FINAL TECHNICAL REPORT

HIGH SPEED HYDROGEN/GRAPHITE INTERACTION

Authors: A. J. Kelly, R. Hamman, O. P. Sharma and D. T. Harrje

Research Supported Under
NGF - 31-001-230

Technical Monitor: Francis C. Schwenk
Atomic Energy Headquarters

Approved by: David T. Harrje
Principal Investigator

May 1974

AMS Report No. 1206

Guggenheim Laboratories for the Aerospace Propulsion Sciences
Department of Aerospace and Mechanical Sciences
PRINCETON UNIVERSITY
Princeton, New Jersey
TABLE OF CONTENTS

TITLE PAGE ................................................................. i
TABLE OF CONTENTS ......................................................... ii
INTRODUCTION ................................................................. iii
SECTION 1 THEORETICAL PREDICTIONS OF HYDROGEN/GRAPHITE EROSION RATES ................................................................. 1
SECTION 2 HIGH TEMPERATURE, NONEQUILIBRIUM HYDROGEN FLOW IN A NOZZLE ................................................................. 4
SECTION 3 MOLECULAR BEAM STUDIES OF HYDROGEN/GRAPHITE EROSION ................................................................. 36
REFERENCES ................................................................. 53
APPENDIX A THEORETICAL DERIVATIONS ................................................................. 55
INTRODUCTION

The following sections of this final report on high speed hydrogen/graphite interaction deal with the various aspects of the research program.

Section 1 concerns the theoretical predictions of hydrogen/graphite erosion rates. Our previous report (1-1) covered this topic area in some detail, however, this phase of the research is continuing under Dr. Sharma's direction and a brief summary of the activities are included in this section.

Section 2 describes high temperature, nonequilibrium hydrogen flow in a nozzle. In this section some detail as to computer programs and subroutines is supplied in order to calculate flow characteristics of nuclear rocket applications. The analysis includes subsonic, transonic and supersonic regimes together with equilibrium and non-equilibrium considerations.

Section 3 describes the molecular beam studies of hydrogen/graphite erosion. This phase of the research has concluded. The findings, together with a description of the approach and experimental apparatus, are summarized here.
SECTION 1

THEORETICAL PREDICTIONS OF HYDROGEN/GRAPHITE EROSION RATES

A theoretical model is developed to predict the erosion rate of graphite coating by a stream of hydrogen gas. It is based on a phenomenological description of turbulent reacting boundary layer flow. It also takes into account the effect of lateral curvature in the nozzle as well as the dissociation of hydrogen gas.

The basic conservation equations with the relevant boundary conditions for this model were summarized in the last report (1-1). The formulation of the problem was done by considering the multicomponent diffusion of species. The detailed description of the transport properties needed for the solution of the equations as well as the transformed forms of the governing equations were also given in the last report (1-1).

A numerical solution is being sought for the set of coupled nonlinear partial differential equations. For this purpose, we are following the general procedure adopted by Herring and Mellor (1-2) for calculating the boundary layer flow of a single component (non-reacting) mixture. Using the Crank-Michelson scheme, the partial differential equations have been transformed into finite difference equations which are then being solved by Gaussian elimination procedure. The expressions are too lengthy for presentation in this report.

There are essentially three successive phases involved in the complete solution of this problem:

[...]

[...]

[...]

[...]

[...]
(a) The flow external to the boundary layer must be known. This task was undertaken by Mr. R. Hamman who provided the numerical data for the non-equilibrium flow field with a given nozzle geometry by neglecting the boundary layer effects (see Section 2). The choice of step-size along the axial direction is consequently restricted by this input data.

(b) In order to solve the governing equations step by step along the axial direction, we use approximate turbulent similarity flow equations at the initial station. Herring and Mellor generalized the results obtained from incompressible equilibrium turbulent boundary layer flow studies to get approximate compressible turbulent similarity flow equations. In the present analysis, we make use of the same prescriptions for the momentum conservation equation expressed in terms of temperature in contrast to enthalpy. Moreover, the same concept is extended to the species conservation equation.

It must be pointed out that since we have included the dependences on temperature and composition for the various physical properties of the mixture, the final expressions are far more complex, and the logic of the computer program also becomes very involved.

(c) Having obtained the results for the similarity flow, the calculations can be easily completed for other stations by considering the general form of the governing equations. No essential difficulty can be expected at this stage. All the relevant details have been worked out.

In view of the unexpected change of location of the in-
vestigator for this phase of the program, Dr. O. P. Sharma, and the necessity of using a smaller computer facility (IBM 7044), the debugging of the Fortran has been rather slow. It is anticipated that the computation will be completed by summer 1974 at no additional expense to the contract.
SECTION 2

HIGH TEMPERATURE, NONEQUILIBRIUM HYDROGEN FLOW IN A NOZZLE

2.1 Analysis

The analysis is composed of three rather distinctive flow cases: subsonic one dimensional flow, transonic flow and supersonic axisymmetric flow. Only a rough outline of the respective theories is given. For more detailed information one is referred to the references for this section.

The subsonic flow analysis consists of a pressure defined one-dimensional non-equilibrium analysis as given in Refs. 2-1 & 2-2. Insufficient reliable information was known to warrant a computer program on a two-dimensional axisymmetric treatment of the subsonic flow.

In the case of transonic flow a model is chosen for a simple, more geometrical treatment analogue to that discussed in Reference 2-2 which gives accurate results compared to experiments. An extensive treatment of the transonic axisymmetric case is given in Reference 2-2, but was rejected for this program as being too complicated.

The analysis of the axisymmetric non-equilibrium supersonic flow employs a method of characteristics solution for the partial differential equations. The finite difference scheme chosen stems from Reference 2-4, being a more simple method than that used in Reference 2-5.

2.1.1 Subsonic one-dimensional flow

The governing differential equations for one-dimensional flow with chemical non-equilibrium are

\[ \frac{g \Delta W}{\lambda} = \text{constant} \]  \hspace{1cm} (continuity) \hspace{1cm} (2.1)

\[ g \frac{dW}{dz} + \frac{dp}{dz} = 0 \]  \hspace{1cm} (momentum) \hspace{1cm} (2.2)
\[ h + \frac{1}{2} w^2 = \text{constant} \quad \text{(energy)} \quad (2.3) \]
\[ \frac{da}{dx} = \frac{c}{w} \quad \text{(chemical relaxation)} \quad (2.4) \]

In case of chemical equilibrium equation (2.4) is replaced by
\[ \alpha = \alpha_e (\rho, T) \quad (2.5) \]
or in case of frozen flow by
\[ \alpha = \alpha_0 \quad \text{constant} \]

In the discussion we will not consider the frozen case, as its method of solution is almost identical to the one for equilibrium flow.

As the set of equations both in the equilibrium and in the non-equilibrium case are to be integrated through the transonic region, the area ratio cannot be used as the independent variable because the area ratio defined set of equations is singular at the sonic point.

Using the velocity or pressure as the independent variable has the extra advantage that the set of four differential equations, which originally required simultaneous integration, is reduced to a set of three equations.

With the flow field the corresponding area ratio can be computed afterwards.

In the non-equilibrium case there exists a coupling of the equations with the area ratio by means of the chemical relaxation equation. This case will have to be solved by iteration of the complete subsonic flowfield until the computed area ratio converges to the area ratio defined by the nozzle shape.
2.1.1. Equilibrium flow

Using velocity as the independent variable equations (2.2) and (2.3) can be written

\[ g_w \, dw + dp = 0 \quad (2.6) \]

\[ dh + wdw = 0 \quad (2.7) \]

Equation (2.4) is replaced by the condition for equilibrium \( \omega = \omega(p,T) \).

As the enthalpy \( h \) is a function of \( \omega \) and \( T \) only

\[ dh = h_T \, dT + h_\omega \, d\omega \]

where

\[ h_T = \frac{\partial h}{\partial T} \]

\[ h_\omega = \frac{\partial h}{\partial \omega} \]

Combining this result with (2.5)

\[ dh = h_T \, dT + h_\omega \left[ \frac{\partial \omega}{\partial p} \, dp + \frac{\partial \omega}{\partial T} \, dT \right] \]

which reduces the set of equations to

\[ g_w \, dw + dp = 0 \]

\[ (h_\omega \frac{\partial \omega}{\partial p} + h_T) \, dT + \left( 1 - h_\omega \frac{\partial \omega}{\partial p} \right) \, wdw = 0 \quad (2.8) \]

Writing this in finite difference form with the velocity as the independent variable

\[ \Delta p = (-g_w) \Delta w \quad (2.9) \]

\[ \Delta T = \left( \frac{h_\omega \frac{\partial \omega}{\partial p} \, \frac{g-1}{\omega} \, w}{h_\omega \frac{\partial \omega}{\partial T} + h_T} \right) \Delta w \quad (2.10) \]
which combined with the condition for chemical equilibrium

\[ \alpha = \alpha_c(P, T) \]

gives a solution for the equilibrium flow properties.

The coefficients in (2.9) and (2.10) are taken to be the average values between two consecutive points, while the density \( \rho \) is computed using the equation of state

\[ \frac{P}{\rho} = \frac{kT(1+\alpha)}{2\rho \mu} \]  \hspace{1cm} (2.11)

The local frozen speed of sound can be found using the equation given in appendix A.

As the mass flow \( \dot{m} \) is constant, it follows from

\[ \rho A \omega = \dot{m} \]

that at the throat, where \( A = \frac{\omega}{A_{\min}} \), \( \omega \) should take a maximum value.

