \rightleftharpoons O_2 + N$

$$K_{38} = \frac{K_{10}}{K_{12}}$$

$$k_{38} = a_{38}T^{-n_{38}} e^{-b_{38}/T}$$

$$X_{38} = \left[K_{38}c_{10}c_{18} - c_{12}c_{17}\right] k_{38}$$

$$\frac{\partial X_{38}}{\partial c_{10}} = K_{38}c_{18}k_{38}$$

$$\frac{\partial X_{38}}{\partial c_{12}} = -c_{17}k_{38}$$

$$\frac{\partial X_{38}}{\partial c_{17}} = -c_{12}k_{38}$$

$$\frac{\partial X_{38}}{\partial c_{18}} = K_{38}c_{10}k_{38}$$

$$\frac{\partial X_{38}}{\partial T} = \left[\frac{1}{K_{10}} \frac{dK_{10}}{dT} - \frac{1}{K_{12}} \frac{dK_{12}}{dT}\right] K_{38}c_{10}c_{18}k_{38} - \left[n_{38} + \frac{b_{38}}{T}\right] \frac{X_{38}}{T}$$

Reaction 39, $O_2 + H \rightleftharpoons OH + O$

$$K_{39} = \frac{K_{12}}{K_{11}}$$

$$k_{39} = a_{39} T^{-n_{39}} e^{-b_{39}/T}$$

$$X_{39} = \left[K_{39} c_{12} c_{16} - c_{11} c_{18}\right] k_{39}$$

$$\frac{\partial X_{39}}{\partial c_{11}} = -c_{18} k_{39}$$

$$\frac{\partial X_{39}}{\partial c_{12}} = K_{39} c_{16} k_{39}$$

$$\frac{\partial X_{39}}{\partial c_{16}} = K_{39} c_{12} k_{39}$$

$$\frac{\partial X_{39}}{\partial c_{18}} = -c_{11} k_{39}$$

$$\frac{\partial X_{39}}{\partial T} = \left[\frac{1}{K_{12}} \frac{dK_{12}}{dT} - \frac{1}{K_{11}} \frac{dK_{11}}{dT}\right] K_{39} c_{12} c_{16} k_{39} - \left[n_{39} + \frac{b_{39}}{T}\right] \frac{X_{39}}{T}$$

4.2.2 Calculation of f_i and $\beta_{i,j}$ for the Chemical Relaxation Equations

For the species of interest, f_i and $\beta_{i,j}$ for the chemical relaxation equations are calculated from the following relationships:

For CO_2,

$$\overline{K}_1 = \frac{44.011 \rho r^*}{V}$$

$$f_1 = -\overline{K}_1 \left[X_1 + X_{13} + X_{14} - X_{18} - X_{21}\right]$$

$$\beta_{1,1} = -\overline{K}_1 \left[\frac{\partial X_1}{\partial c_1} + \frac{\partial X_{13}}{\partial c_1} + \frac{\partial X_{14}}{\partial c_1} - \frac{\partial X_{18}}{\partial c_1} - \frac{\partial X_{21}}{\partial c_1}\right]$$

$$\beta_{1,2} = -\overline{K}_1 \frac{\partial X_1}{\partial c_2}$$

$$\beta_{1,3} = -\overline{K}_1 \left[\frac{\partial X_1}{\partial c_3} + \frac{\partial X_{13}}{\partial c_3} + \frac{\partial X_{14}}{\partial c_3} - \frac{\partial X_{18}}{\partial c_3} - \frac{\partial X_{21}}{\partial c_3}\right]$$

$$\beta_{1,4} = -\overline{K}_1 \frac{\partial X_1}{\partial c_4}$$

$$\beta_{1,5} = -\overline{K}_1 \frac{\partial X_1}{\partial c_5}$$

$$\beta_{1,6} = -\overline{K}_1 \frac{\partial X_1}{\partial c_6}$$

$$\beta_{1,7} = -\overline{K}_1 \frac{\partial X_1}{\partial c_7}$$

$$\beta_{1,8} = -\overline{K}_1 \frac{\partial X_1}{\partial c_8}$$

$$\beta_{1,9} = -\overline{K}_1 \frac{\partial X_1}{\partial c_9}$$

$$\beta_{1,10} = -K_1\left[\frac{\partial X_1}{\partial c_{10}} - \frac{\partial X_{21}}{\partial c_{10}}\right]$$

$$\beta_{1,11} = -K_1\left[\frac{\partial X_1}{\partial c_{11}} + \frac{\partial X_{13}}{\partial c_{11}}\right]$$

$$\beta_{1,12} = -\overline{K}_1\left[\frac{\partial X_1}{\partial c_{12}} + \frac{\partial X_{14}}{\partial c_{12}}\right]$$

$$\beta_{1,13} = -\overline{K}_1\left[\frac{\partial X_1}{\partial c_{13}} - \frac{\partial X_{18}}{\partial c_{13}}\right]$$

$$\beta_{1,14} = -\overline{K}_1 \frac{\partial X_1}{\partial c_{14}}$$

$$\beta_{1,15} = -\overline{K}_1 \frac{\partial X_1}{\partial c_{15}}$$

$$\beta_{1,16} = -\overline{K}_1\left[\frac{\partial X_1}{\partial c_{16}} + \frac{\partial X_{13}}{\partial c_{16}}\right]$$

$$\beta_{1,17} = -K\left[\frac{\partial X_1}{\partial c_{17}} - \frac{\partial X_{21}}{\partial c_{17}}\right]$$

$$\beta_{1,18} = -\overline{K}_1\left[\frac{\partial X_1}{\partial c_{18}} + \frac{\partial X_{14}}{\partial c_{18}}\right]$$

$$\beta_{1,19} = -\frac{1}{V} f_i$$

$$\beta_{1,20} = \frac{1}{\rho} f_i - \overline{K}_1 \frac{\partial X_1}{\partial \rho}$$

$$\beta_{1,21} = -\overline{K}_1\left[\frac{\partial X_1}{\partial T} + \frac{\partial X_{13}}{\partial T} + \frac{\partial X_{14}}{\partial T} - \frac{\partial X_{18}}{\partial T} - \frac{\partial X_{21}}{\partial T}\right]$$

For H_2O,

$$\overline{K}_2 = \frac{18.016\rho r^*}{V}$$

$$f_2 = -\overline{K}_2\left[X_2 + X_{15} + X_{16} - X_{17} - X_{31}\right]$$

$$\beta_{2,1} = -\overline{K}_2\ \frac{\partial X_2}{\partial c_1}$$

$$\beta_{2,2} = -\overline{K}_2\left[\frac{\partial X_2}{\partial c_2} + \frac{\partial X_{15}}{\partial c_2} + \frac{\partial X_{16}}{\partial c_2} + \frac{\partial X_{17}}{\partial c_2} - \frac{\partial X_{31}}{\partial c_2}\right]$$

$$\beta_{2,3} = -K_2\ \frac{\partial X_2}{\partial c_3}$$

$$\beta_{2,4} = -K_2\ \frac{\partial X_2}{\partial c_4}$$

$$\beta_{2,5} = -K_2\ \frac{\partial X_2}{\partial c_5}$$

$$\beta_{2,6} = -\overline{K}_2\left[\frac{\partial X_2}{\partial c_6} + \frac{\partial X_{15}}{\partial c_6}\right]$$

$$\beta_{2,7} = -\overline{K}_2\left[\frac{\partial X_2}{\partial c_7} - \frac{\partial X_{31}}{\partial c_7}\right]$$

$$\beta_{2,8} = -\overline{K}_2\left[\frac{\partial X_2}{\partial c_8} + \frac{\partial X_{16}}{\partial c_8}\right]$$

$$\beta_{2,9} = -\overline{K}_2\ \frac{\partial X_2}{\partial c_9}$$

$$\beta_{2,10} = -\overline{K}_2 \frac{\partial X_2}{\partial c_{10}}$$

$$\beta_{2,11} = -\overline{K}_2 \left[\frac{\partial X_2}{\partial c_{11}} + \frac{\partial X_{15}}{\partial c_{11}} + \frac{\partial X_{16}}{\partial c_{11}} + \frac{\partial X_{17}}{\partial c_{11}} - \frac{\partial X_{31}}{\partial c_{11}} \right]$$

$$\beta_{2,12} = -\overline{K}_2 \frac{\partial X_2}{\partial c_{12}}$$

$$\beta_{2,13} = -\overline{K}_2 \frac{\partial X_2}{\partial c_{13}}$$

$$\beta_{2,14} = -\overline{K}_2 \left[\frac{\partial X_2}{\partial c_{14}} + \frac{\partial X_{15}}{\partial c_{14}} \right]$$

$$\beta_{2,15} = -\overline{K}_2 \left[\frac{\partial X_2}{\partial c_{15}} - \frac{\partial X_{31}}{\partial c_{15}} \right]$$

$$\beta_{2,16} = -\overline{K}_2 \left[\frac{\partial X_2}{\partial c_{16}} + \frac{\partial X_{16}}{\partial c_{16}} \right]$$

$$\beta_{2,17} = -\overline{K}_2 \frac{\partial X_2}{\partial c_{17}}$$

$$\beta_{2,18} = -\overline{K}_2 \left[\frac{\partial X_2}{\partial c_{18}} + \frac{\partial X_{17}}{\partial c_{18}} \right]$$

$$\beta_{2,19} = -\frac{1}{V} f_2$$

$$\beta_{2,20} = \frac{1}{\rho} f_2 - \overline{K}_2 \frac{\partial X_2}{\partial \rho}$$

$$\beta_{2,21} = -\overline{K}_2 \left[\frac{\partial X_2}{\partial T} + \frac{\partial X_{15}}{\partial T} + \frac{\partial X_{16}}{\partial T} + \frac{\partial X_{17}}{\partial T} - \frac{\partial X_{31}}{\partial T} \right]$$

For CO,

$$\overline{K}_3 = \frac{28.011\rho r^*}{V}$$

$$f_3 = \overline{K}_3\left[X_1 - X_3 + X_{13} + X_{14} - 2X_{18} - X_{19} - X_{20} - X_{21} - X_{22}\right]$$

$$\beta_{3,1} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_1} - \frac{\partial X_3}{\partial c_1} + \frac{\partial X_{13}}{\partial c_1} + \frac{\partial X_{14}}{\partial c_1} - 2\frac{\partial X_{18}}{\partial c_1} - \frac{\partial X_{21}}{\partial c_1}\right]$$

$$\beta_{3,2} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_2} - \frac{\partial X_3}{\partial c_2}\right]$$

$$\beta_{3,3} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_3} - \frac{\partial X_3}{\partial c_3} + \frac{\partial X_{13}}{\partial c_3} + \frac{\partial X_{14}}{\partial c_3} - 2\frac{\partial X_{18}}{\partial c_3} - \frac{\partial X_{19}}{\partial c_3} - \frac{\partial X_{20}}{\partial c_3}\right.$$
$$\left. - \frac{\partial X_{21}}{\partial c_3} - \frac{\partial X_{22}}{\partial c_3}\right]$$

$$\beta_{3,4} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_4} - \frac{\partial X_3}{\partial c_4}\right]$$

$$\beta_{3,5} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_5} - \frac{\partial X_3}{\partial c_5}\right]$$

$$\beta_{3,6} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_6} - \frac{\partial X_3}{\partial c_6}\right]$$

$$\beta_{3,7} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_7} - \frac{\partial X_3}{\partial c_7}\right]$$

$$\beta_{3,8} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_8} - \frac{\partial X_3}{\partial c_8}\right]$$

$$\beta_{3,9} = \overline{K}_3\left[\frac{\partial X_1}{\partial c_9} - \frac{\partial X_3}{\partial c_9}\right]$$

$$\beta_{3,10} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{10}} - \frac{\partial X_3}{\partial c_{10}} - \frac{\partial X_{20}}{\partial c_{10}} - \frac{\partial X_{21}}{\partial c_{10}} \right]$$

$$\beta_{3,11} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{11}} - \frac{\partial X_3}{\partial c_{11}} + \frac{\partial X_{13}}{\partial c_{11}} - \frac{\partial X_{19}}{\partial c_{11}} \right]$$

$$\beta_{3,12} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{12}} - \frac{\partial X_3}{\partial c_{12}} + \frac{\partial X_{14}}{\partial c_{12}} - \frac{\partial X_{22}}{\partial c_{12}} \right]$$

$$\beta_{3,13} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{13}} - \frac{\partial X_3}{\partial c_{13}} - 2\,\frac{\partial X_{18}}{\partial c_{13}} - \frac{\partial X_{19}}{\partial c_{13}} - \frac{\partial X_{20}}{\partial c_{13}} - \frac{\partial X_{22}}{\partial c_{13}} \right]$$

$$\beta_{3,14} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{14}} - \frac{\partial X_3}{\partial c_{14}} \right]$$

$$\beta_{3,15} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{15}} - \frac{\partial X_3}{\partial c_{15}} \right]$$

$$\beta_{3,16} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{16}} - \frac{\partial X_3}{\partial c_{16}} + \frac{\partial X_{13}}{\partial c_{16}} - \frac{\partial X_{19}}{\partial c_{16}} \right]$$

$$\beta_{3,17} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{17}} - \frac{\partial X_3}{\partial c_{17}} - \frac{\partial X_{20}}{\partial c_{17}} - \frac{\partial X_{21}}{\partial c_{17}} \right]$$

$$\beta_{3,18} = \overline{K}_3 \left[\frac{\partial X_1}{\partial c_{18}} - \frac{\partial X_3}{\partial c_{18}} + \frac{\partial X_{14}}{\partial c_{18}} - \frac{\partial X_{22}}{\partial c_{18}} \right]$$

$$\beta_{3,19} = -\frac{1}{V} f_3$$

$$\beta_{3,20} = \frac{1}{\rho} f_3 + \overline{K}_3 \left[\frac{\partial X_1}{\partial \rho} - \frac{\partial X_3}{\partial \rho} \right]$$

$$\beta_{3,21} = \overline{K}_3 \left[\frac{\partial X_1}{\partial T} - \frac{\partial X_3}{\partial T} + \frac{\partial X_{13}}{\partial T} + \frac{\partial X_{14}}{\partial T} - 2\frac{\partial X_{18}}{\partial T} - \frac{\partial X_{19}}{\partial T} - \frac{\partial X_{20}}{\partial T} \right.$$

$$\left. + \frac{\partial X_{21}}{\partial T} - \frac{\partial X_{22}}{\partial T} \right]$$

