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TG 456

IBM 7090 PROGRAM FOR COMPLEX CHEMICAL KINETIC FLOW COMBUSTION

by

S. Favin

AP

THE JOHNS HOPKINS UNIVERSITY
APPLIED PHYSICS LABORATORY
8621 GEORGIA AVENUE SILVER SPRING, MARYLAND

Operating under Contract NOw 62-0604-c with the Bureau of Naval Weapons, Department of the Navy

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ABSTRACT

A Fortran computer program has been developed for the calculation of the one-dimensional flow of a reacting gas through a supersonic nozzle. This report describes the equations and their use in the program. In its present form it handles five chemical elements and fifteen chemical species undergoing thirty reversible reactions. These limitations are easily expanded. The initial conditions and equations required for the solutions of a specific problem are discussed. A solution produces temperature, density, chemical composition, velocity and pressure versus distance and/or time through the specific nozzle. Available thermodynamic and kinetic data built into the program are supplied. A H_2-Air problem is used to illustrate the program.

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LIST OF SYMBOLS AND PROGRAM LOCATIONS

AR A	Cross-sectional area ratio relative to throat; function subroutine AREA(Z).
B	$A_o/\dot{m}$, ratio of area at reference (usually the throat) and mass flow rate (cm^2 sec gm^{-1}); location B.
C_i	Heat capacity at constant pressure of i th species (cal mole^{-1} °K^{-1}); computed in subroutine THERM, stored in Y(I).
D(I)	Fortran location for the derivatives of concentration (moles per gram of mixture per cm) for I th species.
DTEMP	Fortran location of intermediate calculations in DAUX, dT/dZ.
DRHØ	Fortran location of intermediate calculations in DAUX, $d\rho/dZ$.
$E(I^*)$	Fortran location for equilibrium constant K.
F_i	Concentration of the i th chemical species (moles per gram of mixture); location F(I).
H_i	Absolute enthalpy of the i th species (cal mole^{-1}); computed in subroutine THERM, stored in Y(I + 20).
J^*	Mechanical equivalent of heat (ergs cal^{-1}).
k	Reaction rate constant; expressions computed in DAUX, stored in location $C(I^*)$.
K	Equilibrium constant; tables of ln K are stored in subroutine TABLE for a temperature range of 300 to 3500°K.
L	Number of chemical elements present in the gas.
$\bar{M}$	Mean molecular weight, $\bar{M} = (\sum_i F_i)^{-1}$; value stored in T(300).

N	Number of chemical species present in the gas.
n_{ei}	Number of atoms of the e th element in a molecule of the i th species.
NEQ	Number of differential RWINT numerically integrates, NEQ = N - L + 2.
$P(I^*)$	Fortran location to keep or eliminate the left hand product for difference of the rate quantity expression.
PR	Pressure (unit depends on R^* unit).
R^*	Universal gas constant.
$R(I^*)$	Fortran location for rate quantity.
r_i	Net volumetric rate of change of i th species concentration due to chemical reaction (moles cm^{-3} sec^{-1}).
T	Absolute static temperature (°K); always found in T(4).
T( )	Fortran locations for pertinent information for RWINT.
V	Flow velocity (cm sec^{-1}).
W	Total mass flow rate per unit throat area (gm cm^{-2} sec^{-1}).
X_i	Mole fraction of the i th species.
Z	Axial distance coordinate in nozzle (cm); always found in T(2).
a,b,c	Fit coefficients; found in location W(I, 3-5).
ρ	Density (g cm^{-3}); Fortran location T(5).
$\Delta H_f^{298.15}$	Heat of formation (cal $mole^{-1}$); found in location W(I, 1).
$\Delta H_{298.15}^{3000.0}$	The fitted value of molar enthalpy change from 298.15 to 3000.0°K; found in W(I, 2).

subscripts:

i	designates a chemical species
I	designates a chemical species in Fortran
o	designates throat conditions, initial condition or reference
I^*	designates order

I. INTRODUCTION

The problem of calculating the one-dimensional flow of a reacting gas through a supersonic nozzle is essentially numerical and involves the solution of a system of ordinary non-linear differential equations of the first order. Many reports in the literature have described the general problem (Refs. 1, 2, 3, 4)[1] but none of the specific machine programs. In view of this, and since there is some duplication of effort in this field, it was felt worthwhile to describe an IBM 7090 General Nozzle Program (G.N.P.) which solves such systems by utilizing a standard integrating routine (RWINT (Ref. 5)). This report describes the program used by Westenberg and Favin (Refs. 3, 4). Because the problem was programmed for the most part in Fortran, most of their symbols are preserved.

G.N.P. has built into it equilibrium constants expressed in tables and thermodynamic data expressed as polynomials. With this information at hand it is only necessary to specify in Fortran the geometry of the nozzle, the input conditions, and the chemical kinetics to be used. Because most information is programmed directly, the required input data are few and only supply initial conditions, precision of RWINT, and controls for input and output. The program contains 17 subroutines, of which a maximum of eight are specific to a given problem. This report presents a description of each subroutine with the available equations and data. Finally, a H_2 - Air problem is used as a specific illustration.

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[1] References are on page 31.

II. GENERAL EQUATIONS

The list of Fortran statements describes the general equations used by Westenberg and Favin (Refs. 3, 4). It should be emphasized that this report does not justify nor commit itself to the validity of the kinetic constants. G.N.P. was flexibly constructed so that both constants and equations could be easily modified. Machine time, in general, is relatively long and increases with the number of differential equations. With this in mind, it becomes more practical to write specific equations rather than to control general ones through input techniques.