After location of this maximum, the throat properties and the equilibrium mass flow can be determined, and the area corresponding with every set of properties \( p, T, \alpha \) and \( \omega \) is known:

\[ \dot{m}_{eq} = (\rho \omega)_{\max} A^n \]  \hspace{1cm} (2.12)

and

\[ A_n = \frac{\dot{m}_{eq}}{(\rho \omega)_n} \]  \hspace{1cm} (2.15)

An expression for the nozzle shape links the area with the axial coordinate, which permits us to use the functions
\[ P = P_{eq}(\lambda) \]
\[ w = w_{eq}(\lambda) \]
\[ T = T_{eq}(\lambda) \]
\[ \alpha = \alpha_{eq}(\lambda) \]

and all derived equilibrium properties, whenever they are needed.

2.1.1.2. Non-equilibrium flow

As the pressure is relatively insensitive for non-equilibrium effects, it is convenient to use it as the independent variable in the kinetic analysis.

Equations (2.2), (2.4) and (2.3) can be written

\[ (gw)dw + \left( \frac{dp}{dn} \right) d\lambda = 0 \]
\[ d\alpha - \left( \frac{w}{w} \right) dw = 0 \]
\[ h_T dT + \left( h_\alpha w w - \frac{1}{3} \left( \frac{dp}{dn} \right) \right) d\lambda = 0 \]

Or

\[ dw = \left[ \frac{-1}{3w} \left( \frac{dp}{dn} \right) \right] d\lambda \]
\[ d\alpha = \left[ \frac{w}{w} \right] d\lambda \]
\[ dT = \left[ - \frac{h_\alpha w w}{h_T} + \frac{1}{3h_T} \left( \frac{dp}{dn} \right) \right] d\lambda \]

The pressure and its derivatives are assumed to be known; as a first approximation is taken to the equilibrium pressure distribution.

A fourth equation can be derived by differentiating the equation of state (2.11)

\[ dg = \left[ \frac{1}{T} \left( \frac{dp}{dn} \right) - \frac{1}{T} \frac{dT}{dn} - \frac{1}{T} \frac{w}{w} \right] g d\lambda \]

These four equations can be rewritten, as shown in appendix A, in the form
\[
\frac{dw}{d\alpha} = f_1 = -\frac{1}{\bar{g} w} \left( \frac{dp}{d\alpha} \right) \quad (2.14)
\]

\[
\frac{d\alpha}{d\alpha} = f_2 = \frac{\dot{w}}{\bar{w}} \quad (2.15)
\]

\[
\frac{dT}{d\alpha} = \left[ \frac{\gamma-1}{\gamma P} \left( \frac{dp}{d\alpha} \right) - B \right] T \quad (2.16)
\]

\[
\frac{dg}{d\alpha} = \left[ \frac{1}{\gamma P} \left( \frac{dp}{d\alpha} \right) - A \right] g \quad (2.17)
\]

where

\[ B = \frac{h_w}{\bar{T} \bar{w}} f_2 \]

\[ A = \frac{f_2}{\bar{w}} - B \]

The integration method is taken from Reference 2-1 with a few minor alterations.

Setting

\[ y_1 = w \]
\[ y_2 = \dot{w} \]
\[ y_3 = \bar{T} \]
\[ y_4 = g \]
\[ k_1 = \Delta w \]
\[ k_2 = \Delta \dot{w} \]
\[ k_3 = \Delta \bar{T} \]
\[ k_4 = \Delta g \]

and

\[ \beta_{ij} = \frac{1}{n} \]
\[ \alpha_{ij} = \frac{1}{n} \]

four second order integration formulae in the increments of \( Y_i \) can be derived of the form...
\[ k_{i,n+1} = \frac{h}{h_{n+1}} \left[ k_{i,n} + (t_{i,n} + \alpha_{i,n} h_{n+1} + \frac{h}{\sum_{j=1}^{n} (\beta_{i,j,n} k_{j,n+1})} h_{n} \right] \]  

where

\[ h_{n} = \text{stepsize for the } n\text{th interval}. \]

The function values \( f_i \) and the derivatives \( \alpha_i \) and \( \beta_{i,j} \) are taken at the \( n \)th point.

As the last increment before the computed increment has to be known to apply equation (2.18), it is necessary to use a different set of formulae for the starting step of the integration.

The first order variant of equation (2.18) is

\[ k_{i,1} = (t_{i,0} + \alpha_{i,0} h + \frac{h}{\sum_{j=1}^{n} (\beta_{i,j,0} k_{j,1})} h) \]  

when applied on the first interval.

The relative error in the increment \( k_{i,n+1} \) for the second order method is

\[ \Delta k_{i,n} = \left| \frac{k_{i,n+1} - 2k_{i,n} + k_{i,n-1}}{2k_{i,n+1} - k_{i,n}} \right| \]

This formula is used to determine the allowable stepsize.

As the error varies as the stepsize squared, the criterion for doubling and halving the stepsize is given as

\[ h_{n+1} = \frac{5}{10} \Delta k_{i,\text{max}} < S \]  

\[ h_{n+1} = \frac{1}{2} h_{n+1} \]  

\[ \Delta k_{i,\text{max}} > S \]  

\[ h_{n+1} = 2 h_{n+1} \]  

\[ \Delta k_{i,\text{max}} < \frac{S}{10} \]

where \( S \) is the maximum error allowed.
Equations (2.18) and (2.19) can be written as four linear algebraic equations

\[ a_l k_{1,u_1} + b_l k_{2,u_1} + c_l k_{3,u_1} + d_l k_{4,u_1} = c_l \]

\[ l = -1, 2, 3, 4 \]

which are solved for the increments \( k_{1,u_1}, i = 1, 2, 3, 4 \).

The integration method is only weakly dependent on the engine size and allows an integration step several orders of magnitude larger than the chemical relaxation length.

The gas properties at the throat and the mass flow are determined the same way as treated in the paragraph on equilibrium flow.

\[ \dot{m} = (\dot{g}w)_{\text{max}} A^+ \]

and

\[ A_n = \frac{\dot{m}}{(\dot{g}w)_n} \]

A convergence criterion is applied on the mass flow and the one-dimensional computation is ended, when sufficient convergence is achieved. If no sufficient convergence is found, the complete one-dimensional non-equilibrium calculation is restarted, using the newly computed pressure profile.

The form of the functions and derivatives in equations (2.18) and (2.19) is given in Appendix A.

2.1.2. Transonic flow

Basis for the analysis is a modified Sauer analysis as given in Reference 22 by Nickerson. The method employs first order perturbation theory to find
a solution for a constant property line at the throat minimum point.

For a more extensive discussion of the theory use Reference 2-2. Only the results of and changes in that theory will be given here.

The constant property line selected is the isobar at the throat minimum point. The coordinates of the isobar are given by

\[ \kappa = \frac{1}{2} (1 - r^2) \left( \frac{2R_2}{\gamma + 1} \right) - \frac{1}{2} \]  \hspace{1cm} (2.21)

where

- \( R_2 \) = downstream normalized throat radius of curvature
- \( \gamma \) = average specific heat ratio in the throat region
- \( r \) = radial normalized coordinate
- \( x \) = axial normalized coordinate.

The average specific heat ratio is determined as

\[ \gamma = \frac{1}{2} \left( \gamma^* + \frac{\sum_{i=1}^{N} r_i \gamma_i}{\sum_{i=1}^{N} r_i} \right) \]  \hspace{1cm} (2.22)

where the asterisk denotes the throat property following from the one-dimen-
sional analysis and \( \gamma_i \) is the property at point \( i \) on the isobar. \( N \) is
the total number of points on the isobar.

The spacing of the points on the isobar is determined such that the mass
flow through each annular element is equal.

Hence

\[ r_i = 0 \]  \hspace{1cm} (2.23)

\[ r_k \sqrt{\frac{A^*}{(n-1)\pi}} \]  \hspace{1cm} (2.24)

and

\[ r_{i+1} = r_i \sqrt{i} \]  \hspace{1cm} \( i = 2, \ldots, (n-1) \)  \hspace{1cm} (2.25)
Denoting all one-dimensional throat properties with an asterisk, it follows for the pressure on the isobar

\[ p = p^* \left( 1 - \frac{Y}{u} \frac{1}{R_2^2 + \frac{Y}{u}} \right) \]  

(2.26)

The axial and radial components of the velocity are

\[ u = a^* \left( 1 + \frac{r^2}{2} - \frac{1}{u} + \left( \frac{2R_3}{v+1} \right)^{\frac{1}{2}} \right) \frac{1}{R_3} \]

\[ v = a^* \left( \frac{1}{u} \left( \frac{r+1}{2} \right)^{\frac{1}{2}} (u^3 - 1) + R_3^{\frac{1}{2}} v \zeta \right) \frac{1}{R_3^{\frac{3}{2}}} \]

Using equation (2.23) these expressions can be simplified into

\[ u = a^* \left( 1 + \frac{1}{uE_3} \right) \]  

(2.27)

\[ v = a^* \left[ \left( \frac{r^2 - 1}{2} \right)^{\frac{1}{2}} \right] \frac{1}{uR_3^{\frac{3}{2}}} \]  

(2.28)

which shows that the axial velocity is constant on the isobar.

The resultant velocity is

\[ w = \sqrt{(u^2 + v^2)} \]  

(2.29)

The streamline angle is found easily by

\[ \Theta = \tan^{-1} \left( \frac{v}{u} \right) \]  

(2.30)

The two other flow properties to be determined are the mass fraction atomic hydrogen and the temperature.

As solving the chemical relaxation equation

\[ \frac{d\xi}{\alpha} = \frac{w}{\omega} \]

ever the relatively large distance from throat to isobar leads to severe
numerical instability for interpolation from the property table provided
by the one-dimensional non-equilibrium analysis. The temperature follows
from the energy equation
\[ h(a, T) = h_o - \frac{1}{2} \omega^2 \]  

2.3 Description of program subroutines

The program subroutines are divided in four groups

- main program and general subroutines used throughout
  the computation
- subroutines used for the computation of the one-dimensional
  subsonic flow
- subroutines for the determination of the transonic line
- subroutines that perform the two-dimensional supersonic
  flow calculation.