For Cl_2,

$$\overline{K}_4 = \frac{70.914 \rho r^*}{V}$$

$$f_4 = - \overline{K}_4 \left[X_4 - X_{23} - X_{24} \right]$$

$$\beta_{4,1} = - \overline{K}_4 \frac{\partial X_4}{\partial c_1}$$

$$\beta_{4,2} = - \overline{K}_4 \frac{\partial X_4}{\partial c_2}$$

$$\beta_{4,3} = - \overline{K}_4 \frac{\partial X_4}{\partial c_3}$$

$$\beta_{4,4} = - \overline{K}_4 \left[\frac{\partial X_4}{\partial c_4} - \frac{\partial X_{23}}{\partial c_4} - \frac{\partial X_{24}}{\partial c_4} \right]$$

$$\beta_{4,5} = - \overline{K}_4 \frac{\partial X_4}{\partial c_5}$$

$$\beta_{4,6} = - \overline{K}_4 \left[\frac{\partial X_4}{\partial c_6} - \frac{\partial X_{23}}{\partial c_6} - \frac{\partial X_{24}}{\partial c_6} \right]$$

$$\beta_{4,7} = - \overline{K}_4 \frac{\partial X_4}{\partial c_7}$$

$$\beta_{4,8} = - \overline{K}_4 \left[\frac{\partial X_4}{\partial c_8} - \frac{\partial X_{24}}{\partial c_8} \right]$$

$$\beta_{4,9} = -\overline{K}_4 \frac{\partial X_4}{\partial c_9}$$

$$\beta_{4,10} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{10}}$$

$$\beta_{4,11} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{11}}$$

$$\beta_{4,12} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{12}}$$

$$\beta_{4,13} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{13}}$$

$$\beta_{4,14} = -\overline{K}_4 \left[\frac{\partial X_4}{\partial c_{14}} - \frac{\partial X_{23}}{\partial c_{14}}\right]$$

$$\beta_{4,15} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{15}}$$

$$\beta_{4,16} = -\overline{K}_4 \left[\frac{\partial X_4}{\partial c_{16}} - \frac{\partial X_{23}}{\partial c_{16}}\right]$$

$$\beta_{4,17} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{17}}$$

$$\beta_{4,18} = -\overline{K}_4 \frac{\partial X_4}{\partial c_{18}}$$

$$\beta_{4,19} = -\frac{\dot{}}{V} f_4$$

$$\beta_{4,20} = \frac{1}{\rho} f_4 - \overline{K}_4 \frac{\partial X_4}{\partial \rho}$$

$$\beta_{4,21} = -\overline{K}_4\left[\frac{\partial X_4}{\partial T} - \frac{\partial X_{23}}{\partial T} - \frac{\partial X_{24}}{\partial T}\right]$$

For F_2,

$$\overline{K}_5 = \frac{38,000\rho r^*}{V}$$

$$f_5 = -\overline{K}_5\left[X_5 - X_{27} - X_{29}\right]$$

$$\beta_{5,1} = -\overline{K}_5 \frac{\partial X_5}{\partial c_1}$$

$$\beta_{5,2} = -\overline{K}_5 \frac{\partial X_5}{\partial c_2}$$

$$\beta_{5,3} = -\overline{K}_5 \frac{\partial X_5}{\partial c_3}$$

$$\beta_{5,4} = -\overline{K}_5 \frac{\partial X_5}{\partial c_4}$$

$$\beta_{5,5} = -\overline{K}_5\left[\frac{\partial X_5}{\partial c_5} - \frac{\partial X_{27}}{\partial c_5} - \frac{\partial X_{29}}{\partial c_5}\right]$$

$$\beta_{5,6} = -\overline{K}_5 \frac{\partial X_5}{\partial c_6}$$

$$\beta_{5,7} = -\overline{K}_5\left[\frac{\partial X_5}{\partial c_7} - \frac{\partial X_{27}}{\partial c_7} - \frac{\partial X_{29}}{\partial c_7}\right]$$

$$\beta_{5,8} = -\overline{K}_5\left[\frac{\partial X_5}{\partial c_8} - \frac{\partial X_{29}}{\partial c_8}\right]$$

$$\beta_{5,9} = -\overline{K}_5 \frac{\partial X_5}{\partial c_9}$$

$$\beta_{5,10} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{10}}$$

$$\beta_{5,11} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{11}}$$

$$\beta_{5,12} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{12}}$$

$$\beta_{5,13} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{13}}$$

$$\beta_{5,14} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{14}}$$

$$\beta_{5,15} = -\overline{K}_5 \left[\frac{\partial X_5}{\partial c_{15}} - \frac{\partial X_{27}}{\partial c_{15}}\right]$$

$$\beta_{5,16} = -\overline{K}_5 \left[\frac{\partial X_5}{\partial c_{16}} - \frac{\partial X_{27}}{\partial c_{16}}\right]$$

$$\beta_{5,17} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{17}}$$

$$\beta_{5,18} = -\overline{K}_5 \frac{\partial X_5}{\partial c_{18}}$$

$$\beta_{5,19} = -\frac{1}{V} f_5$$

$$\beta_{5,20} = \frac{1}{\rho} f_5 - \overline{K}_5 \frac{\partial X_5}{\partial \rho}$$

$$\beta_{5,21} = -\overline{K}_5 \left[\frac{\partial X_5}{\partial T} - \frac{\partial X_{27}}{\partial T} - \frac{\partial X_{29}}{\partial T}\right]$$

For HCl,

$$\overline{K}_6 = \frac{36.465 \rho r^*}{V}$$

$$f_6 = -\overline{K}_6 \left[X_6 - X_{15} + X_{23} + 2X_{24} + X_{25} - X_{26} - X_{32}\right]$$

$$\beta_{6,1} = -\overline{K}_6 \frac{\partial X_6}{\partial c_1}$$

$$\beta_{6,2} = -\overline{K}_6 \left[\frac{\partial X_6}{\partial c_2} - \frac{\partial X_{15}}{\partial c_2}\right]$$

$$\beta_{6,3} = -\overline{K}_6 \frac{\partial X_6}{\partial c_3}$$

$$\beta_{6,4} = -\overline{K}_6 \left[\frac{\partial X_6}{\partial c_4} + \frac{\partial X_{23}}{\partial c_4} + 2 \frac{\partial X_{24}}{\partial c_4}\right]$$

$$\beta_{6,5} = -\overline{K}_6 \frac{\partial X_6}{\partial c_6}$$

$$\beta_{6,6} = -\overline{K}_6 \left[\frac{\partial X_6}{\partial c_6} - \frac{\partial X_{15}}{\partial c_6} + \frac{\partial X_{23}}{\partial c_6} + 2 \frac{\partial X_{24}}{\partial c_6} + \frac{\partial X_{25}}{\partial c_6} - \frac{\partial X_{26}}{\partial c_6} - \frac{\partial X_{32}}{\partial c_6}\right]$$

$$\beta_{6,7} = -\overline{K}_6 \left[\frac{\partial X_6}{\partial c_7} - \frac{\partial X_{26}}{\partial c_7}\right]$$

$$\beta_{6,8} = -\overline{K}_6 \left[\frac{\partial X_6}{\partial c_8} + 2 \frac{\partial X_{24}}{\partial c_8} - \frac{\partial X_{32}}{\partial c_8}\right]$$

$$\beta_{6,9} = -\overline{K}_6 \frac{\partial X_6}{\partial c_9}$$

$$\beta_{6,10} = -\overline{K}_6 \frac{\partial X_6}{\partial c_{10}}$$

$$\beta_{6,11} = -\overline{K}_6\left[\frac{\partial X_6}{\partial c_{11}} - \frac{\partial X_{15}}{\partial c_{11}} + \frac{\partial X_{25}}{\partial c_{11}}\right]$$

$$\beta_{6,12} = -\overline{K}_6 \frac{\partial X_6}{\partial c_{12}}$$

$$\beta_{6,13} = -\overline{K}_6 \frac{\partial X_6}{\partial c_{13}}$$

$$\beta_{6,14} = -\overline{K}_6\left[\frac{\partial X_6}{\partial c_{14}} - \frac{\partial X_{15}}{\partial c_{14}} + \frac{\partial X_{23}}{\partial c_{14}} + \frac{\partial X_{25}}{\partial c_{14}} - \frac{\partial X_{26}}{\partial c_{14}} - \frac{\partial X_{32}}{\partial c_{14}}\right]$$

$$\beta_{6,15} = -\overline{K}_6\left[\frac{\partial X_6}{\partial c_{15}} - \frac{\partial X_{26}}{\partial c_{15}}\right]$$

$$\beta_{6,16} = -\overline{K}_6\left[\frac{\partial X_6}{\partial c_{16}} + \frac{\partial X_{23}}{\partial c_{16}}\right]$$

$$\beta_{6,17} = -\overline{K}_6 \frac{\partial X_6}{\partial c_{17}}$$

$$\beta_{6,18} = -\overline{K}_6\left[\frac{\partial X_6}{\partial c_{18}} + \frac{\partial X_{25}}{\partial c_{18}}\right]$$

$$\beta_{6,19} = -\frac{1}{V} f_6$$

$$\beta_{6,20} = \frac{1}{\rho} f_6 - \overline{K}_6 \frac{\partial X_6}{\partial \rho}$$

$$\beta_{6,21} = -\overline{K}_6\left[\frac{\partial X_6}{\partial T} - \frac{\partial X_{15}}{\partial T} + \frac{\partial X_{23}}{\partial T} + 2\frac{\partial X_{24}}{\partial T} + \frac{\partial X_{25}}{\partial T} - \frac{\partial X_{26}}{\partial T} - \frac{\partial X_{32}}{\partial T}\right]$$

For F_7

$$K_7 = \frac{20.008 \rho r^*}{V}$$

$$f_7 = -K_7 \left[X_7 + X_{26} + X_{27} + X_{28} + 2X_{29} + X_{30} + X_{31} \right]$$

$$\beta_{7,1} = -K_7 \frac{\partial X_7}{\partial c_1}$$

$$\beta_{7,2} = -K_7 \left[\frac{\partial X_7}{\partial c_2} + \frac{\partial X_{31}}{\partial c_2} \right]$$

$$\beta_{7,3} = -K_7 \frac{\partial X_7}{\partial c_3}$$

$$\beta_{7,4} = -K_7 \frac{\partial X_7}{\partial c_4}$$

$$\beta_{7,5} = -K_7 \left[\frac{\partial X_7}{\partial c_5} + \frac{\partial X_{27}}{\partial c_5} + 2 \frac{\partial X_{29}}{\partial c_5} \right]$$

$$\beta_{7,6} = -K_7 \left[\frac{\partial X_7}{\partial c_6} + \frac{\partial X_{26}}{\partial c_6} \right]$$

$$\beta_{7,7} = -K_7 \left[\frac{\partial X_7}{\partial c_7} + \frac{\partial X_{26}}{\partial c_7} + \frac{\partial X_{27}}{\partial c_7} + \frac{\partial X_{28}}{\partial c_7} + 2 \frac{\partial X_{29}}{\partial c_7} + \frac{\partial X_{30}}{\partial c_7} + \frac{\partial X_{31}}{\partial c_7} \right]$$

$$\beta_{7,8} = -K_7 \left[\frac{\partial X_7}{\partial c_8} + \frac{\partial X_{28}}{\partial c_8} + 2 \frac{\partial X_{29}}{\partial c_8} \right]$$

$$\beta_{7,9} = -K_7 \frac{\partial X_7}{\partial c_9}$$

$$\beta_{7,10} = -K_7 \frac{\partial X_7}{\partial c_{10}}$$

$$\beta_{7,11} = -\overline{K}_7\left[\frac{\partial X_7}{\partial c_{11}} + \frac{\partial X_{30}}{\partial c_{11}} + \frac{\partial X_{31}}{\partial c_{11}}\right]$$

$$\beta_{7,12} = -\overline{K}_7 \frac{\partial X_7}{\partial c_{12}}$$

$$\beta_{7,13} = -\overline{K}_7 \frac{\delta X_7}{\partial c_{13}}$$

$$\beta_{7,14} = -\overline{K}_7\left[\frac{\partial X_7}{\partial c_{14}} + \frac{\partial X_{25}}{\partial c_{14}}\right]$$

$$\beta_{7,15} = -\overline{K}_7\left[\frac{\partial X_7}{\partial c_{15}} + \frac{\partial X_{26}}{\partial c_{15}} + \frac{\partial X_{27}}{\partial c_{15}} + \frac{\partial X_{28}}{\partial c_{15}} + \frac{\partial X_{30}}{\partial c_{15}} + \frac{\partial X_{31}}{\partial c_{15}}\right]$$

$$\beta_{7,16} = -\overline{K}_7\left[\frac{\partial X_7}{\partial c_{16}} + \frac{\partial X_{27}}{\partial c_{16}} + \frac{\partial X_{28}}{\partial c_{16}}\right]$$

$$\beta_{7,17} = -\overline{K}_7 \frac{\partial X_7}{\partial c_{17}}$$

$$\beta_{7,18} = -\overline{K}_7\left[\frac{\partial X_7}{\partial c_{18}} + \frac{\partial X_{30}}{\partial c_{18}}\right]$$

$$\beta_{7,19} = -\frac{1}{V} f_7$$

$$\beta_{7,20} = \frac{1}{\rho} f_7 - \overline{K}_7 \frac{\partial X_7}{\partial \rho}$$

$$\beta_{7,21} = -\overline{K}\left[\frac{\partial X_7}{\partial T} + \frac{\partial X_{26}}{\partial T} + \frac{\partial X_{27}}{\partial T} + \frac{\partial X_{28}}{\partial T} + 2\frac{\partial X_{29}}{\partial T} + \frac{\partial X_{30}}{\partial T} + \frac{\partial X_{31}}{\partial T}\right]$$

For H_2,

$$\overline{K}_8 = \frac{2.016\rho r^*}{V}$$

$$f_8 = -\overline{K}_8\left[X_8 - X_{16} - X_{24} - X_{28} - X_{29} + X_{32} + X_{33} + X_{34}\right]$$

$$\beta_{8,1} = -\overline{K}_8 \frac{\partial X_8}{\partial c_1}$$

$$\beta_{8,2} = -\overline{K}_8\left[\frac{\partial X_8}{\partial c_2} - \frac{\partial X_{16}}{\partial c_2}\right]$$

$$\beta_{8,3} = -\overline{K}_8 \frac{\partial X_8}{\partial c_3}$$

$$\beta_{8,4} = -\overline{K}_8\left[\frac{\partial X_8}{\partial c_4} - \frac{\partial X_{24}}{\partial c_4}\right]$$

$$\beta_{8,5} = -\overline{K}_8\left[\frac{\partial X_8}{\partial c_5} - \frac{\partial X_{29}}{\partial c_5}\right]$$

$$\beta_{8,6} = -\overline{K}_8\left[\frac{\partial X_8}{\partial c_6} - \frac{\partial X_{24}}{\partial c_6} + \frac{\partial X_{32}}{\partial c_6}\right]$$

$$\beta_{8,7} = -\overline{K}_8\left[\frac{\partial X_8}{\partial c_7} - \frac{\partial X_{28}}{\partial c_7} - \frac{\partial X_{29}}{\partial c_7}\right]$$

$$\beta_{8,8} = -\overline{K}_8\left[\frac{\partial X_8}{\partial c_8} - \frac{\partial X_{16}}{\partial c_8} - \frac{\partial X_{24}}{\partial c_8} - \frac{\partial X_{23}}{\partial c_8} - \frac{\partial X_{29}}{\partial c_8} + \frac{\partial X_{32}}{\partial c_8} + \frac{\partial X_{33}}{\partial c_8} + \frac{\partial X_{34}}{\partial c_8}\right]$$

$$\beta_{8,9} = -\overline{K}_8 \frac{\partial X_8}{\partial c_9}$$

$$\beta_{8,10} = -\overline{K}_8 \frac{\partial X_8}{\partial c_{10}}$$

$$\beta_{8,11} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial c_{11}} - \frac{\partial X_{16}}{\partial c_{11}} + \frac{\partial X_{33}}{\partial c_{11}} + \frac{\partial X_{34}}{\partial c_{11}}\right]$$

$$\beta_{8,12} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial c_{12}} + \frac{\partial X_{34}}{\partial c_{12}}\right]$$

$$\beta_{8,13} = -\overline{K}_8 \frac{\partial X_8}{\partial c_{13}}$$

$$\beta_{8,14} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial c_{14}} + \frac{\partial X_{32}}{\partial c_{14}}\right]$$

$$\beta_{8,15} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial c_{15}} - \frac{\partial X_{28}}{\partial c_{15}}\right]$$

$$\beta_{8,16} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial c_{16}} - \frac{\partial X_{16}}{\partial c_{16}} - \frac{\partial X_{28}}{\partial c_{16}} + \frac{\partial X_{32}}{\partial c_{16}} + \frac{\partial X_{33}}{\partial c_{16}}\right]$$

$$\beta_{8,17} = -\overline{K}_8 \frac{\partial X_8}{\partial c_{17}}$$

$$\beta_{8,18} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial c_{18}} + \frac{\partial X_{33}}{\partial c_{18}}\right]$$

$$\beta_{8,19} = -\frac{1}{V} f_8$$

$$\beta_{8,20} = \frac{1}{\rho} f_8 - \overline{K}_8 \frac{\partial X_8}{\partial \rho}$$

$$\beta_{8,21} = -\overline{K}_8 \left[\frac{\partial X_8}{\partial T} - \frac{\partial X_{16}}{\partial T} - \frac{\partial X_{24}}{\partial T} - \frac{\partial X_{28}}{\partial T} - \frac{\partial X_{29}}{\partial T} + \frac{\partial X_{32}}{\partial T} + \frac{\partial X_{33}}{\partial T} + \frac{\partial X_{34}}{\partial T} \right]$$

For N_2,

$$\overline{K}_9 = \frac{28.016 \rho r^*}{V}$$

$$f_9 = -\overline{K}_9 \left[X_9 + X_{35} + X_{36} \right]$$

$$\beta_{9,1} = -\overline{K}_9 \frac{\partial X_9}{\partial c_1}$$

$$\beta_{9,2} = -\overline{K}_9 \frac{\partial X_9}{\partial c_2}$$

$$\beta_{9,3} = -\overline{K}_9 \frac{\partial X_9}{\partial c_3}$$

$$\beta_{9,4} = -\overline{K}_9 \frac{\partial X_9}{\partial c_4}$$

$$\beta_{9,5} = -\overline{K}_9 \frac{\partial X_9}{\partial c_5}$$

$$\beta_{9,6} = -\overline{K}_9 \frac{\partial X_9}{\partial c_6}$$

$$\beta_{9,7} = -\overline{K}_9 \frac{\partial X_9}{\partial c_7}$$

$$\beta_{9,8} = -\overline{K}_9 \frac{\partial X_9}{\partial c_8}$$

$$\beta_{9,9} = -\overline{K}_9 \left[\frac{\partial X_9}{\partial c_9} + \frac{\partial X_{35}}{\partial c_9} + \frac{\partial X_{36}}{\partial c_9} \right]$$

$$\beta_{9,10} = -\overline{K}_9 \left[\frac{\partial X_9}{\partial c_{10}} + \frac{\partial X_{35}}{\partial c_{10}} + \frac{\partial X_{36}}{\partial c_{10}} \right]$$

$$\beta_{9,11} = -\overline{K}_9 \frac{\partial X_9}{\partial c_{11}}$$

$$\beta_{9,12} = -\overline{K}_9 \left[\frac{\partial X_9}{\partial c_{12}} + \frac{\partial X_{36}}{\partial c_{12}} \right]$$

$$\beta_{9,13} = -\overline{K}_9 \frac{\partial X_9}{\partial c_{13}}$$

$$\beta_{9,14} = -K_9 \frac{\partial X_9}{\partial c_{14}}$$

$$\beta_{9,15} = -K_9 \frac{\partial X_9}{\partial c_{15}}$$

$$\beta_{9,16} = -\overline{K}_9 \frac{\partial X_9}{\partial c_{16}}$$

$$\beta_{9,17} = -\overline{K}_9 \left[\frac{\partial X_9}{\partial c_{17}} + \frac{\partial X_{35}}{\partial c_{17}} \right]$$

$$\beta_{9,18} = -\overline{K}_9 \frac{\partial X_9}{\partial c_{18}}$$

$$\beta_{9,19} = -\frac{1}{V} f_9$$

$$\beta_{9,20} = \frac{1}{\rho} f_9 - \overline{K}_9 \frac{\partial X_9}{\partial \rho}$$

$$\beta_{9,21} = -\bar{K}_9\left[\frac{\partial X_9}{\partial T} + \frac{\partial X_{35}}{\partial T} + \frac{\partial X_{36}}{\partial T}\right]$$

For NO,

$$\bar{K}_{10} = \frac{30.008\rho r^*}{V}$$

$$f_{10} = -\bar{K}_{10}\left[X_{10} - X_{20} + X_{21} - X_{35} - 2X_{36} + X_{37} + X_{38}\right]$$

$$\beta_{10,1} = -\bar{K}_{10}\left[\frac{\partial X_{10}}{\partial c_1} + \frac{\partial X_{21}}{\partial c_1}\right]$$

$$\beta_{10,2} = -\bar{K}_{10}\,\frac{\partial X_{10}}{\partial c_2}$$

$$\beta_{10,3} = -\bar{K}_{10}\left[\frac{\partial X_{10}}{\partial c_3} - \frac{\partial X_{20}}{\partial c_3} + \frac{\partial X_{21}}{\partial c_3}\right]$$

$$\beta_{10,4} = -\bar{K}_{10}\,\frac{\partial X_{10}}{\partial c_4}$$

$$\beta_{10,5} = -\bar{K}_{10}\,\frac{\partial X_{10}}{\partial c_5}$$

$$\beta_{10,6} = -\bar{K}_{10}\,\frac{\partial X_{10}}{\partial c_6}$$

$$\beta_{10,7} = -\bar{K}_{10}\,\frac{\partial X_{10}}{\partial c_7}$$

$$\beta_{10,8} = -\bar{K}_{10}\,\frac{\partial X_{10}}{\partial c_8}$$

$$\beta_{10,9} = -\bar{K}_{10}\left[\frac{\partial X_{10}}{\partial c_9} - \frac{\partial X_{35}}{\partial c_9} - 2\,\frac{\partial X_{36}}{\partial c_9}\right]$$

$$\beta_{10,10} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{10}} - \frac{\partial X_{20}}{\partial c_{10}} + \frac{\partial X_{21}}{\partial c_{10}} - \frac{\partial X_{35}}{\partial c_{10}} - 2\,\frac{\partial X_{36}}{\partial c_{10}} + \frac{\partial X_{37}}{\partial c_{10}} + \frac{\partial X_{38}}{\partial c_{10}}\right]$$

$$\beta_{10,11} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{11}} + \frac{\partial X_{37}}{\partial c_{11}}\right]$$

$$\beta_{10,12} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{12}} - 2\,\frac{\partial X_{36}}{\partial c_{12}} + \frac{\partial X_{38}}{\partial c_{12}}\right]$$

$$\beta_{10,13} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{13}} - \frac{\partial X_{20}}{\partial c_{13}}\right]$$

$$\beta_{10,14} = -\overline{K}_{10}\,\frac{\partial X_{10}}{\partial c_{14}}$$

$$\beta_{10,15} = -\overline{K}_{10}\,\frac{\partial X_{10}}{\partial c_{15}}$$

$$\beta_{10,16} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{16}} + \frac{\partial X_{37}}{\partial c_{16}}\right]$$

$$\beta_{10,17} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{17}} - \frac{\partial X_{20}}{\partial c_{17}} + \frac{\partial X_{21}}{\partial c_{17}} - \frac{\partial X_{35}}{\partial c_{17}} + \frac{\partial X_{37}}{\partial c_{17}} + \frac{\partial X_{38}}{\partial c_{17}}\right]$$

$$\beta_{10,18} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial c_{18}} - \frac{\partial X_{35}}{\partial c_{18}} + \frac{\partial X_{38}}{\partial c_{18}}\right]$$

$$\beta_{10,19} = -\frac{1}{V}\,f_{10}$$

$$\beta_{10,20} = \frac{1}{\rho}\,f_{10} - \overline{K}_{10}\,\frac{\partial X_{10}}{\partial \rho}$$

$$\beta_{10,21} = -\overline{K}_{10}\left[\frac{\partial X_{10}}{\partial T} - \frac{\partial X_{20}}{\partial T} + \frac{\partial X_{21}}{\partial T} - \frac{\partial X_{35}}{\partial T} - 2\,\frac{\partial X_{36}}{\partial T} + \frac{\partial X_{37}}{\partial T} + \frac{\partial X_{38}}{\partial T}\right]$$

For OH,

$$\overline{K}_{11} = \frac{17.008\rho r^*}{V}$$

$$f_{11} = \overline{K}_{11}\Big[X_2 - X_{11} + X_{13} + X_{15} + X_{16} + 2X_{17} + X_{19} + X_{25} + X_{30}$$

$$- X_{31} + X_{33} + 2X_{34} + X_{37} + X_{39}\Big]$$

$$\beta_{11,1} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_1} - \frac{\partial X_{11}}{\partial c_1} + \frac{\partial X_{13}}{\partial c_1}\right]$$

$$\beta_{11,2} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_2} - \frac{\partial X_{11}}{\partial c_2} + \frac{\partial X_{15}}{\partial c_2} + \frac{\partial X_{16}}{\partial c_2} + 2\,\frac{\partial X_{17}}{\partial c_2} - \frac{\partial X_{31}}{\partial c_2}\right]$$

$$\beta_{11,3} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_3} - \frac{\partial X_{11}}{\partial c_3} + \frac{\partial X_{13}}{\partial c_3} + \frac{\partial X_{19}}{\partial c_3}\right]$$

$$\beta_{11,4} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_4} - \frac{\partial X_{11}}{\partial c_4}\right]$$

$$\beta_{11,5} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_5} - \frac{\partial X_{11}}{\partial c_5}\right]$$

$$\beta_{11,6} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_6} - \frac{\partial X_{11}}{\partial c_6} + \frac{\partial X_{15}}{\partial c_6} + \frac{\partial X_{25}}{\partial c_6}\right]$$

$$\beta_{11,7} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_7} - \frac{\partial X_{11}}{\partial c_7} + \frac{\partial X_{30}}{\partial c_7} - \frac{\partial X_{31}}{\partial c_7}\right]$$

$$\beta_{11,8} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_8} - \frac{\partial X_{11}}{\partial c_8} + \frac{\partial X_{16}}{\partial c_8} + \frac{\partial X_{33}}{\partial c_8} + 2\,\frac{\partial X_{34}}{\partial c_8}\right]$$

$$\beta_{11,9} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial c_9} - \frac{\partial X_{11}}{\partial c_9}\right]$$

$$\beta_{11,10} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{10}} - \frac{\partial X_{11}}{\partial c_{10}} + \frac{\partial X_{37}}{\partial c_{10}}\right]$$

$$\beta_{11,11} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{11}} - \frac{\partial X_{11}}{\partial c_{11}} + \frac{\partial X_{13}}{\partial c_{11}} + \frac{\partial X_{15}}{\partial c_{11}} + \frac{\partial X_{16}}{\partial c_{11}} + 2\,\frac{\partial X_{17}}{\partial c_{11}} + \frac{\partial X_{19}}{\partial c_{11}}\right.$$

$$\left.\frac{\partial X_{25}}{\partial c_{11}} + \frac{\partial X_{30}}{\partial c_{11}} - \frac{\partial X_{31}}{\partial c_{11}} + \frac{\partial X_{33}}{\partial c_{11}} + 2\,\frac{\partial X_{34}}{\partial c_{11}} + \frac{\partial X_{37}}{\partial c_{11}} + \frac{\partial X_{39}}{\partial c_{11}}\right]$$

$$\beta_{11,12} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{12}} - \frac{\partial X_{11}}{\partial c_{12}} + 2\,\frac{\partial X_{34}}{\partial c_{12}} + \frac{\partial X_{39}}{\partial c_{12}}\right]$$

$$\beta_{11,13} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{13}} - \frac{\partial X_{11}}{\partial c_{13}} + \frac{\partial X_{19}}{\partial c_{13}}\right]$$