2.4 Main program and supporting subroutines

The subroutines in this group are

MAIN PROGRAM
SUBROUTINE CONSTA
CHEMEQ
EQUIL
GAMMA
TEMP

2.4.1 Main calling program

MAIN PROGRAM
2.4.2 Input and physical constants

SUBROUTINE CONSTA

In this subroutine the physical constants used in the program are initialized and the nozzle shape and case parameters are read in. The variables, used in the internal computation, are derived from the data given in the nozzle shape parameters.

Finally the values of the input parameters are printed.

Physical constants

The physical constants, as they are given in the subroutine, are

- $AA$ constant in the expression for the reaction rate $FKP = \frac{AA}{T}$, where $T$ is the temperature in degrees K.
- $PM$ mass of a hydrogen atom
- $FK$ Boltzmann constant
- $THID$ characteristic temperature for dissociation of hydrogen
- $THIK$ characteristic temperature for vibration of hydrogen
- $PI$ geometrical constant
- $WI$ atomic weight of hydrogen

The constants are set at the values

$AA = 0.7 \times 10^{18} \text{ cm}^6 \text{ g}^{-1} \text{ mole}^{-2} \text{ sec}^{-1}$
$PM = 0.1674 \times 10^{-25} \text{ g}$
$FK = 0.138 \times 10^{-17} \text{ erg} \text{ cm}^{-3} \text{ mole}^{-1}$
$THED = 54733 \text{ K}$
$THIK = 6140.0 \text{ K}$
$PI = 3.14159$
$WI = 1.008 \text{ g/mole}$
\[ A1 = \frac{\text{REXIT} - \text{REE} - \text{THEX} \cdot \tan(\text{THSUP})}{\text{THEX}^2} \]

\[ B1 = \tan(\text{THSUP}) - 2 \cdot A1 \cdot \text{XEE} \]

\[ \text{XEF} = \text{XEE} + \text{THEX} \]

\[ \text{THEX} = \text{atan} \left( 2 \cdot A1 \cdot \text{XEF} + B1 \right) \quad \text{(rad)} \]

\[ \text{IF (LENGTH.EQ.0)} \]

\[ \text{XEF} = \frac{2(\text{REXIT} - 1 - \text{THEX} \cdot (1 - \cos(\text{THSUP})))}{\tan(\text{THEX}) + \tan(\text{THSUP})} + \text{XEE} \]

and generally

\[ \text{COL} = \frac{(\text{XEF} - \text{XEE}) \cdot \tan(\text{THSUP})}{\tan(\text{THSUP}) - \tan(\text{THEX})} \]

The parameters IWALL, IPERF, IPROP, INTER, NPNTS, IOUT and LENGTH determine the case that has to be computed and the shape and quantity of the output.

**PROGRAM INPUT**

- \( P^\circ \) stagnation pressure (dyne/cm\(^2\))
- \( T^\circ \) stagnation temperature (°K)

**PROGRAM OUTPUT**

- internal constants
- PRINT

**CALLING DATA**

**SUBROUTINE EQUIL**

**CALLED BY**

**MAIN PROGRAM**

2.4.3 **General subroutines**

**SUBROUTINE CHEMEQ**

**EQUIL**

**GAMMA**

**TEMP**
Nozzle shape parameters

The nozzle shape is assumed to be composed out of circular arcs, straight lines and a parabolic supersonic expansion section.

Read in are

- RCHAM combustion chamber radius
- RONE nozzle inlet radius of curvature
- RTWP upstream throat radius of curvature
- RTDRE downstream throat radius of curvature
- NSTAR throat radius (cm)
- RXEXIT nozzle exit radius
- THSUB maximum nozzle inlet angle (rad)
- THSUP maximum nozzle exit angle (rad)
- THEX IF (LENGTH.EQ.0) nozzle exit angle (rad)
  IF (LENGTH.GT.0) length of parabolic nozzle section

All values, with the exception of NSTAR and the angles, are dimensionless with respect to the throat radius.

The internal nozzle shape parameters, which can be derived

\[
XBE = R\text{ONE} \cdot \sin (\text{THSUB})
\]

\[
XCE = R\text{CHAM} - 1 - RTWP (1 - \cos (\text{THSUB})) + \frac{1}{R\text{ONE} \left( \frac{1}{\cos (\text{THSUB})} - 1 \right)} + \frac{R\text{ONE} \left( \frac{1}{\cos (\text{THSUB})} - 1 \right)}{\tan (\text{THSUB})}
\]

\[
XDE = XCE + RTWP \cdot \sin (\text{THSUB})
\]

\[
XEE = XDE + RTDRE \cdot \sin (\text{THSUP})
\]

\[
RBE = R\text{CHAM} + R\text{ONE} \left( \frac{1}{\cos (\text{THSUB})} - 1 \right)
\]

\[
RCE = 1 + RTWP \left( 1 - \cos (\text{THSUB}) \right)
\]

\[
REE = 1 + RTDRE \left( 1 - \cos (\text{THSUP}) \right)
\]
SUBROUTINE CHEMSY (T,FKP,DFKP)

This subroutine is used during the complete computation to provide the other subroutines with the value of the equilibrium constant FKP \((\text{dyne/cm}^2)^{\frac{1}{2}}\) and the derivative DFKP \(\left(\frac{d}{dT}(\ln(FKP))\right)\) at a given temperature T for the reaction \(\text{H}_2 \rightarrow \text{H}\).

The first time the subroutine is called two arrays, S and TAB, are read in. Immediately afterwards a flag is set

\[ \text{NFLAG}=1 \]

which prevents that the next time, when the subroutine is called, it will try to read the values for S and TAB again. TAB and S are defined

\[ \text{TAB} = 10 \log K_p, \quad K_p \text{ in (atmospheres)}^{\frac{1}{2}} \]

\[ S \text{ corresponding temperature in degrees K.} \]

and are taken from the JANAF tables, Reference 2-6. The range of temperatures covered runs from 0°K until 6000°K.

At the required value of the temperature T the corresponding value of FKP is found by logarithmic interpolation, and the result is converted to the output units. In the same loop the value of the derivative \(\frac{d}{dT}(\ln K_p)\) is determined.

<table>
<thead>
<tr>
<th>PROGRAM INPUT</th>
<th>T</th>
<th>temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROGRAM OUTPUT</td>
<td>FKP</td>
<td>equilibrium constant ((\text{dyne/cm}^2)^{\frac{1}{2}})</td>
</tr>
<tr>
<td></td>
<td>DFKP</td>
<td>logarithmic derivative of the equilibrium constant ((°K)^{-1})</td>
</tr>
</tbody>
</table>

CALLING DATA

CALLED BY SUBROUTINE
SUBROUTINE EQUIL (P,T,ALP)

Calculates at given pressure P and temperature T the corresponding value of the mass fraction atomic hydrogen ALP at chemical equilibrium conditions according to the relation

\[ ALP = \text{DSQRT}(1./(1.+4.*P/(FKP*FKP))) \]

where FKP is the value of the equilibrium constant at \( T \, ^{\circ}\text{K} \).

**PROGRAM INPUT**

<table>
<thead>
<tr>
<th>P</th>
<th>pressure (dyn/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>temperature (°K)</td>
</tr>
</tbody>
</table>

**PROGRAM OUTPUT**

| ALP | mass fraction atomic hydrogen at equilibrium conditions. |

**CALLING**

SUBROUTINE CHMEQ

**CALLED BY**

SUBROUTINE
SUBROUTINE GAMMA (P, T, ALP, GAM, AF2, HIF)

At given
- pressure P
- temperature T
- mass fraction atomic hydrogen ALP

are computed
- specific heat ratio GAM of the mixture
- squared frozen speed of sound AF2
- density HIF

according to the expressions (A1), (A7) and (AH) of appendix A.

PROGRAM INPUT
- P pressure (dyne/cm²)
- T temperature (°K)
- ALP mass fraction atomic hydrogen

PROGRAM OUTPUT
- GAM specific heat ratio
- AF2 squared frozen speed of sound (cm²/sec²)
- HIF density (g/cm³)

CALLED BY
- SUBROUTINE
2.5 Subsonic flow

The subroutines in this group are split in two subsections, the first one dealing with one-dimensional equilibrium flow, the second one with one-dimensional non-equilibrium flow. It contains

SUBROUTINE C0EQ
CORTAB
EQUIN
STOUT1
TABLE
CHECK
FINISH
PUNPUT
SOLVE
SUBC1
SUBC2
SUBEX

2.5.1 Equilibrium flow

SUBROUTINE C0EQ
CORTAB
EQUIN
STOUT1
TABLE
SUBROUTINE C2EQ (P,T,W,ALP,CQ1,CQ2)

The coefficients of the two finite difference equations for integration of the one-dimensional equilibrium flow field (c.f. section 2.1.1.1; equations (2.9) and (2.10))

\[ CQ1 = \frac{dC}{dp} \]
\[ CQ2 = \frac{\frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g - \frac{dC}{dt} g} {h_a + \frac{dC}{dt} g + \frac{dC}{dt} g} \]

are computed here. The expressions for the partial derivatives

\[ \frac{dC}{dp} \quad \text{and} \quad \frac{dC}{dt} \]

can be found in appendix A (equations (A12a) and (A12b)).

PROGRAM INPUT

| P | pressure (dyne/cm²) |
| T | temperature (°K) |
| W | velocity (cm/sec) |
| ALP | mass fraction atomic hydrogen |

PROGRAM OUTPUT

| CQ1 | coefficient in equation (2.9) |
| CQ2 | coefficient in equation (2.10) |

CALLING

SUBROUTINE CHMEQ

CALLED BY

SUBROUTINE EQUIN
SUBROUTINE CHRTAB (W,X,M,WE,EX,J)

The subroutine modifies a table \((W,X)\) with \(M\) entries into a table \((WE,EX)\) with \(J\) entries with the result that between each two values of the array \(EX\) in the second table a constant interval is constructed.

The interpolation between two values of \(X\) is achieved with the formula

\[
WE(I) = W(I) \cdot \left( \frac{W(I+1)}{W(I)} \right) \left( \frac{EX(J) - X(I)}{X(I+1) - X(I)} \right)
\]

where

\[EX(J) = EX(J-1) + \text{RELL}\]

\[\text{RELL} = 0.03 \times \text{HSTAB}\]

\[EX(1) = X(1)\]

A logarithmic interpolation method is chosen as it represents most accurately the shape of the function \(W=W(X)\) between two subsequent points.

**PROGRAM INPUT**
- \(W\) velocity (cm/sec)
- \(X\) axial coordinate (cm)
- \(M\) number of entries in \((W,X)\) table

**PROGRAM OUTPUT**
- \(WE\) velocity (cm/sec)
- \(EX\) axial coordinate (cm)
- \(J\) number of entries in \((WE,EX)\) table

**CALLED BY**
SUBROUTINE EQUIN
SUBROUTINE EQUIN (P0, T0, IMASS, M, X, P, TS, WS, AS, PHIG)

The subroutine computes the equilibrium pressure distribution P as a function of the axial coordinate X and the equilibrium mass flow FMASS.

Two main calculations can be distinguished. After the computation of the initial flow conditions from the stagnation pressure P0 and stagnation temperature T0, which uses the common expression for the temperature ratio in compressible flow as a function of the Mach number and the specific heat ratio, the energy equation and the condition for chemical equilibrium, a table of the equilibrium gas properties

- velocity W
- pressure P
- temperature T
- mass fraction atomic hydrogen ALP
- density RI0
- frozen Mach number FMA

is computed, using the relations described in section 2.1.1.1.

During this calculation the maximum value of the product (RH0mW) is determined, from which the equilibrium mass flow FMASS follows.

After computation of the sets of gas properties corresponding with the area by applying continuity, follows the construction of a table of the velocity WE as a function of the axial coordinate EX by means of SUBROUTINE TABLE, which employs an analytic expression for the nozzle geometry.

At the same time the nozzle inlet conditions

- pressure PHIG=PS
- temperature TS
- mass fraction atomic hydrogen AS
- velocity WS
This subroutine provides the regular output of the results of the one-dimensional performance calculation.

The nozzle area is converted in the area ratio by dividing by (RSTANe RSTANEPI). Printed are for all stations

- area ratio $A$
- axial coordinate $X$ (cm)
- pressure $P$ (dyne/cm²)
- temperature $T$ (°K)
- density $\text{H}_2\text{O}$ (g/cm³)
- mass fraction atomic hydrogen $\text{ALP}$
- velocity $W$ (cm/sec)
- frozen Mach number $\text{FMACH}$

When the frozen Mach number becomes greater than unity, the vacuum specific impulse is computed according to

$$SPI = \frac{1}{981} \left( W - \frac{P}{\text{H}_2\text{O}} \right)$$

and printed.

**PROGRAM INPUT**

- $P$: pressure (dyne/cm²)
- $T$: temperature (°K)
- $\text{ALP}$: mass fraction atomic hydrogen
- $\text{H}_2\text{O}$: density (g/cm³)
- $W$: velocity (cm/sec)
- $A$: nozzle area (cm²)
- $X$: axial coordinate (cm)

**PROGRAM OUTPUT**

- $\text{FMACH}$: frozen Mach number

**PRINT**

**CALLED BY**

SUBROUTINE EQUIN

SUBEX
The table \((we, ex)\) is corrected with the aid of SUBROUTINE CMIITAB to ensure an equal stepsize \(dx\) in the resulting table \((w, x)\), which furnishes the new input for the second run through the equilibrium flow integration. The final pressure table \((p, x)\) is obtained again with the aid of SUBROUTINE TABLE.

SUBROUTINE STPUT1 takes care of the standard print output of the results.

**Program Input**
- \(p_s\): stagnation pressure (dyne/cm\(^2\))
- \(T_s\): stagnation temperature (°K)

**Program Output**
- \(FM\): equilibrium mass flow (g/sec)
- \(M\): number of entries in the arrays \(P\) and \(X\)
- \(X\): axial coordinate (cm)
- \(P\): pressure (dyne/cm\(^2\))
- \(TS, WS, AS\): temperature (°K), velocity (cm/sec) and mass fraction atomic hydrogen corresponding with the first entry in the \((P, X)\) table
- \(P_{Ein}\): nozzle inlet pressure (dyne/cm\(^2\))

**Calling**
- SUBROUTINE CMIMEQ
- CMIMEQ
- CMITAB
- EQUIL
- GAMMA
- STPUT1
- TABLE

**Called By**
- SUBROUTINE SUISEX
SUBROUTINE TABLE (P,A,N,ASTAR,T,W,ALP,X,Q,M,TS,WS,AS,NSTAR)

The property/area table (P,A) with N entries is converted in a property/axial coordinate table (Q,X) with M entries.

The values of the other three one-dimensional flow properties TS, WS and AS corresponding with the first entry in the (Q,X) table are interpolated from the input arrays T, W and ALP. NSTAR is the index of the entries at the nozzle throat.

The relations that link the axial coordinate X with the nozzle area A, non-dimensionalizing the axial coordinate X and the radial coordinate by dividing through the throat radius NSTAR, are:

\[ R(J) = \frac{\sqrt{A(J)/ASTAR}}{ } \]

- if \( R(J) \), LT.RCHAM

\[ X(J) = \sqrt{R^2 - (R(J) - RCHAM + HNE)^2} \]

- if \( R(J) \), LT.RHE

\[ X(J) = RCHAM - R(J) + HNE \left( \frac{1}{\cos(TISUB)} - 1 \right) \tan(TISUB) \]

- if \( R(J) \), LT.RHE

\[ X(J) = XDE - \sqrt{(HTWP^2 - (HTWP + H(J))^2)} \]

- if \( J, GT,NSTAR \)

\[ X(J) = XDE + \sqrt{(HTWP^2 - (H(J) - 1 - HTWP)^2)} \]

- if \( J, GT,NSTAR \)

\[ X(J) = XDE + C\Phi L \left( 1 - \sqrt{1 - \frac{R(J) - RHE}{C\Phi L \tan(TISUP)}} \right) \]

Finally all computed X values are dimensionalized

\[ X(J) = X(J) \cdot NSTAR \]

PROGRAM INPUT

P.A : gas property/nozzle area table to be converted; A in cm²

N : number of entries in (P,A) table
- 28 -

N entries

NSTAR index of properties at the nozzle throat

PROGRAM OUTPUT

q,X gas property/axial coordinate table; X in cm

M number of entries in (q,X) table

TS,WS,AS with (q(1),X(1)) corresponding values of the arrays T, W and ALP

CALLED BY

SUINQUTINE EQUIN

SUBEX

3.2.2. Non-equilibrium flow

SUINQUTINE CHECK

DERISB
PUNQUT
SOLVE
SUINCG1
SUINCG2
SUBEX

This subroutine computes at known
- pressure P
- temperature T
- density HI\(\phi\)
- mass fraction atomic hydrogen ALP
- velocity W
- pressure first derivative DPX
- pressure second derivative DP2X

the functions F1, F2, F3, F4 and their derivatives with respect to x, w, \(\alpha\), T and \(\rho\), according to the expressions given in appendix A (equations (A13) through (A16) and following), which will be used for the calculation of the coefficients of the first and second order integration methods for one-dimensional non-equilibrium flow.

**PROGRAM INPUT**

- P pressure (dyne/cm\(^2\))
- T temperature (°K)
- HI\(\phi\) density (g/cm\(^3\))
- ALP mass fraction atomic hydrogen
- W velocity
- DPX pressure first derivative (dyne/cm\(^3\))
- DP2X pressure second derivative (dyne/cm\(^4\))

**PROGRAM OUTPUT**

- F1, F2, F3, F4 and their derivatives (c.f. appendix A)

**CALLING**

SUBROUTINE CHIMEQ

**CALLED BY**

SUBROUTINE SUBRO1

SUBRO2
Four linear algebraic equations in four unknowns are solved using Kramer's Rule. The equations are of the form

\[ a_1DW + b_1DA + c_1DT + d_1Dt = e_1 \]

and are the rearranged integration formulae from section 2.1.1.2, equations (2.18) and (2.19).

The coefficients \( a_1, b_1, c_1, d_1 \) and \( e_1 \) are computed in subroutine SUBCI (first order method, applied only for the initial integration interval, if (NONE.EQ.1)) and subroutine SUBC2 (second order method, used for all subsequent steps).