$$\beta_{11,14} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{14}} - \frac{\partial X_{11}}{\partial c_{14}} + \frac{\partial X_{15}}{\partial c_{14}} + \frac{\partial X_{25}}{\partial c_{14}}\right]$$

$$\beta_{11,15} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{15}} - \frac{\partial X_{11}}{\partial c_{15}} + \frac{\partial X_{30}}{\partial c_{15}} - \frac{\partial X_{31}}{\partial c_{15}}\right]$$

$$\beta_{11,16} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{16}} - \frac{\partial X_{11}}{\partial c_{16}} + \frac{\partial X_{13}}{\partial c_{16}} + \frac{\partial X_{16}}{\partial c_{16}} + \frac{\partial X_{19}}{\partial c_{16}} + \frac{\partial X_{33}}{\partial c_{16}} + \frac{\partial X_{37}}{\partial c_{16}} + \frac{\partial X}{\partial c}\right.$$

$$\beta_{11,17} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{17}} - \frac{\partial X_{11}}{\partial c_{17}} + \frac{\partial X_{37}}{\partial c_{17}}\right]$$

$$\beta_{11,18} = \bar{K}_{11}\left[\frac{\partial X_2}{\partial c_{18}} - \frac{\partial X_{11}}{\partial c_{18}} + 2\,\frac{\partial X_{17}}{\partial c_{18}} + \frac{\partial X_{25}}{\partial c_{18}} + \frac{\partial X_{30}}{\partial c_{18}} + \frac{\partial X_{33}}{\partial c_{18}} + \frac{\partial X_{39}}{\partial c_{18}}\right]$$

$$\beta_{11,19} = -\frac{1}{V} f_{11}$$

$$\beta_{11,20} = \frac{1}{\rho} f_{11} + \bar{K}_{11}\left[\frac{\partial X_2}{\partial \rho} - \frac{\partial X_{11}}{\partial \rho}\right]$$

$$\beta_{11,21} = \overline{K}_{11}\left[\frac{\partial X_2}{\partial T} - \frac{\partial X_{11}}{\partial T} + \frac{\partial X_{13}}{\partial T} + \frac{\partial X_{15}}{\partial T} + \frac{\partial X_{16}}{\partial T} + 2\frac{\partial X_{17}}{\partial T} + \frac{\partial X_{19}}{\partial T}\right.$$

$$\left.\frac{\partial X_{25}}{\partial T} + \frac{\partial X_{30}}{\partial T} - \frac{\partial X_{31}}{\partial T} + \frac{\partial X_{33}}{\partial T} + 2\frac{\partial X_{34}}{\partial T} + \frac{\partial X_{37}}{\partial T} + \frac{\partial X_{39}}{\partial T}\right]$$

For O_2,

$$\overline{K}_{12} = \frac{32.000}{V}\rho r^*$$

$$f_{12} = -\overline{K}_{12}\left[X_{12} - X_{14} - X_{22} + X_{34} + X_{36} - X_{38} + X_{39}\right]$$

$$\beta_{12,1} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_1} - \frac{\partial X_{14}}{\partial c_1}\right]$$

$$\beta_{12,2} = -\overline{K}_{12}\frac{\partial X_{12}}{\partial c_2}$$

$$\beta_{12,3} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_3} - \frac{\partial X_{14}}{\partial c_3} - \frac{\partial X_{22}}{\partial c_3}\right]$$

$$\beta_{12,4} = -\overline{K}_{12}\frac{\partial X_{12}}{\partial c_4}$$

$$\beta_{12,5} = -\overline{K}_{12}\frac{\partial X_{12}}{\partial c_5}$$

$$\beta_{12,6} = -\overline{K}_{12}\frac{\partial X_{12}}{\partial c_6}$$

$$\beta_{12,7} = -\overline{K}_{12}\frac{\partial X_{12}}{\partial c_7}$$

$$\beta_{12,8} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_8} + \frac{\partial X_{34}}{\partial c_8}\right]$$

$$\beta_{12,9} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_9} + \frac{\partial X_{36}}{\partial c_9}\right]$$

$$\beta_{12,10} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{10}} + \frac{\partial X_{36}}{\partial c_{10}} - \frac{\partial X_{38}}{\partial c_{10}}\right]$$

$$\beta_{12,11} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{11}} + \frac{\partial X_{34}}{\partial c_{11}} + \frac{\partial X_{39}}{\partial c_{11}}\right]$$

$$\beta_{12,12} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{12}} - \frac{\partial X_{14}}{\partial c_{12}} - \frac{\partial X_{22}}{\partial c_{12}} + \frac{\partial X_{34}}{\partial c_{12}} + \frac{\partial X_{36}}{\partial c_1} - \frac{\partial X_{38}}{\partial c_1} + \frac{\partial X_{39}}{\partial c_1}\right]$$

$$\beta_{12,13} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{13}} - \frac{\partial X_{22}}{\partial c_{13}}\right]$$

$$\beta_{12,14} = -\overline{K}_{12}\,\frac{\partial X_{12}}{\partial c_{14}}$$

$$\beta_{12,15} = -\overline{K}_{12}\,\frac{\partial X_{12}}{\partial c_{15}}$$

$$\beta_{12,16} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{16}} + \frac{\partial X_{39}}{\partial c_{16}}\right]$$

$$\beta_{12,17} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{17}} - \frac{\partial X_{38}}{\partial c_{17}}\right]$$

$$\beta_{12,18} = -\overline{K}_{12}\left[\frac{\partial X_{12}}{\partial c_{18}} - \frac{\partial X_{14}}{\partial c_{18}} - \frac{\partial X_{22}}{\partial c_{18}} - \frac{\partial X_{38}}{\partial c_{18}} + \frac{\partial X_{39}}{\partial c_{18}}\right]$$

$$\beta_{12,19} = -\frac{1}{V}\,f_{12}$$

$$\beta_{12,20} = \frac{1}{\rho}\,f_{12} - \overline{K}_{12}\,\frac{\partial X_{12}}{\partial \rho}$$

$$\beta_{12,21} = -K_{12}\left[\frac{\partial X_{12}}{\partial T} - \frac{\partial X_{14}}{\partial T} - \frac{\partial X_{22}}{\partial T} + \frac{\partial X_{34}}{\partial T} + \frac{\partial X_{36}}{\partial T} - \frac{\partial X_{38}}{\partial T} + \frac{\partial X_{39}}{\partial T}\right]$$

For C,

$$\overline{K}_{13} = \frac{12.011}{V}\rho r^*$$

$$f_{13} = \overline{K}_{13}\left[X_3 + X_{18} + X_{19} + X_{20} + X_{22}\right]$$

$$\beta_{13,1} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_1} + \frac{\partial X_{18}}{\partial c_1}\right]$$

$$\beta_{13,2} = \overline{K}_{13}\frac{\partial X_3}{\partial c_2}$$

$$\beta_{13,3} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_3} + \frac{\partial X_{18}}{\partial c_3} + \frac{\partial X_{19}}{\partial c_3} + \frac{\partial X_{20}}{\partial c_3} + \frac{\partial X_{22}}{\partial c_3}\right]$$

$$\beta_{13,4} = \overline{K}_{13}\frac{\partial X_3}{\partial c_4}$$

$$\beta_{13,5} = \overline{K}_{13}\frac{\partial X_3}{\partial c_5}$$

$$\beta_{13,6} = \overline{K}_{13}\frac{\partial X_3}{\partial c_6}$$

$$\beta_{13,7} = \overline{K}_{13}\frac{\partial X_3}{\partial c_7}$$

$$\beta_{13,8} = \overline{K}_{13}\frac{\partial X_3}{\partial c_8}$$

$$\beta_{13,9} = \overline{K}_{13}\frac{\partial X_3}{\partial c_9}$$

$$\beta_{13,10} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{10}} + \frac{\partial X_{20}}{\partial c_{10}}\right]$$

$$\beta_{13,11} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{11}} + \frac{\partial X_{19}}{\partial c_{11}}\right]$$

$$\beta_{13,12} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{12}} + \frac{\partial X_{22}}{\partial c_{12}}\right]$$

$$\beta_{13,13} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{13}} + \frac{\partial X_{18}}{\partial c_{13}} + \frac{\partial X_{19}}{\partial c_{13}} + \frac{\partial X_{20}}{\partial c_{13}} + \frac{\partial X_{22}}{\partial c_{13}}\right]$$

$$\beta_{13,14} = \overline{K}_{13}\ \frac{\partial X_3}{\partial c_{14}}$$

$$\beta_{13,15} = \overline{K}_{13}\ \frac{\partial X_3}{\partial c_{15}}$$

$$\beta_{13,16} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{16}} + \frac{\partial X_{19}}{\partial c_{16}}\right]$$

$$\beta_{13,17} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{17}} + \frac{\partial X_{20}}{\partial c_{17}}\right]$$

$$\beta_{13,18} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial c_{18}} + \frac{\partial X_{22}}{\partial c_{18}}\right]$$

$$\beta_{13,19} = -\frac{1}{V} f_{13}$$

$$\beta_{13,20} = \frac{1}{\rho} f_{13} + \overline{K}_{13}\ \frac{\partial X_3}{\partial \rho}$$

$$\beta_{13,21} = \overline{K}_{13}\left[\frac{\partial X_3}{\partial T} + \frac{\partial X_{18}}{\partial T} + \frac{\partial X_{19}}{\partial T} + \frac{\partial X_{20}}{\partial T} + \frac{\partial X_{22}}{\partial T}\right]$$

For Cl,

$$\overline{K}_{14} = \frac{35.457}{V} \rho r^*$$

$$f_{14} = \overline{K}_{14}\left[2X_4 + X_6 - X_{15} - X_{23} + X_{25} - X_{26} - X_{32}\right]$$

$$\beta_{14,1} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_1} + \frac{\partial X_6}{\partial c_1}\right]$$

$$\beta_{14,2} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_2} + \frac{\partial X_6}{\partial c_2} - \frac{\partial X_{15}}{\partial c_2}\right]$$

$$\beta_{14,3} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_3} + \frac{\partial X_6}{\partial c_3}\right]$$

$$\beta_{14,4} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_4} + \frac{\partial X_6}{\partial c_4} - \frac{\partial X_{23}}{\partial c_4}\right]$$

$$\beta_{14,5} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_5} + \frac{\partial X_6}{\partial c_5}\right]$$

$$\beta_{14,6} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_6} + \frac{\partial X_6}{\partial c_6} - \frac{\partial X_{15}}{\partial c_6} - \frac{\partial X_{23}}{\partial c_6} + \frac{\partial X_{25}}{\partial c_6} - \frac{\partial X_{26}}{\partial c_6} - \frac{\partial X_{32}}{\partial c_6}\right]$$

$$\beta_{14,7} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_7} + \frac{\partial X_6}{\partial c_7} - \frac{\partial X_{26}}{\partial c_7}\right]$$

$$\beta_{14,8} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_8} + \frac{\partial X_6}{\partial c_8} - \frac{\partial X_{32}}{\partial c_8}\right]$$

$$\beta_{14,9} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_9} + \frac{\partial X_6}{\partial c_9}\right]$$

$$\beta_{14,10} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{10}} + \frac{\partial X_6}{\partial c_{10}}\right]$$

$$\beta_{14,11} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{11}} + \frac{\partial X_6}{\partial c_{11}} - \frac{\partial X_{15}}{\partial c_{11}} + \frac{\partial X_{25}}{\partial c_{11}}\right]$$

$$\beta_{14,12} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{12}} + \frac{\partial X_6}{\partial c_{12}}\right]$$

$$\beta_{14,13} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{13}} + \frac{\partial X_6}{\partial c_{13}}\right]$$

$$\beta_{14,14} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{14}} + \frac{\partial X_6}{\partial c_{14}} - \frac{\partial X_{15}}{\partial c_{14}} - \frac{\partial X_{23}}{\partial c_{14}} + \frac{\partial X_{25}}{\partial c_{14}} - \frac{\partial X_{26}}{\partial c_{14}} - \frac{\partial X_{32}}{\partial c_{14}}\right]$$

$$\beta_{14,15} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{15}} + \frac{\partial X_6}{\partial c_{15}} - \frac{\partial X_{26}}{\partial c_{15}}\right]$$

$$\beta_{14,16} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{16}} + \frac{\partial X_6}{\partial c_{16}} - \frac{\partial X_{23}}{\partial c_{16}} - \frac{\partial X_{32}}{\partial c_{16}}\right]$$

$$\beta_{14,17} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{17}} + \frac{\partial X_6}{\partial c_{17}}\right]$$

$$\beta_{14,18} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial c_{18}} + \frac{\partial X_6}{\partial c_{18}} + \frac{\partial X_{25}}{\partial c_{18}}\right]$$

$$\beta_{14,19} = -\frac{1}{V} f_{14}$$

$$\beta_{14,20} = \frac{1}{\rho} f_{14} + \overline{K}_{14}\left[2\frac{\partial X_4}{\partial \rho} + \frac{\partial X_6}{\partial \rho}\right]$$

$$\beta_{14,21} = \overline{K}_{14}\left[2\frac{\partial X_4}{\partial T} + \frac{\partial X_6}{\partial T} - \frac{\partial X_{15}}{\partial T} - \frac{\partial X_{23}}{\partial T} + \frac{\partial X_{25}}{\partial T} - \frac{\partial X_{26}}{\partial T} - \frac{\partial X_{32}}{\partial T}\right]$$