**PROGRAM INPUT**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Pressure at last calculated ( (n^{th}) ) point (dyne/cm(^2))</td>
</tr>
<tr>
<td>T</td>
<td>Temperature at ( n^{th} ) point ((^o)K)</td>
</tr>
<tr>
<td>WI5H</td>
<td>Density at ( n^{th} ) point (g/cm(^3))</td>
</tr>
<tr>
<td>ALP</td>
<td>Mass fraction atomic hydrogen at ( n^{th} ) point</td>
</tr>
<tr>
<td>W</td>
<td>Velocity at ( n^{th} ) point (cm/sec)</td>
</tr>
<tr>
<td>DX</td>
<td>Axial distance between ( n^{th} ) and ( (n+1)^{th} ) point (cm)</td>
</tr>
<tr>
<td>DPX</td>
<td>Value of ( \frac{\partial P}{\partial x} ) at the ( n^{th} ) point (dyne/cm(^3))</td>
</tr>
<tr>
<td>DP2X</td>
<td>Value of ( \frac{\partial^2 P}{\partial x^2} ) at ( n^{th} ) point (dyne/cm(^4))</td>
</tr>
<tr>
<td>DWN</td>
<td>Increment in velocity between ( (n-1)^{th} ) and ( n^{th} ) point (cm/sec)</td>
</tr>
<tr>
<td>DTN</td>
<td>Increment in temperature between ( (n-1)^{th} ) and ( n^{th} ) point ((^o)K)</td>
</tr>
<tr>
<td>DHN</td>
<td>Increment in density between ( (n-1)^{th} ) and ( n^{th} ) point (g/cm(^3))</td>
</tr>
</tbody>
</table>
DAN  increment in mass fraction atomic hydrogen between (n-1)\text{th} and n\text{th} point

NONE  n

DX1  axial distance between (n-1)\text{th} and n\text{th} point (cm)

PROGRAM OUTPUT

DW  increment in velocity between n\text{th} and (n+1)\text{th} point (cm/sec)

DT  increment in temperature between n\text{th} and (n+1)\text{th} point (°K)

DH  increment in density between n\text{th} and (n+1)\text{th} point (g/cm\textsuperscript{3})

DA  increment in mass fraction atomic hydrogen between n\text{th} and (n+1)\text{th} point

CALLING

SUBROUTINE SUBC\textsuperscript{1}

SUBC\textsuperscript{2}

CALLED BY

SUBROUTINE SUBEX
SUHJOTINE subroutine SUBG1 (P,T,HI,LP,W,DPX,DP2X,A1,A2,A3,A4,W3,W1,C2,C3,
C4,D1,D2,D3,D4,E1,E2,E3,E4,DX)

Computation of the coefficients of the four linear algebraic equations, 
obtained from the first order integration method, c.f. section 2.1.1.2, 
equation (2.19).

The values and the derivatives of the functions F1, F2, F3 and F4 at 
given P, T, H, LP and W (equations (A13) through (A18), appendix A) 
are computed in SUHJOTINE DERISB.

The coefficients A1, A2, etc. are defined

\[ A1 = F1W^{1/2} \]
\[ A2 = F2W \]
\[ A3 = F3W \]
\[ A4 = F4W \]
\[ B2 = F2A^{1/2} \]
\[ B3 = F3A \]
\[ B4 = F4A \]
\[ C2 = F2T \]
\[ C3 = F3T^{1/2} \]
\[ C4 = F4T \]
\[ D1 = F1X \]
\[ D2 = F2X \]
\[ D3 = F3X \]
\[ D4 = F4X^{1/2} \]
\[ E1 = F1 - F1X, DX \]
\[ E2 = F2 \]
\[ E3 = F3 - F3X, DX \]
\[ E4 = F4 - F4X, DX \]
**PROGRAM INPUT**

- **P** pressure (dyne/cm²)
- **T** temperature (°K)
- **HI** density (g/cm³)
- **ALP** mass fraction atomic hydrogen
- **W** velocity (cm/sec)
- **DP** derivative dp/dx (dyne/cm³)
- **DP2** derivative d²p/dx² (dyne/cm⁴)
- **DX** axial interval (cm)

**PROGRAM OUTPUT**

- A₁, A₂, ..., E₃, E₄ coefficients of linear algebraic equations

**CALLING**

- SUBROUTINE DERISH

**CALLED BY**

- SUBROUTINE SOLVE
Computation of the four linear algebraic equations, obtained from the second order integration method, c.f. section 2.1.1.2, equation (2.18).

The values and the derivatives of the functions F1, F2, F3 and F4 (equations (A13) through (A18), appendix A) are calculated in SUBROUTINE DERISH.

Setting

\[ P = \frac{Dx1(Dx+Dx1)}{Dx} \]
\[ PQ = \frac{Dx(Dx+Dx1)}{(2Dx+Dx1)} \]

the coefficients A1, A2, etc. are defined

\[ A1 = \frac{F1W-1}{PQ} \]
\[ B2 = \frac{F2A-1}{PQ} \]
\[ C3 = \frac{F3T-1}{PQ} \]
\[ D4 = \frac{F4K-1}{PQ} \]
\[ E1 = -\frac{DWN}{Q} - F1X.DX - F1 \]
\[ E2 = -\frac{DAN}{Q} - F2 \]
\[ E3 = -\frac{DTN}{Q} - F3X.DX - F3 \]
\[ E4 = -\frac{DIN}{Q} - F4X.DX - F4 \]

A2, A3, A4, H3, H4, C2, C4, D1, D2 and D3 have the same definition as in SUBROUTINE SUBC01.

**PROGRAM INPUT**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>pressure (dyne/cm²)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (°K)</td>
</tr>
<tr>
<td>RH</td>
<td>density (g/cm³)</td>
</tr>
<tr>
<td>ALP</td>
<td>mass fraction atomic hydrogen</td>
</tr>
<tr>
<td>W</td>
<td>velocity (cm/sec)</td>
</tr>
<tr>
<td>DPX</td>
<td>derivative dp/dx (dyne/cm³)</td>
</tr>
</tbody>
</table>
axial interval between last computed point and next following point (cm)

down increment in velocity between last computed point and the point before (cm/sec)

D TN increment in temperature between last computed point and the point before (°K)

d DN increment in density between last computed point and the point before (g/cm³)

DAN increment in mass fraction atomic hydrogen between last computed point and the point before

dx1 axial interval before dx (cm)

program output
A1, A2, ..., E3, E4 coefficients of linear algebraic equations

calling
SUBROUTINE DERISH

called by
SUBROUTINE SAILVE

3.3 Transonic flow

This group is composed of only one subroutine

SUBROUTINE INLINE
SECTION 3

MOLECULAR BEAM STUDIES OF HYDROGEN/GRAPHITE EROSION

Introduction

As part of its contoured exhaust nozzle, the NERVA solid core nuclear rocket flight engine (Ref.3-1) was designed to incorporate a radiatively cooled graphite skirt. The choice of graphite for this skirt, extending from an area ratio of 24 to 1 to the exit plane (area ratio 100 to 1), rather than the more commonly used refractory metals, was based upon the superior nucleonic properties of low atomic weight graphite as opposed to those of high atomic weight metals. While the thermo-mechanical properties of graphite are quite adequate for its application as a skirt material, there exists however a question of its long term compatibility with the high temperature hydrogen propellant.

It is well established (Ref.3-2,-3,-4) that at high temperature (1000°K) and particularly under conditions of high temperatures and pressures (0 (1) atm) hot graphite will react with hydrogen to form simple hydrocarbons. Such a reaction, if sufficiently vigorous, would have a pronounced effect upon the utility of the nozzle skirt for multiple missions requiring cumulative burn times on the order of 10 hours or so. Consequently, it was deemed of importance to have definitive information available concerning the details of hydrogen-carbon surface reaction under conditions anticipated to be present at the surface of
the skirt during all phases of NERVA engine operation.

The mechanisms by which graphite surfaces react with heated hydrogen have been studied basically under equilibrium conditions. Clarke and Fox (Ref. 3-2) employed a filament to investigate the reaction of hydrogen and graphite over a temperature range 2000°K to 3400°K and pressures from 10⁻² to 1 atm. These experiments, conducted at low total hydrogen flow rates, permitted them to conclude that at temperatures below 3000°K and pressures between 10⁻² and 1 atm, the rate of reaction at the surface of the graphite is directly proportional to the hydrogen pressure and to the square root of the dissociation constant for this gas. At higher temperatures the sublimation rate of graphite is controlling, and C₂H₂ and C₃H₄ are predominant as reaction products.

Sanders (Ref. 3-2) of Lewis Research Center measured weight loss from graphite test samples heated in the range 1820°K to 2430°K at atmospheric pressure. The flow rate of hydrogen was low (47 cm³/sec) and equilibrium was maintained throughout the test series. The data collected from these tests at temperatures in excess of 2070°K, correlate quite well with thermodynamic calculations of the equilibrium reaction of carbon and hydrogen. Divergence between the data and computed reaction rates in the temperature range between 1820°K and 2070°K was attributed to a lack of thermodynamic equilibrium induced by the low, but significant, hydrogen flow rate employed during the tests. In addition to predicting the reaction rate, the calculations
indicated that acetylene (C₂H₂) would be the primary reaction product. Earlier, Heddon (Ref.3-4) determined the rate of methane production for graphite reacting with hydrogen at pressures from 10¹ to 10² atmospheres and temperatures from 1270°K to 1520°K. It was concluded that the rate determining step in this pressure and temperature regime consisted of hydrogenation of CH₂-CH₂-groups at the graphite lattice coupled with a splitting of the -CH₂-CH₂- bond. It was further concluded that the reaction rate was negligible at temperatures below 1270°K.

These studies, all conducted under equilibrium conditions, have but limited applicability to the problem of establishing the erosion rate of a contoured nozzle. It is necessary, when trying to establish the chemical erosion rate of the graphite nozzle skirt in question, to not only have knowledge of the graphite-hydrogen reaction mechanism, but also to have a fully developed model for the flow field and its interaction with the boundary.

The nozzle skirt under continuous operating conditions will attain an equilibrium temperature which varies as a function of longitudinal position, assuming axial symmetry, and is determined by a balance between the heat flux to the surface through the reacting boundary layer inside and thermal radiation from the outside surface. Consequently, the conditions existing at the graphite-hydrogen interface will be very much different from those maintained in the experiments referenced. In particular, it is difficult to determine the influence surface temperature
has upon the overall reaction rate from, for instance, the
effect of hydrogen temperature or velocity. Such information
is necessary for the proper development of a coherent model
of the reacting boundary layer in the skirt.