For F,

$$\overline{K}_{15} = \frac{19.000}{V} \rho r^*$$

$$f_{15} = \overline{K}_{15} \left[2X_5 + X_7 + X_{26} - X_{27} + X_{28} + X_{30} + X_{31} \right]$$

$$\beta_{15,1} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_1} + \frac{\partial X_7}{\partial c_1} \right]$$

$$\beta_{15,2} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_2} + \frac{\partial X_7}{\partial c_2} + \frac{\partial X_{31}}{\partial c_2} \right]$$

$$\beta_{15,3} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_3} + \frac{\partial X_7}{\partial c_3} \right]$$

$$\beta_{15,4} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_4} + \frac{\partial X_7}{\partial c_4} \right]$$

$$\beta_{15,5} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_5} + \frac{\partial X_7}{\partial c_5} - \frac{\partial X_{27}}{\partial c_5} \right]$$

$$\beta_{15,6} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_6} + \frac{\partial X_7}{\partial c_6} + \frac{\partial X_{26}}{\partial c_6} \right]$$

$$\beta_{15,7} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_7} + \frac{\partial X_7}{\partial c_7} + \frac{\partial X_{26}}{\partial c_7} - \frac{\partial X_{27}}{\partial c_7} + \frac{\partial X_{28}}{\partial c_7} + \frac{\partial X_{30}}{\partial c_7} + \frac{\partial X_{31}}{\partial c_7} \right]$$

$$\beta_{15,8} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_8} + \frac{\partial X_7}{\partial c_8} + \frac{\partial X_{28}}{\partial c_8} \right]$$

$$\beta_{15,9} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_9} + \frac{\partial X_7}{\partial c_9} \right]$$

$$\beta_{15,10} = \overline{K}_{15} \left[2 \frac{\partial X_5}{\partial c_{10}} + \frac{\partial X_7}{\partial c_{10}} \right]$$

$$\beta_{15,11} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{11}} + \frac{\partial X_7}{\partial c_{11}} + \frac{\partial X_{30}}{\partial c_{11}} + \frac{\partial X_{31}}{\partial c_{11}}\right]$$

$$\beta_{15,12} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{12}} + \frac{\partial X_7}{\partial c_{12}}\right]$$

$$\beta_{15,13} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{13}} + \frac{\partial X_7}{\partial c_{13}}\right]$$

$$\beta_{15,14} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{14}} + \frac{\partial X_7}{\partial c_{14}} + \frac{\partial X_{26}}{\partial c_{14}}\right]$$

$$\beta_{15,15} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{15}} + \frac{\partial X_7}{\partial c_{15}} + \frac{\partial X_{26}}{\partial c_{15}} - \frac{\partial X_{27}}{\partial c_{15}} + \frac{\partial X_{28}}{\partial c_{15}} + \frac{\partial X_{30}}{\partial c_{15}} + \frac{\partial X_{31}}{\partial c_{15}}\right]$$

$$\beta_{15,16} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{16}} + \frac{\partial X_7}{\partial c_{16}} - \frac{\partial X_{27}}{\partial c_{16}} + \frac{\partial X_{28}}{\partial c_{16}}\right]$$

$$\beta_{15,17} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{17}} + \frac{\partial X_7}{\partial c_{17}}\right]$$

$$\beta_{15,18} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial c_{18}} + \frac{\partial X_7}{\partial c_{18}} + \frac{\partial X_{30}}{\partial c_{18}}\right]$$

$$\beta_{15,19} = -\frac{1}{V} f_{15}$$

$$\beta_{15,20} = \frac{1}{\rho} f_{15} + \overline{K}_{15}\left[2\frac{\partial X_5}{\partial \rho} + \frac{\partial X_7}{\partial \rho}\right]$$

$$\beta_{15,21} = \overline{K}_{15}\left[2\frac{\partial X_5}{\partial T} + \frac{\partial X_7}{\partial T} + \frac{\partial X_{26}}{\partial T} - \frac{\partial X_{27}}{\partial T} + \frac{\partial X_{28}}{\partial T} + \frac{\partial X_{30}}{\partial T} + \frac{\partial X_{31}}{\partial T}\right]$$

For H,

$$\overline{K}_{16} = \frac{1.008}{V} \rho r^*$$

$$f_{16} = \overline{K}_{16}\Big[X_2 + X_6 + X_7 + 2X_8 + X_{11} - X_{13} - X_{16} - X_{19} + X_{23} + X_{27} - X_{28} + X_{32} + X_{33} - X_{37} - X_{39}\Big]$$

$$\beta_{16,1} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_1} + \frac{\partial X_6}{\partial c_1} + \frac{\partial X_7}{\partial c_1} + 2\frac{\partial X_8}{\partial c_1} + \frac{\partial X_{11}}{\partial c_1} - \frac{\partial X_{13}}{\partial c_1}\right]$$

$$\beta_{16,2} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_2} + \frac{\partial X_6}{\partial c_2} + \frac{\partial X_7}{\partial c_2} + 2\frac{\partial X_8}{\partial c_2} + \frac{\partial X_{11}}{\partial c_2} - \frac{\partial X_{16}}{\partial c_2}\right]$$

$$\beta_{16,3} = K_{16}\left[\frac{\partial X_2}{\partial c_3} + \frac{\partial X_6}{\partial c_3} + \frac{\partial X_7}{\partial c_3} + 2\frac{\partial X_8}{\partial c_3} + \frac{\partial X_{11}}{\partial c_3} - \frac{\partial X_{13}}{\partial c_3} - \frac{\partial X_{19}}{\partial c_3}\right]$$

$$\beta_{16,4} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_4} + \frac{\partial X_6}{\partial c_4} + \frac{\partial X_7}{\partial c_4} + 2\frac{\partial X_8}{\partial c_4} + \frac{\partial X_{11}}{\partial c_4} + \frac{\partial X_{23}}{\partial c_4}\right]$$

$$\beta_{16,5} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_5} + \frac{\partial X_6}{\partial c_5} + \frac{\partial X_7}{\partial c_5} + 2\frac{\partial X_8}{\partial c_5} + \frac{\partial X_{11}}{\partial c_5} + \frac{\partial X_{23}}{\partial c_5}\right]$$

$$\beta_{16,6} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_6} + \frac{\partial X_6}{\partial c_6} + \frac{\partial X_7}{\partial c_6} + 2\frac{\partial X_8}{\partial c_6} + \frac{\partial X_{11}}{\partial c_6} + \frac{\partial X_{23}}{\partial c_6} + \frac{\partial X_{32}}{\partial c_6}\right]$$

$$\beta_{16,7} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_7} + \frac{\partial X_6}{\partial c_7} + \frac{\partial X_7}{\partial c_7} + 2\frac{\partial X_8}{\partial c_7} + \frac{\partial X_{11}}{\partial c_7} + \frac{\partial X_{27}}{\partial c_7} - \frac{\partial X_{28}}{\partial c_7}\right]$$

$$\beta_{16,8} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_8} + \frac{\partial X_6}{\partial c_8} + \frac{\partial X_7}{\partial c_8} + 2\frac{\partial X_8}{\partial c_8} + \frac{\partial X_{11}}{\partial c_8} - \frac{\partial X_{16}}{\partial c_8} - \frac{\partial X_{28}}{\partial c_8} + \frac{\partial X_{32}}{\partial c_8} + \frac{\partial X_{33}}{\partial c_8}\right]$$

$$\beta_{16,9} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_9} + \frac{\partial X_6}{\partial c_9} + \frac{\partial X_7}{\partial c_9} + 2\,\frac{\partial X_8}{\partial c_9} + \frac{\partial X_{11}}{\partial c_9}\right]$$

$$\beta_{16,10} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{10}} + \frac{\partial X_6}{\partial c_{10}} + \frac{\partial X_7}{\partial c_{10}} + 2\,\frac{\partial X_8}{\partial c_{10}} + \frac{\partial X_{11}}{\partial c_{10}} - \frac{\partial X_{39}}{\partial c_{10}}\right]$$

$$\beta_{16,11} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{11}} + \frac{\partial X_6}{\partial c_{11}} + \frac{\partial X_7}{\partial c_{11}} + 2\,\frac{\partial X_8}{\partial c_{11}} + \frac{\partial X_{11}}{\partial c_{11}} - \frac{\partial X_{13}}{\partial c_{11}} - \frac{\partial X_{16}}{\partial c_{11}}\right.$$

$$\left. - \frac{\partial X_{19}}{\partial c_{11}} + \frac{\partial X_{33}}{\partial c_{11}} - \frac{\partial X_{37}}{\partial c_{11}} - \frac{\partial X_{39}}{\partial c_{11}}\right]$$

$$\beta_{16,12} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{12}} + \frac{\partial X_6}{\partial c_{12}} + \frac{\partial X_7}{\partial c_{12}} + 2\,\frac{\partial X_8}{\partial c_{12}} + \frac{\partial X_{11}}{\partial c_{12}} - \frac{\partial X_{39}}{\partial c_{12}}\right]$$

$$\beta_{16,13} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{13}} + \frac{\partial X_6}{\partial c_{13}} + \frac{\partial X_7}{\partial c_{13}} + 2\,\frac{\partial X_8}{\partial c_{13}} + \frac{\partial X_{11}}{\partial c_{13}} - \frac{\partial X_{19}}{\partial c_{13}}\right]$$

$$\beta_{16,14} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{14}} + \frac{\partial X_6}{\partial c_{14}} + \frac{\partial X_7}{\partial c_{14}} + 2\,\frac{\partial X_8}{\partial c_{14}} + \frac{\partial X_{11}}{\partial c_{14}} + \frac{\partial X_{23}}{\partial c_{14}} + \frac{\partial X_{32}}{\partial c_{14}}\right]$$

$$\beta_{16,15} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{15}} + \frac{\partial X_6}{\partial c_{15}} + \frac{\partial X_7}{\partial c_{15}} + 2\,\frac{\partial X_8}{\partial c_{15}} + \frac{\partial X_{11}}{\partial c_{15}} + \frac{\partial X_{27}}{\partial c_{15}} - \frac{\partial X_{28}}{\partial c_{15}}\right]$$

$$\beta_{16,16} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{16}} + \frac{\partial X_6}{\partial c_{16}} + \frac{\partial X_7}{\partial c_{16}} + 2\,\frac{\partial X_8}{\partial c_{16}} + \frac{\partial X_{11}}{\partial c_{16}} - \frac{\partial X_{13}}{\partial c_{16}} - \frac{\partial X_{16}}{\partial c_{16}} - \frac{\partial X_{19}}{\partial c_{16}}\right.$$

$$\left. + \frac{\partial X_{23}}{\partial c_{16}} + \frac{\partial X_{27}}{\partial c_{16}} - \frac{\partial X_{28}}{\partial c_{16}} + \frac{\partial X_{32}}{\partial c_{16}} + \frac{\partial X_{33}}{\partial c_{16}} - \frac{\partial X_{37}}{\partial c_{16}} - \frac{\partial X_{39}}{\partial c_{16}}\right]$$

$$\beta_{16,17} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{17}} + \frac{\partial X_6}{\partial c_{17}} + \frac{\partial X_7}{\partial c_{17}} + 2\,\frac{\partial X_8}{\partial c_{17}} + \frac{\partial X_{11}}{\partial c_{17}} - \frac{\partial X_{37}}{\partial c_{17}}\right]$$

$$\beta_{16,18} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial c_{18}} + \frac{\partial X_6}{\partial c_{18}} + \frac{\partial X_7}{\partial c_{18}} + 2\,\frac{\partial X_8}{\partial c_{18}} + \frac{\partial X_{11}}{\partial c_{18}} + \frac{\partial X_{33}}{\partial c_{18}} - \frac{\partial X_{39}}{\partial c_{18}}\right]$$

$$\beta_{16,19} = -\frac{1}{V} f_{16}$$

$$\beta_{16,20} = \frac{1}{\rho} f_{16} + \overline{K}_{16}\left[\frac{\partial X_2}{\partial \rho} + \frac{\partial X_6}{\partial \rho} + \frac{\partial X_7}{\partial \rho} + 2\frac{\partial X_8}{\partial \rho} + \frac{\partial X_{11}}{\partial \rho}\right]$$

$$\beta_{16,21} = \overline{K}_{16}\left[\frac{\partial X_2}{\partial T} + \frac{\partial X_6}{\partial T} + \frac{\partial X_7}{\partial T} + 2\frac{\partial X_8}{\partial T} + \frac{\partial X_{11}}{\partial T} - \frac{\partial X_{13}}{\partial T} - \frac{\partial X_{16}}{\partial T} - \frac{\partial X_{19}}{\partial T}\right.$$
$$\left. + \frac{\partial X_{23}}{\partial T} + \frac{\partial X_{27}}{\partial T} - \frac{\partial X_{28}}{\partial T} + \frac{\partial X_{32}}{\partial T} + \frac{\partial X_{33}}{\partial T} - \frac{\partial X_{37}}{\partial T} - \frac{\partial X_{39}}{\partial T}\right]$$

For N,

$$\overline{K}_{17} = \frac{14.008}{V} \rho r^*$$

$$f_{17} = \overline{K}_{17}\left[2X_9 + X_{10} - X_{20} + X_{21} + X_{35} + X_{37} + X_{38}\right]$$

$$\beta_{17,1} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_1} + \frac{\partial X_{10}}{\partial c_1} + \frac{\partial X_{21}}{\partial c_1}\right]$$

$$\beta_{17,2} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_2} + \frac{\partial X_{10}}{\partial c_2}\right]$$

$$\beta_{17,3} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_3} + \frac{\partial X_{10}}{\partial c_3} - \frac{\partial X_{20}}{\partial c_3} + \frac{\partial X_{21}}{\partial c_3}\right]$$

$$\beta_{17,4} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_4} + \frac{\partial X_{10}}{\partial c_4}\right]$$

$$\beta_{17,5} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_5} + \frac{\partial X_{10}}{\partial c_5}\right]$$

$$\beta_{17,6} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_6} + \frac{\partial X_{10}}{\partial c_6}\right]$$

$$\beta_{17,7} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_7} + \frac{\partial X_{10}}{\partial c_7}\right]$$

$$\beta_{17,8} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_8} + \frac{\partial X_{10}}{\partial c_8}\right]$$

$$\beta_{17,9} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_9} + \frac{\partial X_{10}}{\partial c_9} + \frac{\partial X_{35}}{\partial c_9}\right]$$

$$\beta_{17,10} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{10}} + \frac{\partial X_{10}}{\partial c_{10}} - \frac{\partial X_{20}}{\partial c_{10}} + \frac{\partial X_{21}}{\partial c_{10}} + \frac{\partial X_{35}}{\partial c_{10}} + \frac{\partial X_{37}}{\partial c_{10}} + \frac{\partial X_{38}}{\partial c_{10}}\right]$$

$$\beta_{17,11} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{11}} + \frac{\partial X_{10}}{\partial c_{11}} + \frac{\partial X_{37}}{\partial c_{11}}\right]$$

$$\beta_{17,12} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{12}} + \frac{\partial X_{10}}{\partial c_{12}} + \frac{\partial X_{38}}{\partial c_{12}}\right]$$

$$\beta_{17,13} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{13}} + \frac{\partial X_{10}}{\partial c_{13}} - \frac{\partial X_{20}}{\partial c_{13}}\right]$$

$$\beta_{17,14} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{14}} + \frac{\partial X_{10}}{\partial c_{14}}\right]$$

$$\beta_{17,15} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{14}} + \frac{\partial X_{10}}{\partial c_{14}}\right]$$

$$\beta_{17,16} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{16}} + \frac{\partial X_{10}}{\partial c_{16}} + \frac{\partial X_{37}}{\partial c_{16}}\right]$$

$$\beta_{17,17} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{17}} + \frac{\partial X_{10}}{\partial c_{17}} - \frac{\partial X_{20}}{\partial c_{17}} + \frac{\partial X_{21}}{\partial c_{17}} + \frac{\partial X_{35}}{\partial c_{17}} + \frac{\partial X_{37}}{\partial c_{17}} + \frac{\partial X_{38}}{\partial c_{17}}\right]$$

$$\beta_{17,18} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial c_{18}} + \frac{\partial X_{10}}{\partial c_{18}} + \frac{\partial X_{35}}{\partial c_{18}} + \frac{\partial X_{38}}{\partial c_{18}}\right]$$

$$\beta_{17,19} = -\frac{1}{V} f_{17}$$

$$\beta_{17,20} = \frac{1}{\rho} f_{17} + \overline{K}_{17}\left[2\frac{\partial X_9}{\partial \rho} + \frac{\partial X_{10}}{\partial \rho}\right]$$

$$\beta_{17,21} = \overline{K}_{17}\left[2\frac{\partial X_9}{\partial T} + \frac{\partial X_{10}}{\partial T} - \frac{\partial X_{20}}{\partial T} + \frac{\partial X_{21}}{\partial T} + \frac{\partial X_{35}}{\partial T} + \frac{\partial X_{37}}{\partial T} + \frac{\partial X_{38}}{\partial T}\right]$$