A practical engineering assault on the problem of graphite
skirt erosion (Ref.3-5,-6) has shown that, on the basis of model tests
employing AGCarb-101 material as a test sample, and pressures
and temperatures commensurate with those anticipated to be
encountered, erosion rates will be acceptable. Similar tests
conducted with helium rather than hydrogen failed to cause
erosion. It might be concluded that this is an unambiguous
indication of a purely chemical, as opposed to mechanical,
erosion mechanism. However, the question can be raised as to
whether the surface is not acting as a catalyst for the re-
combination of the dissociated hydrogen present in the flow
leading to intensified reactivity in excess of that to be
anticipated from purely thermal considerations. A more exten-
sive series of tests employing other gases (e.g., N₂) would be
enlightening.

While the model tests seemingly appear to provide a solid
basis for the verification of the suitability of the existing
skirt design, i.e., indicated acceptably low erosion rates,
these tests have constantly failed to duplicate the low pressure
high velocity and Mach number conditions to be experienced by
the skirt. It is not possible at this point, on the basis
of these or the earlier tests to predict with any assurance
what the erosion rate will be in the actual nozzle skirt flow
regime. This statement is particularly true with regard to future higher temperature versions of the NERVA engine. As indicated earlier, to do so would require a comprehensive description of the reacting boundary layer coupled with a realistic description of the reaction mechanisms present when hydrogen impinges on a heated graphite surface.

It was the purpose of the experimental program undertaken during this contract to provide information concerning the detailed mechanisms by which hydrogen reacts with solid carbon (graphite) surfaces.
Experimental Program

Approach

In order for any experiment directed toward the investigation of the interaction of hydrogen with graphite surfaces to provide meaningful results it is mandatory that the basic physical characteristics of both the hydrogen gas and the graphite surface be known with precision and be independently controllable over a substantial range of values. An experiment so designed would then permit the pertinent parameters associated with the surface reactions to be independently varied and their effect upon the overall reaction schematic to be unambiguously assayed.

The use of a molecular beam nozzle generating a precisely controlled jet of hydrogen having known physical properties impinging on an accurately controlled graphite surface was chosen as the most straightforward means to satisfy the basic objectives of the study.

Experimental Apparatus

The experiment consisted then of four basic elements:

A. Hydrogen molecular beam nozzle
B. Graphite surface and its holder and power supply
C. Diagnostic instrumentation
D. Vacuum facility in which the experiment was conducted

The following brief description of each of these components serve to detail the salient characteristics of the experiment.

A. Hydrogen Molecular Beam Nozzle

Figure 1 is a photograph of the hydrogen molecular beam
nozzle. In the nozzle design gaseous hydrogen is introduced as shown and, by splitting the flow, is caused to enter both ends of the resistively heated rhenium nozzle tube. A small hole (31 μm diameter) drilled midway between the ends of the tube, along a radius, forms the nozzle proper.

By controlling the stagnation pressure and the stagnation temperature (by adjustment of the current level through the tube) a wide range of flow conditions could be obtained. Stagnation pressures of up to 20 atmospheres at stagnation temperatures up to 2800°K were possible, at flow rates up to a maximum (determined by the facility pumping capacity) of $10^{20}$ particles/sec.

The Mach numbers of the beam generated by such a nozzle were sufficiently high ($\text{M} = 10$) so that for the purposes of the experiment the energy distribution could within narrow limits (i.e., ±10%) be considered mono-energetic. The use of an almost mono-energetic beam allows the influence of particle velocity on the overall reaction kinetic rate to be precisely determined.

B. Graphite Sample and Holder

Candidate graphite samples were mounted in a sample holder which would permit the surface to be oriented over $2\pi$ steradians with respect to the center line of the beam. By varying the beam impingment angle the influence of surface anisotropies upon the surface kinetics could be weighed. In addition, provision was made for the samples to be resistively heated to
predetermined, controlled temperature levels to allow the influence of surface temperature to be compared with the effects of hydrogen particle energy.

- Diagnostic Instrumentation

A series of increasingly sophisticated instrumentation was available for this study. Initial studies of surface erosion under various beam and surface conditions were to be conducted by qualitative and quantitative evaluation of the amount of material removed by the reaction process. By using these data as a guide a detailed investigation using a mass spectrometer to assess the reaction products would then permit a detailed evaluation of the specific surface reactions contributing to surface erosion.

- Vacuum Facility

The use of a high vacuum environment was essential to this program. By maintaining the background pressure in the range of $10^{-4}$ torr two important advantages were obtained; the absence of significant extraneous material that could mask the effects of the reaction was assured and the reaction could be observed free from the influence of additional interactions due to multiple collisions in the vicinity of the surface. The pumping capacity associated with the vacuum facility limits the maximum nozzle flow rate that can be used.

All experiments conducted in this program were run in the Guggenheim Physical Laboratory facility which permitted pressures of $10^{-4}$ torr to be maintained at particle flow rates of up to $10^{20}$ sec$^{-1}$. Pressure levels below $10^{-4}$ torr correspond to mean
free paths in excess of one meter insuring favorable conditions for the observation of the reaction at the surface.

It should be noted that, in all but one respect, the physical characteristics of the hydrogen beam are quite similar to those anticipated to be present in the nozzle skirt of the NERVA flight engine. The one exception to this correspondence is the particle density. The hydrogen density at the surface of the graphite test sample, when being impinged upon by the beam, was on the order of $10^{13}$ to $10^{14}$ particles/cm$^3$ as compared to $10^{16}$ to $10^{17}$ particles/cm$^3$ in the actual nozzle. The simulation of nozzle skirt surface operating conditions was not the goal of this work. It is purely coincidental that the experimental parameters approximate those anticipated to be present.

Overall Progress

Considerable effort was devoted, during the early phases of the program, toward the development of a nozzle capable of providing the requisite hydrogen flows at the pressures and temperatures required for the test program. Initial attempts to produce a nozzle beam using tantalum nozzle tubes revealed that operation at modest temperatures (ie, $(0) 1000 \, K$) soon led to catastrophic failure because of embrittlement. As a consequence the use of rhenium nozzle tubes was pioneered.

A supply of vapor deposited rhenium, and tungsten-25%, rhenium nozzle tubes were secured and tested for long term compatibility with hydrogen under conditions of interest for this experiment series. The rhenium tubes supplied by The Advanced Rocket Technology Corporation of Irvine, California
proved to be more than adequate to the task and superior to the more brittle tungsten/rhenium alloy tubes tested.

The use of rhenium as a nozzle material necessitated the development of special drilling techniques to produce the microscopic holes required for the generation of high Mach number beams. By using specially ground tungsten carbide drill bits and a microdrilling apparatus purchased from National Jet Company of Cumberland, Maryland a number of nozzles were fabricated for use in the program.

An extensive series of tests were conducted to accurately determine the velocity distribution of the hydrogen beam produced by these nozzles when operated over a wide range of stagnation pressures and temperatures. These tests, using existing time of flight velocity distribution apparatus, revealed the Mach number to be in the range of 10 to 20 for all operating conditions and therefore adequate for the initial series of erosion tests.

The first series of tests had as its goal the qualitative evaluation of the various molded graphite skirt materials, listed in Table 1. For these tests the unheated 2 cm x 4 cm polished samples were mounted normal to the beam center line and 5 cm from the nozzle exit plane. Meticulous attention was devoted to assuring that the test conditions were maintained the same for each sample. By operating at a stagnation temperature of 2000°K and a pressure of 3 atmospheres hydrogen
particle mean energy of 0.6 ev was obtained. Each sample was 
irradiated for a period of three (3) hours, during which the flow 
rate and particle energy was maintained constant within 2%.

A thin tantalum shadow strip was afixed across the center 
of the sample piece to facilitate comparison of irradiated and 
unexposed surfaces. Figure 2 is a photograph taken in visible 
light of an irradiated sample. In this photograph the light 
horizontal band is the unirradiated surface, the darker areas 
having been exposed to the hydrogen beam. The small light 
rectangular areas at the corners were shielded from the 
impinging beam by clips used to restrain the sample in the 
holder.

The sample shown in this photograph (Sample 172) was 
visually quite similar to the other seven tested. In all 
cases visual inspection failed to reveal any marked differences 
amongst the samples studied. The demarcation between irradiated and 
umirradiated areas of the samples studied was sharp and quite 
distinct even for the areas shielded by the clips whose edges 
were raised somewhat above the sample surface, (the tantalum 
shield was in direct contact with the sample surface).

Because of this unambiguous visual evidence of beam 
impingement induced surface alteration it was anticipated that 
photomicrographs taken with a scanning electron microscope 
(SEM) would permit a quantitative measurement of surface 
erosion to be made. The strategy employed was to orient the 
sample such that the step in the surface (viewing from the eroded,
irradiated surface toward the shielded surface) could be clearly imaged and its elevation measured.

Figure 3 is a photomicrograph of the boundary region between the irradiated area (right and below) and the shielded area (left and above) of sample 172. This material displayed the highest degree of surface alteration of all the samples studied with the SEM. In fact it was the only sample of the eight (8) tested in which it was possible to detect the boundary region at any level of magnification.

This result was most unexpected because of the exceptionally sharp, distinct visual evidence all of the samples displayed for beam induced alteration. Inspection of figure 3 and a similar photograph of this sample surface obtained at a magnification of 4000X (displayed as figure 4) showed that the radiated surface has undergone what can best be described as mild excoriation. Surface irregularities in the irradiated area are observed to be softly rounded and generally subdued as compared to the shielded zone.

Close scrutiny of the photomicrographs taken of the eight (8) test samples at various view angles and at magnifications up to 4000X reveal, at most, marginal changes in the surface textures of all except #172. On the basis of this evidence the sample #172 material can be considered to be more susceptible to attack by energetic hydrogen atoms than the others tested.

This conclusion must be mollified by the realization that the surface changes apparent could very well have resulted from a process that was initially quite pronounced during the three (3)
hour test period and that no or very little change occurred thereafter. The resolution of this question is a moot point pending further tests involving both shorter and longer irradiation times with higher surface temperature, higher beam particle energies and varied sample orientations.

Although planned these tests were not implemented during this contract because the overall emphasis of the program was shifted soon after the data were collected and in the process of being analyzed. At the conclusion of the reported sample test series major effort was devoted toward the refinement of the rhenium, high pressure, high temperature nozzle design. As a result of these refinements to the nozzle design stemming from an extended series of tests at temperatures in the 2600 to 2700 K range at pressures in excess of one atmosphere total nozzle longevity has been extended to 30 hours at 2700 K.

On the basis of the known crystallographic and sublimation properties of rhenium a 30 hour useful life at 2700 K corresponds to virtually indefinite (1000 hours) service life at operating temperatures below 2400 K. As a consequence a high temperature, high pressure molecular beam nozzle is now available for the acceleration of all non-oxidizing gases and vapors, a signal advance in the field of molecular beam research.
## TABLE I

**Manufacturing Histories of Molded Graphite**  (1)

### TEST SAMPLES

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Filler</th>
<th>Binder</th>
<th>Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>143&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>POCO PCD (-OQ)</td>
<td>CAI&lt;sup&gt;(4)&lt;/sup&gt;</td>
<td>2800</td>
</tr>
<tr>
<td>152&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>CAI (1000 °C)</td>
<td>ITX&lt;sup&gt;(4)&lt;/sup&gt;</td>
<td>2800</td>
</tr>
<tr>
<td>162&lt;sup&gt;(2,3)&lt;/sup&gt;</td>
<td>ITX (1000)</td>
<td>ITX</td>
<td>2800</td>
</tr>
<tr>
<td>169&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>POCO PCD (-9) Q</td>
<td>ITX</td>
<td>2800</td>
</tr>
<tr>
<td>171&lt;sup&gt;(2)&lt;/sup&gt;</td>
<td>POCO PCD (-0) Q</td>
<td>ITX</td>
<td>2800</td>
</tr>
<tr>
<td>172</td>
<td>POCO PCD (-9) Q</td>
<td>Ashland 240 Pitch</td>
<td>2800</td>
</tr>
<tr>
<td>175</td>
<td>ITX (700 °C)</td>
<td>ITX</td>
<td>2800</td>
</tr>
<tr>
<td>POCOAXF5Q Commercial - No History</td>
<td></td>
<td></td>
<td>2500</td>
</tr>
</tbody>
</table>

(1) Filler and binder molded at 1600 psi and 1400 °C, except for POCO AXF5Q. Heated without pressure to 2800 °C.

(2) Impregnated with CAI Polymer.

(3) Same graphite as 175 except 162 was impregnated.

(4) CAI - Cinnamylideneindene.

**NOTES:**

1. These materials were made for NERVA Program, SNC-95.

2. Supplied by Mr. J. M. Napier, Nuclear Division, Union Carbide Corporation P.O. Box Y, Oak Ridge, Tennessee 37330.
ETHANOL COOLING

CURRENT INPUT

HYDROGEN INLET

RHENIUM NOZZLE TUBE

NOZZLE HOLE

ETHANOL COOLING

HYDROGEN MOLECULAR BEAM NOZZLE ASSEMBLY

FIGURE 1
Figure 2. Photograph of graphite sample # 172.
Figure 3. Scanning Electron Microscope Photograph of Boundary between irradiated surface (on right) and shielded surface (magnification X2000), Sample #172.

Figure 4. Same as figure 3 but magnification X4000.
REFERENCES


2-6 Dergazarian, T. E., e.a., "JANNAF Thermochemical Data," Thermal Laboratory, Dow Chemical Company, Midland, December 1960.


REFERENCES CON'T.


APPENDIX A

THEORETICAL DERIVATIONS

Considering a mixture of hydrogen atoms and molecules, and defining \( \alpha \) as the ratio of the mass of hydrogen atoms present in the mixture to the total mass of the mixture, the number densities of \( \text{H} \) and \( \text{H}_2 \) can be determined as

\[
n_{\text{H}} = \frac{\alpha}{m_{\text{H}}} = \frac{2\alpha}{2m_{\text{H}}}
\]

and

\[
n_{\text{H}_2} = \frac{1-\alpha}{m_{\text{H}_2}} = \frac{1-\alpha}{2m_{\text{H}}}
\]

where \( m_{\text{H}} \) is the mass of a hydrogen atom.

Using these expressions the equation of state can be written

\[
\frac{P}{\beta} = kT \left( \sum_i n_i \right) = \frac{k}{2m_{\text{H}}} (1+\alpha)T
\]

where \( k \) is the Boltzmann constant.

From equation (A1) can be deduced

\[
\frac{P}{\beta} = \frac{k}{2m_{\text{H}}} (1+\alpha)T = \frac{\mathcal{R}}{m_{\text{w.mixture}}} T
\]

Or, as

\[
m_{\text{w.mixture}} = \frac{2w_{\text{H}}}{1+\alpha}
\]

where \( w_{\text{H}} \) is the atomic weight of hydrogen and \( \mathcal{R} \) is the universal gas constant, it follows

\[
\frac{\mathcal{R}}{w_{\text{H}}} = \frac{k}{m_{\text{H}}}
\]

(A2)

The enthalpy is defined

\[
h = \frac{P}{\beta} + e
\]

where \( e \) is the specific internal energy of the mixture, with zero energy taken to be that of the atomic species at absolute zero temperature.

As only vibrational, rotational, translational and dissociation energies of the species are considered (electronic excitation is neglected), \( e \) can be written
\[
e = \sum_{i} n_i (E_{\text{dissociation}_i} + E_{\text{translation}_i} + E_{\text{vibration}_i} + E_{\text{rotation}_i})
\]

summed over both species \(i\) in the mixture.

Translation, rotation and vibration are assumed to be in equilibrium, i.e. they have a Maxwell-Boltzmann distribution.

Expressions for the energies are then
\[
E_{\text{rot}_i} = kT/	heta_{V_i}
\]
\[
E_{\text{vib}_i} = \frac{\theta_{V_i}}{e^{\theta_{V_i}/T}} - 1
\]
\[
E_{\text{tr}_i} = 3/2 kT
\]
\[
E_{\text{dis}_i} = k\theta_{D_i}
\]

where
\[
\theta_{V_i} = \text{characteristic vibrational temperature of species } i
\]
\[
\theta_{D_i} = \text{characteristic dissociation temperature of species } i.
\]

As the atomic species has only translational energy, one obtains for the internal energy
\[
e = \frac{k}{2m_H} (\frac{\alpha}{2} + 5/2 + \frac{1-\alpha}{T}(\theta_{V_i}/(e^{\theta_{V_i}/T} - 1) + \theta_{D_i}))T \tag{A3}
\]
and for the enthalpy
\[
h = \frac{k}{2m_H} (3\alpha/2 + 7/2 + \frac{1-\alpha}{T}(\theta_{V_i}/(e^{\theta_{V_i}/T} - 1) + \theta_{D_i}))T \tag{A4}
\]
or
\[
e = e(\alpha, T)
\]
\[
h = h(\alpha, T)
\]

\(\theta_V\) and \(\theta_D\) are the characteristic temperatures of molecular hydrogen.

For the calculation of the specific heat ratio \(\gamma\) and of some other quantities we will need the partial derivatives of the enthalpy.
\[
\frac{\partial h}{\partial T} = h_T = \frac{k}{2\omega_H} \left[ \frac{3}{2} \alpha - \frac{1}{T} \left( \frac{\Theta_v}{e^\Theta_v / T - 1} \right) \right]
\]

\[
\frac{\partial \Theta_v}{\partial T} = \Theta_v \left[ \frac{3}{2} \alpha + \frac{7}{2} + (1 - \alpha) c_6 \right]
\]

where

\[
c_6 = \left( \frac{\Theta_v}{T(e^{\Theta_v / T} - 1)} \right)^2 e^{\Theta_v}
\]

As the specific heat at constant volume \(c_v\) is defined

\[
c_v = \frac{\partial e}{\partial T} = \frac{2}{T} \left( h - \frac{P}{\gamma} \right) = h_T - R
\]

where

\[
R = \frac{(1 + \alpha) \mathcal{P}}{2w_H}
\]

is the specific gas constant of the mixture, and

\[
\gamma = \frac{c_p}{c_v} = 1 + \frac{R}{c_v}
\]

it follows

\[
\gamma = \frac{1}{1 - \frac{k(1 + \alpha)}{2w_H h_T}} \quad (A7)
\]

For the local frozen speed of sound can now be written

\[
a_T = \sqrt{\gamma RT} = \sqrt{\frac{k}{2w_H \gamma(1 + \alpha)T}} \quad (A8)
\]
\[ H_2 + H \xrightarrow{k_f} 2H + H \]

\[ H_2 + H_2 \xrightarrow{k_f} 2H + H_2 \]

where

\[ k_f = \text{forward reaction rate of the } i\text{th third body reaction} \]

\[ k_{b_i} = \text{backward reaction rate of the } i\text{th third body reaction}, \]

the dissociation rate becomes (c.f. ref. 2-7)

\[
\omega = \frac{d\alpha}{dt} = \left( k_{f_1} \alpha + k_{f_2} \left( \frac{1-\alpha}{2} \right) \right) \frac{S}{w_H} \left( 1 - \alpha - \frac{29\alpha^2}{w_H K_C} \right) \quad (A9)
\]

where

\[ K_C = \frac{k_{f_1}}{k_{b_1}} = \text{the equilibrium constant based on concentrations per unit volume for the reaction } H_2 = 2H. \]

As the third body has no effect on the equilibrium concentrations, one can write

\[ k_{f_1} = K_C k_{b_1} \quad \text{and} \quad k_{f_2} = K_C k_{b_2} \]