For O,

$$\overline{K}_{18} = \frac{16.000}{V} \rho r^*$$

$$f_{18} = \overline{K}_{18}\left[X_1 + X_3 + X_{10} + X_{11} + 2X_{12} - X_{14} - X_{17} - X_{22} - X_{25} - X_{30} - X_{33} - X_{35} - X_{38} + X_{39}\right]$$

$$\beta_{18,1} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_1} + \frac{\partial X_3}{\partial c_1} + \frac{\partial X_{10}}{\partial c_1} + \frac{\partial X_{11}}{\partial c_1} + 2\frac{\partial X_{12}}{\partial c_1} - \frac{\partial X_{14}}{\partial c_1}\right]$$

$$\beta_{18,2} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_2} + \frac{\partial X_3}{\partial c_2} + \frac{\partial X_{10}}{\partial c_2} + \frac{\partial X_{11}}{\partial c_2} + 2\frac{\partial X_{12}}{\partial c_2} - \frac{\partial X_{17}}{\partial c_2}\right]$$

$$\beta_{18,3} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_3} + \frac{\partial X_3}{\partial c_3} + \frac{\partial X_{10}}{\partial c_3} + \frac{\partial X_{11}}{\partial c_3} + 2\frac{\partial X_{12}}{\partial c_3} - \frac{\partial X_{14}}{\partial c_3} - \frac{\partial X_{22}}{\partial c_3}\right]$$

$$\beta_{18,4} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_4} + \frac{\partial X_3}{\partial c_4} + \frac{\partial X_{10}}{\partial c_4} + \frac{\partial X_{11}}{\partial c_4} + 2\frac{\partial X_{12}}{\partial c_4}\right]$$

$$\beta_{18,5} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_5} + \frac{\partial X_3}{\partial c_5} + \frac{\partial X_{10}}{\partial c_5} + \frac{\partial X_{11}}{\partial c_5} + 2\frac{\partial X_{12}}{\partial c_5}\right]$$

$$\beta_{18,6} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_6} + \frac{\partial X_3}{\partial c_6} + \frac{\partial X_{10}}{\partial c_6} + \frac{\partial X_{11}}{\partial c_6} + 2\frac{\partial X_{12}}{\partial c_6} - \frac{\partial X_{25}}{\partial c_6}\right]$$

$$\beta_{18,7} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_7} + \frac{\partial X_3}{\partial c_7} + \frac{\partial X_{10}}{\partial c_7} + \frac{\partial X_{11}}{\partial c_7} + 2\frac{\partial X_{12}}{\partial c_7} - \frac{\partial X_{30}}{\partial c_7}\right]$$

$$\beta_{18,8} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_8} + \frac{\partial X_3}{\partial c_8} + \frac{\partial X_{10}}{\partial c_8} + \frac{\partial X_{11}}{\partial c_8} + 2\,\frac{\partial X_{12}}{\partial c_8} - \frac{\partial X_{35}}{\partial c_8}\right]$$

$$\beta_{18,9} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_9} + \frac{\partial X_3}{\partial c_9} + \frac{\partial X_{10}}{\partial c_9} + \frac{\partial X_{11}}{\partial c_9} + 2\,\frac{\partial X_{12}}{\partial c_9} - \frac{\partial X_{35}}{\partial c_9}\right]$$

$$\beta_{18,10} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{10}} + \frac{\partial X_3}{\partial c_{10}} + \frac{\partial X_{10}}{\partial c_{10}} + \frac{\partial X_{11}}{\partial c_{10}} + 2\,\frac{\partial X_{12}}{\partial c_{10}} - \frac{\partial X_{35}}{\partial c_{10}} - \frac{\partial X_{38}}{\partial c_{10}}\right]$$

$$\beta_{18,11} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{11}} + \frac{\partial X_3}{\partial c_{11}} + \frac{\partial X_{10}}{\partial c_{11}} + \frac{\partial X_{11}}{\partial c_{11}} + 2\,\frac{\partial X_{12}}{\partial c_{11}} - \frac{\partial X_{17}}{\partial c_{11}} - \frac{\partial X_{25}}{\partial c_{11}} - \frac{\partial X_{30}}{\partial c_{11}} - \frac{\partial X_{33}}{\partial c_{11}} + \frac{\partial X_{39}}{\partial c_{11}}\right]$$

$$\beta_{18,12} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{12}} + \frac{\partial X_3}{\partial c_{12}} + \frac{\partial X_{10}}{\partial c_{12}} + \frac{\partial X_{11}}{\partial c_{12}} + 2\,\frac{\partial X_{12}}{\partial c_{12}} - \frac{\partial X_{14}}{\partial c_{12}} - \frac{\partial X_{22}}{\partial c_{12}} - \frac{\partial X_{38}}{\partial c_{12}} + \frac{\partial X_{39}}{\partial c_{12}}\right]$$

$$\beta_{18,13} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{13}} + \frac{\partial X_3}{\partial c_{13}} + \frac{\partial X_{10}}{\partial c_{13}} + \frac{\partial X_{11}}{\partial c_{13}} + 2\,\frac{\partial X_{12}}{\partial c_{13}} - \frac{\partial X_{22}}{\partial c_{13}}\right]$$

$$\beta_{18,14} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{14}} + \frac{\partial X_3}{\partial c_{14}} + \frac{\partial X_{10}}{\partial c_{14}} + \frac{\partial X_{11}}{\partial c_{14}} + 2\,\frac{\partial X_{12}}{\partial c_{14}} - \frac{\partial X_{25}}{\partial c_{14}}\right]$$

$$\beta_{18,15} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{15}} + \frac{\partial X_3}{\partial c_{15}} + \frac{\partial X_{10}}{\partial c_{15}} + \frac{\partial X_{11}}{\partial c_{15}} + 2\,\frac{\partial X_{12}}{\partial c_{15}} - \frac{\partial X_{30}}{\partial c_{15}}\right]$$

$$\beta_{18,16} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{16}} + \frac{\partial X_3}{\partial c_{16}} + \frac{\partial X_{10}}{\partial c_{16}} + \frac{\partial X_{11}}{\partial c_{16}} + 2\,\frac{\partial X_{12}}{\partial c_{16}} - \frac{\partial X_{33}}{\partial c_{16}} + \frac{\partial X_{39}}{\partial c_{16}}\right]$$

$$\beta_{18,17} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{17}} + \frac{\partial X_3}{\partial c_{17}} + \frac{\partial X_{10}}{\partial c_{17}} + \frac{\partial X_{11}}{\partial c_{17}} + 2\,\frac{\partial X_{12}}{\partial c_{17}} - \frac{\partial X_{35}}{\partial c_{17}} - \frac{\partial X_{38}}{\partial c_{17}}\right]$$

$$\beta_{18,18} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial c_{18}} + \frac{\partial X_3}{\partial c_{18}} + \frac{\partial X_{10}}{\partial c_{18}} + \frac{\partial X_{11}}{\partial c_{18}} + 2\frac{\partial X_{12}}{\partial c_{18}} - \frac{\partial X_{14}}{\partial c_{18}} - \frac{\partial X_{17}}{\partial c_{18}}\right.$$

$$\left. - \frac{\partial X_{22}}{\partial c_{18}} - \frac{\partial X_{25}}{\partial c_{18}} - \frac{\partial X_{30}}{\partial c_{18}} - \frac{\partial X_{33}}{\partial c_{18}} - \frac{\partial X_{35}}{\partial c_{18}} - \frac{\partial X_{38}}{\partial c_{18}} + \frac{\partial X_{39}}{\partial c_{18}}\right]$$

$$\beta_{18,19} = -\frac{1}{V} f_{18}$$

$$\beta_{18,20} = \frac{1}{\rho} f_{18} + \overline{K}_{18}\left[\frac{\partial X_1}{\partial \rho} + \frac{\partial X_3}{\partial \rho} + \frac{\partial X_{10}}{\partial \rho} + \frac{\partial X_{11}}{\partial \rho} + 2\frac{\partial X_{12}}{\partial \rho}\right]$$

$$\beta_{18,21} = \overline{K}_{18}\left[\frac{\partial X_1}{\partial T} + \frac{\partial X_3}{\partial T} + \frac{\partial X_{10}}{\partial T} + \frac{\partial X_{11}}{\partial T} + 2\frac{\partial X_{12}}{\partial T} - \frac{\partial X_{14}}{\partial T} - \frac{\partial X_{17}}{\partial T}\right.$$

$$\left. - \frac{\partial X_{22}}{\partial T} - \frac{\partial X_{25}}{\partial T} - \frac{\partial X_{30}}{\partial T} - \frac{\partial X_{33}}{\partial T} - \frac{\partial X_{35}}{\partial T} - \frac{\partial X_{38}}{\partial T} + \frac{\partial X_{39}}{\partial T}\right]$$

4.2.3 Calculation of the Pressure and Pressure Derivatives

For subsonic flows, the pressure distribution is given by the pressure table and the pressure and pressure derivatives are calculated from

$$P = P(x_n) + \left.\frac{dP}{dx}\right|_{x_n}(x - x_n) + \frac{1}{2}\left.\frac{d^2P}{dx^2}\right|_{x_n}(x - x_n)^2$$

$$\frac{dP}{dx} = \left.\frac{dP}{dx}\right|_{x_n} + \left.\frac{d^2P}{dx^2}\right|_{x_n}(x - x_n)$$

$$\frac{d^2P}{dx^2} = \left.\frac{d^2P}{dx^2}\right|_{x_n}$$

where $(1/2)(x_{n-1} + x_n) \leq x \leq (1/2)(x_n + x_{n+1})$ and the subscript n refers to the nth entry in the pressure and pressure derivative tables.

For supersonic flows, the pressure is determined by integration.

4.2.4 Calculation of the Area and Area Derivatives

For supersonic flow, the area and area derivatives are calculated from

$$a = \left\{ 1 + R^* - \left[R^{*2} - x^2 \right]^{1/2} \right\}^2$$

$$\frac{da}{dx} = \frac{2x}{\left[R^{*2} - x^2 \right]^{1/2}} \left\{ 1 + R^* - \left[R^{*2} - x^2 \right]^{1/2} \right\}$$

$$\frac{d^2a}{dx^2} = \left\{ \frac{2}{\left[R^{*2} - x^2 \right]^{1/2}} + \frac{2x^2}{\left[R^* - x^2 \right]^{3/2}} \right\} \cdot \left\{ 1 + R^* - \left[R^* - x^2 \right]^{1/2} \right\}$$

$$+ \frac{2x^2}{R^{*2} - x^2}$$

when $x \leq x_t$ and

$$a = \left\{ r_1 + \left[x - x_1 \right] \tan \theta_1 \right\}^2$$

$$\frac{da}{dx} = 2 \left\{ r_1 + \left[x - x_1 \right] \tan \theta_1 \right\} \tan \theta_1$$

$$\frac{d^2a}{dx^2} = 2 \tan^2 \theta_1$$

when $x > x_t$

4.2.5 Calculation of M^2 and Its Partial Derivatives

For supersonic flows, M^2 and its partial derivatives are calculated from

$$M^2 = \frac{V^2}{\gamma R t}$$

$$\frac{\partial M^2}{\partial c_j} = -\frac{M^2}{\gamma}\frac{\partial \gamma}{\partial c_j} - \frac{M^2}{R} R_j \quad , \quad j = 1, 2, \cdots , 18.$$

$$\frac{\partial M^2}{\partial V} = \frac{2M^2}{V}$$

$$\frac{\partial M^2}{\partial T} = -\frac{M^2}{T}$$

where only the $(\partial M^2/\partial c_j)$'s of interest are calculated.

4.2.6 Calculation of S_1 and S_2 and Their Partial Derivatives

The summation terms S_1 and S_2 and their partial derivatives are calculated from

$$S_1 = \frac{1}{R}\sum_{i=1}^{18} f_i R_i$$

$$\frac{\partial S_1}{\partial c_j} = \frac{1}{R}\sum_{i=1}^{18} \beta_{i,j} R_i - \frac{S_1 R_j}{R} \quad , \quad j = 1, 2, \cdots, 18.$$

$$\frac{\partial S_1}{\partial V} = \frac{1}{R}\sum_{i=1}^{18} \beta_{i,19} R_i$$

$$\frac{\partial S_1}{\partial \rho} = \frac{1}{R}\sum_{i=1}^{18} \beta_{i,20} R_i$$

$$\frac{\partial S_1}{\partial T} = \frac{1}{R}\sum_{i=1}^{18} \beta_{i,21} R_i$$

$$S_2 = \frac{1}{RT} \sum_{i=1}^{18} f_i h_i$$

$$\frac{\partial S_2}{\partial c_j} = \frac{1}{RT} \sum_{i=1}^{18} \beta_{i,j} h_i - \frac{S_2}{R} R_j \quad , \quad j = 1, 2, \cdots, 18.$$

$$\frac{\partial S_2}{\partial V} = \frac{1}{RT} \sum_{i=1}^{18} \beta_{i,19} h_i$$

$$\frac{\partial S_2}{\partial \rho} = \frac{1}{RT} \sum_{i=1}^{18} \beta_{i,20} h_i$$

$$\frac{\partial S_2}{\partial T} = \frac{1}{RT} \sum_{i=1}^{18} \beta_{i,21} h_i + \frac{1}{RT} \sum_{i=1}^{18} f_i C_{pi} - \frac{S_2}{T}$$

where the sums are performed only over the species of interest and only the $(\partial S_1/\partial c_j)$'s and $(\partial S_2/\partial c_j)$'s of interest are calculated.

4.2.7 Calculation of B and Its Partial Derivatives

The energy exchange term B and its partial derivatives are calculated from

$$B = \frac{\gamma - 1}{\gamma} S_2$$

$$\frac{\partial B}{\partial c_j} = \frac{\gamma - 1}{\gamma} \frac{\partial S_2}{\partial c_j} + \frac{1}{\gamma^2} S_2 \frac{\partial \gamma}{\partial c_j} \quad , \quad j = 1, 2, \cdots, 18$$

$$\frac{\partial B}{\partial V} = \frac{\gamma - 1}{\gamma} \frac{\partial S_2}{\partial V}$$

$$\frac{\partial B}{\partial \rho} = \frac{\gamma - 1}{\gamma} \frac{\partial S_2}{\partial \rho}$$

$$\frac{\partial B}{\partial T} = \frac{\gamma - 1}{\gamma} \frac{\partial S_2}{\partial T} + \frac{1}{\gamma^2} S_2 \frac{\partial r}{\partial T}$$

where only the $(\partial B/\partial c_j)$'s of interest are calculated.

4.2.8 Calculation of A and Its Partial Derivatives

The diabatic heat addition term A and its partial derivatives are calculated from

$$A = S_1 - B$$

$$\frac{\partial A}{\partial c_j} = \frac{\partial S_1}{\partial c_j} - \frac{\partial B}{\partial c_j}, \quad j = 1, 2, \cdots, 18.$$

$$\frac{\partial A}{\partial V} = \frac{\partial S_1}{\partial V} - \frac{\partial B}{\partial V}$$

$$\frac{\partial A}{\partial \rho} = \frac{\partial S_1}{\partial \rho} - \frac{\partial B}{\partial \rho}$$

$$\frac{\partial A}{\partial T} = \frac{\partial S_1}{\partial T} - \frac{\partial B}{\partial T}$$

where only the $(\partial A/\partial c_j)$'s of interest are calculated.

4.2.9 Caluclation of f_i, α_i and $\beta_{i,j}$ for the Fluid Dynamic Equations

For subsonic flows, f_i, α_i and $\beta_{i,j}$ for the fluid dynamic equations are calculated from the following relationships:

For V,

$$f_{19} = -\frac{1}{\rho V}\frac{dP}{dx}$$

$$\alpha_{19} = -\frac{1}{\rho V}\frac{d^2P}{dx^2}$$

$$\beta_{19,19} = -\frac{1}{\rho} f_{19}$$

$$\beta_{19,21} = -\frac{1}{V} f_{19}$$

For ρ,

$$f_{20} = \left[\frac{1}{\gamma P}\frac{dP}{dx} - A\right]\rho$$

$$a_{20} = \left[\frac{d^2P}{dx^2} - \frac{1}{P}\left(\frac{dP}{dx}\right)^2\right]\frac{\rho}{\gamma P}$$

$$\beta_{20,j} = -\frac{\rho}{\gamma^2 P}\frac{dP}{dx}\frac{\partial\gamma}{\partial c_j} - \rho\frac{\partial A}{\partial c_j}\quad , \quad j = 1, 2, \cdots, 18.$$

$$\beta_{20,19} = -\rho\frac{\partial A}{\partial V}$$

$$\beta_{20,20} = \frac{1}{\rho} f_{20} - \rho\frac{\partial A}{\partial \rho}$$

$$\beta_{20,21} = -\rho\frac{\partial A}{\partial T} - \frac{\rho}{\gamma^2 P}\frac{dP}{dx}\frac{\partial r}{\partial T}$$

where only the $\beta_{20,j}$'s of interest are calculated.

For T,

$$f_{21} = \left[\frac{\gamma - 1}{\gamma}\frac{1}{P}\frac{dP}{dx} - B\right] T$$

$$a_{21} = \frac{\gamma - 1}{\gamma}\left[\frac{d^2P}{dx^2} - \frac{1}{P}\left(\frac{dP}{dx}\right)^2\right]\frac{T}{P}$$

$$\beta_{21,j} = \frac{1}{\gamma^2}\frac{T}{P}\frac{dP}{dx}\frac{\partial\gamma}{\partial c_j} - T\frac{\partial B}{\partial c_j}\quad , \quad j = 1, 2, \cdots, 18.$$

$$\beta_{21,19} = -T\frac{\partial B}{\partial V}$$

$$\beta_{21,20} = -T\frac{\partial B}{\partial \rho}$$

$$\beta_{21,21} = \frac{1}{T} f_{21} - T\frac{\partial B}{\partial T} + \frac{1}{\gamma^2}\frac{T}{P}\frac{dP}{dx}\frac{\partial\gamma}{\partial T}$$

where only the $\beta_{21,j}$'s of interest are calculated.

For supersonic flows, f_i, α_i and $\beta_{i,j}$ for the fluid dynamic equations are calculated from the following relationships:

For V,

$$f_{19} = \left[\frac{1}{a}\frac{da}{dx} - A\right]\frac{V}{M^2 - 1}$$

$$\alpha_{19} = \frac{1}{a}\left[\frac{d^2a}{dx^2} - \frac{1}{a}\left(\frac{da}{dx}\right)^2\right]\frac{V}{M^2 - 1}$$

$$\beta_{19,j} = -\frac{1}{M^2 - 1} f_{19}\frac{\partial M^2}{\partial c_j} - \frac{V}{M^2 - 1}\frac{\partial A}{\partial c_j}, \quad j = 1, 2, \cdots, 18.$$

$$\beta_{19,19} = \frac{1}{V} f_{19} - \frac{1}{M^2 - 1} f_{19}\frac{\partial M^2}{\partial V} - \frac{V}{M^2 - 1}\frac{\partial A}{\partial V}$$

$$\beta_{19,20} = -\frac{V}{M^2 - 1}\frac{\partial A}{\partial \rho}$$

$$\beta_{19,21} = -\frac{1}{M^2 - 1} f_{19}\frac{\partial M^2}{\partial T} - \frac{V}{M^2 - 1}\frac{\partial A}{\partial T}$$

where only the $\beta_{19,j}$'s of interest are calculated.

For ρ,

$$f_{20} = \left\{\left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{M^2}{M^2 - 1} - A\right\}\rho$$

$$\alpha_{20} = -\frac{1}{a}\left[\frac{d^2a}{dx^2} - \frac{1}{a}\left(\frac{da}{dx}\right)^2\right]\frac{\rho M^2}{M^2 - 1}$$

$$\beta_{20,j} = -\frac{\rho}{\left(M^2 - 1\right)^2}\left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{\partial M^2}{\partial c_j} - \frac{\rho}{M^2 - 1}\frac{\partial A}{\partial c_j}, \quad j = 1, 2, \cdots, 18.$$

$$\beta_{20,19} = -\frac{\rho}{\left(M^2 - 1\right)^2}\left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{\partial M^2}{\partial V} - \frac{\rho}{M^2 - 1}\frac{\partial A}{\partial V}$$

$$\beta_{20,20} = \frac{1}{\rho} f_{20} - \frac{\rho}{M^2 - 1}\frac{\partial A}{\partial \rho}$$

$$\beta_{20,21} = -\frac{\rho}{\left(M^2 - 1\right)^2}\left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{\partial M^2}{\partial T} - \frac{\rho}{M^2 - 1}\frac{\partial A}{\partial T}$$

where only the $\beta_{20,j}$'s of interest are calculated.

For T,

$$f_{21} = \left\{(\gamma - 1)\left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{M^2}{M^2 - 1} - B\right\} T$$

$$\alpha_{21} = -\frac{\gamma - 1}{a}\left[\frac{d^2 a}{dx^2} - \frac{1}{a}\left(\frac{da}{dx}\right)^2\right]\frac{TM^2}{M^2 - 1}$$

$$\beta_{21,j} = -\frac{(\gamma - 1)T}{\left(M^2 - 1\right)^2}\left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{\partial M^2}{\partial c_j} + (\gamma - 1)\frac{TM^2}{M^2 - 1}\frac{\partial A}{\partial c_j} - T\frac{\partial B}{\partial c_j}$$

$$+ \left[A - \frac{1}{a}\frac{da}{dx}\right]\frac{TM^2}{M^2 - 1}\frac{\partial \gamma}{\partial c_j}, \quad j = 1, 2, \cdots, 18.$$

$$\beta_{21,19} = -\frac{(\gamma - 1)T}{\left(M^2 - 1\right)^2}\left[\frac{A}{\gamma} - \frac{1}{a}\frac{da}{dx}\right]\frac{\partial M^2}{\partial V} + (\gamma - 1)\frac{TM^2}{M^2 - 1}\frac{\partial A}{\partial V} - T\frac{\partial B}{\partial V}$$

$$\beta_{21,20} = (\gamma - 1)\frac{TM^2}{M^2 - 1}\frac{\partial A}{\partial \rho} - T\frac{\partial B}{\partial \rho}$$

$$\beta_{21,21} = \frac{1}{T} f_{21} - \frac{(\gamma - 1)T}{\left(M^2 - 1\right)^2} \left[\frac{A}{\gamma} - \frac{1}{a}\frac{da}{dx}\right] \frac{\partial M^2}{\partial T} + (\gamma - 1) \frac{TM^2}{M^2 - 1} \frac{\partial A}{\partial T}$$

$$- T \frac{\partial B}{\partial T} + \left[A - \frac{1}{a}\frac{da}{dx}\right] \frac{TM^2}{M^2 - 1} \frac{\partial \gamma}{\partial T}$$

where only the $\beta_{21,j}$'s of interest are calculated.

For P,

$$f_{22} = \left[A - \frac{1}{a}\frac{da}{dx}\right] \frac{\gamma M^2}{M^2 - 1} P$$

$$a_{22} = -\frac{1}{a}\left[\frac{d^2a}{dx^2} - \frac{1}{a}\left(\frac{da}{dx}\right)^2\right] \frac{\gamma M^2}{M^2 - 1} P$$

$$\beta_{22,j} = -\frac{1}{M^2(M^2 - 1)} f_{22} \frac{\partial M^2}{\partial c_j} + \frac{\gamma P M^2}{M^2 - 1} \frac{\partial A}{\partial c_j} + \frac{f_{22}}{\gamma} \frac{\partial \gamma}{\partial c_j}, \quad j = 1, 2, \cdots, 18$$

$$\beta_{22,19} = -\frac{1}{M^2(M^2 - 1)} f_{22} \frac{\partial M^2}{\partial V} + \frac{\gamma P M^2}{M^2 - 1} \frac{\partial A}{\partial V}$$

$$\beta_{22,20} = \frac{\gamma P M^2}{M^2 - 1} \frac{\partial A}{\partial \rho}$$

$$\beta_{22,21} = -\frac{1}{M^2(M^2 - 1)} f_{22} \frac{\partial M^2}{\partial T} + \frac{\gamma P M^2}{M^2 - 1} \frac{\partial A}{\partial T} + \frac{f_{22}}{\gamma} \frac{\partial \gamma}{\partial T}$$

$$\beta_{22,22} = \frac{1}{\rho} f_{22}$$

where only the $\beta_{22,j}$'s of interest are calculated.

4.3 INTEGRATION SUBROUTINE

Given the derivatives (f_i) and partial derivatives (α_i and $\beta_{i,j}$) of the chemical relaxation equations and the fluid dynamic equations, this subroutine integrates these equations using the second order implicit integration method described in Section 3. The subroutine also determines the integration step size required to maintain the integration accuracy within prescribed bounds. These calculations are performed in the following order:

- Predicted values of the species concentrations and the fluid dynamic variables at the next point in the nozzle are calculated from the predictor formulas.
- Predicted values of the derivatives and partial derivatives at the forward point are obtained from the Derivative Evaluation Subroutine (described in Section 4.2) using the predicted values of the species concentrations and fluid dynamic variables.
- Corrected values of the species concentrations and the fluid dynamic variables at the next point in the nozzle are calculated from the corrector formulas.
- The maximum allowable integration step size which will maintain the integration accuracy within the prescribed bounds is calculated from the error formulas for the integration step.
- On input option, corrected values of the derivatives and partial derivatives at the new point are obtained from the Derivative Evaluation Subroutine (described in Section 4.2) using the corrected values of the species concentrations and the fluid dynamic variables.
- The integration then proceeds using a step size of 0.9, the maximum allowable step size calculated for the previous step.

If at any integration step, the step size exceeds the maximum allowable step size for that step, the integration is repeated using a step size of 0.9, the maximum allowable step size for that step.

The calculations performed in this subroutine are described in the following sections.