Substitution of these expressions in equation (A9) yields

\[
\omega = K_C \left( k_{b_1} \alpha + k_{b_2} \left( \frac{1-\alpha}{2} \right) \right) \frac{S}{w_H} \left[ 1 - \alpha - \frac{29\alpha^2}{w_H K_C} \right] \quad (A10)
\]

Ref. 2-10 gives for the values of \( k_{b_1} \) and \( k_{b_2} \) the empirical expressions
Substituting in the equation for \( \omega \), one obtains

\[
\omega = \frac{9 k_H k_f}{w_H} \left( \frac{1}{2} \alpha + \frac{1-\alpha}{2} \right) \left( 1 - \alpha - \frac{29 \alpha^2}{w_H k_c} \right)
\]

or

\[
\omega = \frac{9 k_f}{2w_H} \left[ (1-\alpha)k_c - \frac{29 \alpha^2}{w_H} \right]
\]

As ref. 2-6 gives the equilibrium constant based on partial pressures, we will have to convert the last equation with the aid of

\[
K_c = \frac{k_f^2}{RT} = \frac{w_H k_f^2}{k T u}
\]

where \( K_p \) is the equilibrium constant based on partial pressures, which results in

\[
\omega = \frac{9 k_f}{2w_H^2} \left( \frac{w_H k_f^2}{k} \frac{1-\alpha}{T} - 29 \alpha^2 \right) \quad (A10a)
\]

Eliminating \( p \) with the equation of state (A1) it follows

\[
\omega = \frac{2w_H^2}{k_T (1+\alpha) w_H} k_f \left[ \frac{k_f^2}{4} (1-\alpha^2) - \alpha^2 \right] \quad (A10b)
\]

For equilibrium flow and chemically frozen flow the rate of dissociation is equal to zero, which gives us for frozen flow

\[ f = \text{constant} \]

and for equilibrium flow
\[
\frac{k_p^2}{4P} (1 - \alpha_e^2) - \alpha_e^2 = 0
\]

hence
\[
\alpha_e = \sqrt{\frac{1}{1 + \frac{4P}{k_p^2}}}
\]  \hspace{1cm} (A11)

As \( K_p \) is a function of \( T \) only, \( \alpha_e \) is a function of \( p \) and \( T \) only. The partial derivatives with respect to \( p \) and \( T \) are
\[
\frac{\partial \alpha_e}{\partial p} = -\frac{2\alpha_e^3}{k_p^2} \\
\frac{\partial \alpha_e}{\partial T} = \frac{4P \alpha_e^3}{k_p^2} \frac{d}{dT} (\ln k_p)
\]  \hspace{1cm} (A12a, b)

One-Dimensional Non-Equilibrium Flow

For one-dimensional flow the equations of conservation of momentum and energy and the chemical relaxation equation can be written
\[
h_T \frac{dT}{d\xi} + h_\kappa \frac{w}{w} - \frac{1}{\beta} \frac{dp}{d\xi} = 0
\]
\[
\rho w \frac{d\rho}{d\xi} + \frac{dp}{d\xi} = 0
\]
\[
\frac{d\alpha}{d\xi} = \frac{w}{w}
\]
as shown in 2.1.1.2.

A fourth differential equation for \( \gamma \) can be derived by differentiating the equation of state (A1)
\[
\frac{d\gamma}{d\xi} = \left[ \frac{1}{P} \frac{dp}{d\xi} - \frac{1}{T} \frac{dT}{d\xi} - \frac{1}{1 + \kappa} \frac{d\kappa}{d\xi} \right] \gamma
\]
Rearranging these equations
\[
\frac{dw}{du} = f_1 = -\frac{1}{gw} \frac{dp}{du}
\]
\[
\frac{da}{du} = f_2 = \frac{w}{w}
\]
\[
\frac{dT}{du} = \left[ -\frac{1}{gT^2} \frac{dp}{du} - \frac{l x}{kT} \frac{1}{T} \frac{w}{w} \right] T
\]
\[
\frac{dp}{du} = \left[ -\frac{1}{T^2} \frac{dT}{du} + \frac{1}{T} \frac{dp}{du} - \frac{1}{1 + \alpha} \frac{w}{w} \right]
\]

Combining equations (A1) and (A7) \( \gamma \) can be written

\[
\gamma = \frac{1}{1 - \frac{p}{T_k T}}
\]
or

\[
T_k T = \frac{\gamma p}{\gamma - 1}
\]

Substituting this result in the expressions for the functions \( f_1, f_2, f_3 \) and \( f_4 \) and rearranging them

\[
f_1 = -\frac{1}{gw} \frac{dp}{du} \tag{A13}
\]
\[
f_2 = \frac{w}{w} \tag{A14}
\]
\[
f_3 = \left[ \frac{\gamma - 1}{T} \frac{dp}{du} - B \right] T \tag{A15}
\]
\[
f_4 = \left[ \frac{1}{T} \frac{dp}{du} - A \right] \gamma \tag{A16}
\]

where

\[
B = \frac{l x}{kT_k T} \quad (A17)
\]
\[
A = \frac{1}{1 + \alpha} - B \quad (A18)
\]
For the computation of the one-dimensional non-equilibrium flow we will need the partial derivatives of the functions $f_i$, $B$ and $A$ with respect to $x$, $v$, $\alpha$, $T$ and $g$.

Defining

$$
\begin{align*}
C_2 &= \frac{gkt-k^2(1-u)}{T} \frac{w_H}{2w_H^2} \\
C_3 &= \frac{g^2kt}{w_H^2} \\
C_4 &= \frac{1}{kt} \frac{dk}{dT} \\
C_5 &= \frac{1}{k_T} \frac{dk}{dT} \\
C_6 &= \frac{h_T}{k_T} - \frac{1}{k_T} \left[ \frac{k}{2w_H} \left( \frac{3}{2} e - c_6 \right) \right] \\
C_7 &= \frac{h_T}{k_T} - \frac{1}{k_T} \left[ \frac{k}{2w_H} \left( \frac{3}{2} e - c_6 \right) \right] \\
C_8 &= \frac{h_T}{k_T} = \frac{c_6}{T} \frac{k(1-u)}{2w_H} \left[ \frac{\Theta v}{T} \frac{T+1}{T-1} - 2 \right] ; \quad e = e_{\frac{T}{T}}
\end{align*}
$$

and setting

$$
\frac{\partial}{\partial y_j} f_i = f_i y_j , \quad y_j = \alpha, \omega, w, T \text{ and } g
$$

these derivatives can easily be shown to be

$$
\begin{align*}
\frac{\partial f_i}{\partial \alpha} &= -\frac{1}{g^2w} \frac{d^2p}{d\alpha^2} \\
\frac{\partial f_i}{\partial w} &= -\frac{f_i}{w} \\
\frac{\partial f_i}{\partial T} &= 0
\end{align*} \quad (A13)
$$
\[ t'_{4a} = 0 \]
\[ t'_{3y} = -\frac{1}{2} \]
\[ t'_{2w} = \frac{1}{2} \]
\[ t'_{2a} = -\frac{1}{w} \left[ \frac{c_2}{1-\alpha} + \frac{2c_3}{\alpha} \right] \]
\[ t'_{2T} = \frac{1}{w} \left[ (c_4 + 2c_5 - \frac{1}{T})c_2 - cu c_3 \right] \]
\[ t'_{2y} = \frac{1}{9w} \left[ c_2 - 2c_3 \right] \]

\[ B_w = -\frac{B}{w} \quad \text{(A17)} \]
\[ B_a = \left( \frac{t'_{2a} - c_7}{t_2} \right) B \]
\[ B_T = \left( c_8 + \frac{t'_{2T}}{t_2} - c_9 - \frac{1}{T} \right) B \]
\[ B_y = \frac{t'_{2y}}{t_2} B \]
\[ B_{za} = 0 \quad \text{(A18)} \]

\[ A_w = 0 \]
\[ A_w = -\frac{A}{w} \]
\[ A_a = \frac{t'_{2a}}{1+\alpha} - \frac{t_2}{(1+\alpha)^2} - B_a \]
\[ A_T = \frac{t_2 T}{1+a} - B_T \]
\[ A_\alpha = \frac{t_2 \alpha}{1+\alpha} - B_\alpha \]

\[ t_{3,u} = \frac{Y-1}{Y^2} \left[ \frac{d^2 p}{d u^2} - \frac{1}{p} \frac{dp}{du} \right] T \]
\[ t_{3,w} = -B_w T \]
\[ t_{3,\alpha} = T \left[ \frac{1}{Y^2 p} \left( \frac{d p}{d u} \right) Y_\alpha - B_\alpha \right] \]
\[ t_{3,T} = \frac{t_3}{T} + T \left[ \frac{1}{Y^2 p} \left( \frac{d p}{d u} \right) Y_T - B_T \right] \]
\[ t_{3,\gamma} = -T B_\gamma \]

\[ t_{4,u} = \frac{S}{Y p} \left[ \frac{d^2 p}{d u^2} - \frac{1}{p} \left( \frac{dp}{du} \right)^2 \right] \]
\[ t_{4,w} = -A_w S \]
\[ t_{4,\alpha} = -S \left[ \frac{1}{Y^2 p} \left( \frac{d p}{d u} \right) + A_\alpha \right] \]
\[ t_{4,T} = -S \left[ \frac{1}{Y^2 p} \left( \frac{d p}{d u} \right) + A_T \right] \]
\[ t_{4,\gamma} = \frac{t_4}{S} + S A_\gamma \]

The derivatives \( Y_T \) and \( Y_\alpha \) of the specific heat ratio can be shown to be from equation (A7)

\[ Y_\alpha = Y \left[ \frac{\kappa}{k_\text{eq}} \frac{T}{k_T} - (r-1)c_\alpha \right] \]
\[ Y_T = Y(r-1)c_\alpha \]