4.3.1 Prediction-Corrector Calculation

Predicted values of the species concentrations and the fluid dynamic variables at the forward point are calculated by solving the set of nonhomogeneous algebraic equations

$$\left(1 - \beta_{i,i,n} h + \beta^2_{i,i,n} \frac{h^2}{2}\right) k_i^{(P)} - \sum_{j=1}^{N} \delta_{ij}\beta_{i,j,n}\left(1 - \sum_{i=1}^{N} \beta_{i,j,n} \frac{h}{2}\right) k_j^{(P)} h$$

$$= \left(1 - \beta_{i,i,n} \frac{h}{2}\right)(f_{i,n} + a_{i,n} h)h - \sum_{j=1}^{N} \delta_{ij}\beta_{i,j,n}(f_{j,n} + a_{j,n} h) \frac{h^2}{2}$$

where the sums are performed only over the species of interest. Using the predicted values of the species concentrations and fluid dynamic variables, predicted values of the derivatives and partial derivatives at the forward point are obtained from the Derivative Evaluation Subroutine. Corrected values of the species concentrations and the fluid dynamic variables at the forward point are calculated by solving the set of nonhomogeneous algebraic equations

$$\left(1 - \beta_{i,i,n+1} h + \beta^2_{i,i,n+1} \frac{h^2}{2}\right) k_i^{(C)} - \sum_{j=1}^{N} \delta_{ij}\beta_{i,j,n+1}\left(1 - \sum_{i=1}^{N} \beta_{i,j,n+1} \frac{h}{2}\right) k_j^{(C)} h$$

$$= \left(1 - \beta_{i,i,n+1} \frac{h}{2}\right) f_{i,n+1} h - \sum_{j=1}^{N} \delta_{ij}\beta_{i,j,n+1} f_{j,n+1} \frac{h^2}{2} - a_{i,n+1} \frac{h^2}{2}$$

$$- \sum_{j=1}^{N} \beta_{i,j,n+1}\left(1 - \sum_{i=1}^{N} \beta_{i,j,n+1} \frac{h}{2}\right) k_j^{(P)} h$$

In the subsonic nozzle inlet, the number of equations (N) to be solved is 21 while in the supersonic nozzle expansion cone, the number of equations to be solved is 22 since the pressure is determined from the pressure table in the subsonic nozzle inlet.

4.3.2 Maximum Allowable Integration Step Size Calculation

The maximum allowable integration step size for each equation is calculated from

$$h_{i,max} = \left[\left| \frac{6\delta_i k_i^{(C)}}{\alpha_{i,n} + \sum_{j=1}^{N} \beta_{i,j,n} f_{j,n} - \left(\alpha_{i,n+1} + \sum_{j=1}^{N} \beta_{i,j,n+1} f_{j,n+1} \right)} \right| \right]^{1/2}$$

The smallest $h_{i,max}$ is taken as the maximum allowable integration step size for the integration step. If at any integration step, the step size exceeded the maximum allowable step size for that step, the integration is repeated using a step size of 0.9, the maximum allowable step size for that step. On input option, corrected values of the derivatives and partial derivatives at the new point are obtained from the Derivative Evaluation Subroutine using the corrected values of the species concentrations and the fluid dynamic variables. The integration then proceeds using a step size of 0.9, the maximum allowable step size calculated for the previous step.

4.4 SPECIES THERMAL FUNCTION SUBROUTINE

Given the temperature, this subroutine calculates the species free energy (F_i), enthalpy (h_i), heat capacity (C_{pi}) and the heat capacity temperature derivative (dC_{pi}/dT). For the species of interest, these quantities are calculated from

$$F_i = F_i(n\Delta T_T) + \frac{F_i(n\Delta T_T) - h_i(n\Delta T_T)}{n\Delta T_T}(T - r\,\Delta T_T) - \frac{1}{2}\frac{C_{pi}(n\Delta T_T)}{n\Delta T_T}\left(T - n\Delta T_T\right)^2$$

$$h_i = h_i(n\Delta T_T) + C_{pi}(n\Delta T_T)(T - n\Delta T_T) + \frac{1}{2}\left.\frac{dC_{pi}}{dT}\right|_{n\Delta T_T}\left(T - n\Delta T_T\right)^2$$

$$C_{pi} = C_{pi}(n\Delta T_T) + \left.\frac{dC_{pi}}{dT}\right|_{n\Delta T_T}(T - n\Delta T_T) + \frac{1}{2}\left.\frac{d^2C_{pi}}{dT^2}\right|_{n\Delta T_T}\left(T - n\Delta T_T\right)^2$$

$$\frac{dC_{pi}}{dT} = \left.\frac{dC_{pi}}{dT}\right|_{n\Delta T_T} + \left.\frac{d^2C_{pi}}{dT^2}\right|_{n\Delta T_T}(T - n\Delta T_T)$$

when $|T - n\Delta T_T| \leq (1/2)n\Delta T_T$. If $|T - n\Delta T_T| > (1/2)n\Delta T_T$, n is set equal to the integer nearest $T/\Delta T_T$ and new values of $F_i(n\Delta T_T)$, $h_i(n\Delta T_T)$, $C_{pi}(n\Delta T_T)$, $dC_{pi}/dT|_{n\Delta T_T}$ and $d^2C_{pi}/dT^2|_{n\Delta T_T}$ are obtained from the thermal function tables.

4.5 EQUILIBRIUM FUNCTION SUBROUTINE

Given the temperature and species thermal functions, this subroutine calculates the dissociation-recombination reaction equilibrium constants and their temperature derivatives. For the reactions of interest, these quantities are calculated from

Reaction 1, $CO_2 + M \rightleftharpoons CO + O + M$

$$K_1 = \frac{13.9430}{T}\, e^{-\left[(\Delta H_1/T) + F_1 - F_3 - F_{18}\right]}$$

$$\frac{dK_1}{dT} = \left[\frac{\Delta H}{T} \text{[illegible]} + F_3 + F_{18} + h_1 - h_3 - h_{18} - 1\right]\frac{K_1}{T}$$

Reaction 2, $H_2O + M \rightleftharpoons OH + H + M$

$$K_2 = \frac{1.30295}{T} e^{-\left[(\Delta H_2/T)+F_2-F_{11}-F_{16}\right]}$$

$$\frac{dK_2}{dT} = \left(\frac{\Delta H_2}{T} - F_2 + F_{11} + F_{16} + h_2 - h_{11} - h_{16} - 1\right)\frac{K_2}{T}$$

Reaction 3, $CO + M \rightleftharpoons C + O + M$

$$K_3 = \frac{9.39381}{T} e^{-\left[(\Delta H_3/T)+F_3-F_{13}-F_{18}\right]}$$

$$\frac{dK_3}{dT} = \left(\frac{\Delta H_3}{T} - F_3 + F_{13} + F_{18} + h_3 - h_{13} - h_{18} - 1\right)\frac{K_3}{T}$$

Reaction 4, $Cl_2 + M \rightleftharpoons 2Cl + M$

$$K_4 = \frac{24.2742}{T} e^{-\left[(\Delta H_4/T)+F_4-2F_{14}\right]}$$

$$\frac{dK_4}{dT} = \left(\frac{\Delta H_4}{T} - F_4 + 2F_{14} + h_4 - 2h_{14} - 1\right)\frac{K_4}{T}$$

Reaction 5, $F_2 + M \rightleftharpoons 2F + M$

$$K_5 = \frac{13.0076}{T} e^{-\left[(\Delta H_5/T)+T_5-2F_{15}\right]}$$

$$\frac{dK_5}{dT} = \left(\frac{\Delta H_5}{T} - F_5 + 2F_{15} + h_5 - 2h_{15} - 1\right)\frac{K_5}{T}$$

Reaction 6, $HCl + M \rightleftharpoons H + Cl + M$

$$K_6 = \frac{1.34206}{T} e^{-\left[(\Delta H_6/T)+F_6-F_{14}-F_{16}\right]}$$

$$\frac{dK_6}{dT} = \left(\frac{\Delta H_6}{T} - F_6 + F_{14} + F_{16} + h_6 - h_{14} - h_{16} - 1\right)\frac{K_6}{T}$$

Reaction 7, $HF + M \rightleftharpoons H + F + M$

$$K_7 = \frac{1.31064}{T} e^{-\left[(\Delta H_7/T)+F_7-F_{15}-F_{16}\right]}$$

$$\frac{dK_7}{dT} = \left(\frac{\Delta H_7}{T} - F_7 + F_{15} + F_{16} - h_7 - h_{15} - h_{16} - 1\right)\frac{K_7}{T}$$

Reaction 8, $H_2 + M \rightleftharpoons 2H + M$

$$K_8 = \frac{0.690093}{T} e^{-\left[(\Delta H_8/T)+F_8-2F_{16}\right]}$$

$$\frac{dK_8}{dT} = \left(\frac{\Delta H_8}{T} - F_8 + 2F_{16} + h_8 - 2h_{16} - 1\right)\frac{K_8}{T}$$

Reaction 9, $N_2 + M \rightleftharpoons 2N + M$

$$K_9 = \frac{9.59012}{T} e^{-\left[(\Delta H_9/T)+F_9-2F_{17}\right]}$$

$$\frac{dK_9}{dT} = \left(\frac{\Delta H_9}{T} - F_9 + 2F_{17} + h_9 - 2h_{17} - 1\right)\frac{K_9}{T}$$

Reaction 10, $NO + M \rightleftharpoons N + O + M$

$$K_{10} = \frac{10.2267}{T} e^{-\left[(\Delta H_{10}/T)+F_{10}-F_{17}-F_{18}\right]}$$

$$\frac{dK_{10}}{dT} = \left(\frac{\Delta H_{10}}{T} - F_{10} + F_{11} + F_{18} + h_{10} - h_{17} - h_{18} - 1\right)\frac{K_{10}}{T}$$

Reaction 11, $OH + M \rightleftharpoons O + H + M$

$$K_{11} = \frac{1.29840}{T} e^{-\left[(\Delta H_{11}/T)+F_{11}-F_{16}-F_{18}\right]}$$

$$\frac{dK_{11}}{dT} = \left(\frac{\Delta H_{11}}{T} - F_{11} + F_{16} + F_{18} + h_{11} - h_{16} - h_{18} - 1\right)\frac{K_{11}}{T}$$

Reaction 12, $O_2 + M \rightleftharpoons 2O + M$

$$K_{12} = \frac{10.9339}{T} e^{-\left[(\Delta H_{12}/T)+F_{12}-2F_{18}\right]}$$

$$\frac{dK_{12}}{dT} = \left(\frac{\Delta H_{12}}{T} - F_{12} + 2F_{18} + h_{12} - 2h_{18} - 1\right)\frac{K_{12}}{T}$$

4.6 GAS THERMAL FUNCTION SUBROUTINE

Given the flow properties at a point, this subroutine calculates the mixture gas constant, heat capacity, gamma and it's partial derivative of gamma from the following relationships

$$R = \sum_{i=1}^{18} c_i R_i$$

$$C_p = \sum_{i=1}^{18} c_i C_{pi}$$

$$\gamma = \frac{C_p}{C_p - R}$$

$$\frac{\partial \gamma}{\partial c_j} = \gamma(\gamma - 1)\left(\frac{R_j}{R} - \frac{C_{pj}}{C_p}\right), \qquad j = 1, 2, \cdots, 18$$

$$\frac{\partial \gamma}{\partial T} = -\frac{\gamma(\gamma - 1)}{C_p} \sum_{i=1}^{18} c_i \frac{dC_{pi}}{dT}$$

The sums are performed only over the species of interest.

4.7 OUTPUT SUBROUTINE

The output subroutine processes the output data, converts the data to the proper units and calculates the required output quantities. These calculations are performed in the following order.

- The pressure is converted to psia.
- The species mass fractions are converted to mole fractions.
- The performance parameters are calculated.
- The gas static enthalpy and the percentage total enthalpy change during the integration from the chamber are calculated.
- The entropy change from the chamber is calculated.
- The average expansion coefficients are calculated.

The calculations performed by this subroutine are described in the following sections.

4.7.1 Pressure Conversion

The pressure (in psia) is calculated from

$$P(\text{psia}) = \frac{P}{4633.056}$$

4.7.2 Species Concentration Conversion

The species mole fractions are calculated from

$$c_{i,m} = \frac{R_i}{R} c_i$$

4.7.3 Performance Parameter Calculation

At the throat, the characteristic exhaust velocity is calculated from

$$C^* = \frac{P_c}{\rho^* V^*}$$

The vacuum specific impulse is calculated from

$$I_{sp} = \frac{1}{32.174}\left(V + \frac{P}{\rho V}\right)$$

The vacuum thrust coefficient is calculated from

$$C_F = 32.174 \frac{I_{sp}}{c^*}$$

4.7.4 Enthalpy Calculations

The gas static enthalpy is calculated from

$$h = \sum_{i=1}^{18} c_i h_i$$

where the sum is performed only over the species of interest. The percentage total enthalpy change during the integration from the chamber is calculated from

$$\Delta H_T(\%) = 100\left[1 - \frac{h + \frac{1}{2} V^2}{H_c}\right]$$

4.7.5 Entropy Change Calculation

The entropy change from the chamber is calculated from

$$\Delta S(\mathrm{Btu/lb}\ ^{\circ}\mathrm{R}) = \frac{3.9952 \cdot 10^{-5}}{T} \sum_{i=1}^{18} c_i(h_i - F_i) - S_c$$

where the sum is performed only over the species of interest.

4.7.6 Average Expansion Coefficient Calculations

At the throat, the average temperature expansion coefficient is calculated from

$$N_T^* = 2\frac{T_c}{T^*} - 1.$$

In the expansion cone, the average temperature expansion coefficient is calculated by iteration from

$$N_T^{(n+1)} = \frac{L^{(n)} + 1}{L^{(n)} - 1}$$

where

$$L^{(n)} = \frac{\ln\left[\dfrac{2}{N_T^{(n)} - 1}\,\epsilon^2\left(\dfrac{T_c}{T} - 1\right)\right]}{\ln\left[\dfrac{2}{N_T^{(n)} + 1}\,\dfrac{T_c}{T}\right]}$$

and $N_T^{(1)}$ is the last average temperature expansion coefficient calculated.

The average pressure expansion coefficient is calculated by iteration from

$$N_P^{(n+1)} = -2 \ln \frac{P}{P_c}\left[\ln\left\{\frac{2}{N_P^{(n)} - 1}\,\epsilon^2\left[1 - \left(\frac{P}{P_c}\right)^{N_P^{(n)} - 1/N_P^{(1)}}\right] \left(\frac{N_P^{(1)} + 1}{2}\right)^{N_P^{(n)} + 1/N_P^{(n)} - 1}\right\}\right]^{-1}$$

where $N_P^{(1)}$ is the last average temperature expansion coefficient calculated.

The average expansion gamma is calculated from

$$\bar{\gamma} = \frac{\ln \dfrac{P}{P_c}}{\ln \dfrac{\rho}{\rho_c}}$$

5. REFERENCES

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