The problem is put in the following mathematical terms:

(a) L element conservation equations of the form

$$\sum_{i=1}^{N} n_{ei} F_i = \text{constant} \quad (e = 1, 2, \ldots, L) \qquad (1)$$

L = number of elements in the gas mixture

N = number of chemical species

F_i = concentration of the <u>i</u> <u>th</u> species in moles per gram of mixture

n_{ei} = number of atoms of element <u>e</u> in a molecule of species <u>i</u>.

(b) N - L species continuity relations of the form

$$\frac{dF_i}{dZ} = ABr_i \quad (i = 1, 2, \ldots, N - L) \qquad (2)$$

r_i = net rate of change in the concentration of species i due to chemical reactions

A = cross-sectional area ratio relative to some reference (usually the throat)

B = W^{-1}, where W has been defined as the total mass flow rate per unit reference (usually the throat) area (Ref. 3).

(c) Temperature (T) and density (ρ) derivatives as

$$\frac{dT}{dZ} = \frac{J\left[(R^*\sum_i F_i)^{-1} - T\rho^2A^2W^{-2}\right]\sum_i H_i\left(\frac{dF_i}{dZ}\right) + T\left[A^{-1}\left(\frac{dA}{dZ}\right) - \left(\sum_i F_i\right)^{-1}\sum_i\left(\frac{dF_i}{dZ}\right)\right]}{1 - J\left[(R^*\sum_i F_i)^{-1} - T\rho^2A^2W^{-2}\right]\sum_i F_iC_i} \qquad (3)$$

and

$$\frac{d\rho}{dZ} = \rho^3A^2W^{-2}\left\{\frac{(dT/dZ) - T\left[A^{-1}(dA/dZ) - \left(\sum_i F_i\right)^{-1}\sum(dF_i/dZ)\right]}{(R^*\sum_i F_i)^{-1} - T\rho^2A^2W^{-2}}\right\} \qquad (4)$$

H_i = absolute molar enthalpies

C_i = molar heat capacity at constant pressure

J^* = mechanical equivalent of heat

R^* = universal gas constant.

NEQ = Expressions (2) - (4) constitutes a set of N - L + 2) ordinary first order, nonlinear differential equations. The derivatives of the L elementary equations are calculated directly from Eq. (1).

(d) Miscellaneous side calculations.

Pressure (PR) and flow velocity (v) can be calculated from equations of state and over-all continuity, respectively.

$$PR = \rho RT \sum_i F_i \tag{5}$$

$$v = \frac{W}{\rho A} \tag{6}$$

Mean molecular weight ($\bar{M}$) and mole fraction (X_i) are defined as

$$\bar{M} = \sum_i F_i \tag{7}$$

and

$$X_i = F_i \bar{M} \tag{8}$$

III. DESCRIPTION OF SUBROUTINES

"Order" plays an important role in the ease of handling composition, its derivatives and corresponding thermodynamic data, and expressions and tables defining kinetics. This is accomplished with the use of DIMENSIØN and EQUIVALENT statements. In the main, information flows from one subroutine to another via CØMMØN statements.

At the present time the concentration of hydrogen molecule is ordered first. Its value can be found in the cell symbolically named FH2 which is EQUIVALENT to the name F(1). The value of its derivative is found in D(1). F(2) has been arbitrarily assigned to FH2Ø; its derivative is called D(2); and so forth. (See Appendix A for present order.) In this paper, I is for species order and I^* is for kinetic order.

The subroutines fall into one of three categories:

(a) variable,
(b) fixed, and
(c) service.

Types (a) and (b) have been written by the author and can be changed to meet the problem. Type (b) should be changed only when new species are added. Type (c) should never need editing. The list of names and their categories is given in Table I.

Table I

SUBROUTINES AND THEIR CATEGORIES

(a) Variable	(b) Fixed	(c) Service
DAUX	MAIN-P	RWINT
DERSP	INCØN	TØDAY
AREA	CØNSER	NTRP11
DAREA	THERM	ECØE
INPUT	TABLE	
TERM		
WØT		
CMAS		

The subroutines are described below in the order of their logical appearance. Appropriate examples are given in Section IV.

MAIN-Program

The MAIN routine is the driver program. It calls for the subroutines at the proper time.

TØDAY

An accurate log of runs made is quite helpful. The data read in is printed with page numbers on each page of output.

INCØN

This subroutine and CØNSER and INPUT are entered only once per problem. INCØN initializes certain variables and always reads in 3 cards (see Appendix B).

INPUT

The initial conditions can be presented here. If desired, they can be read in as data on data cards.

(See Appendix B.II.) NEQ, the number of differential equations seen by the integration routine, is stated at this time.

<u>CØNSER</u>

Constants for the element conservation Eqs. (1) are computed and stored in symbolic location CØN (L). At present the constant for

hydrogen is stored in CØN (1),
oxygen, in CØN (2),
nitrogen, in CØN (3), and
carbon, in CØN (4).

<u>RWINT</u> ... INT and INTM

Subroutine RWINT is a FAP coded subprogram designed to integrate a set of simultaneous, first order differential equations numerically. Calling sequence for the set up (performed prior to initiating the integration) is INT; INTM is called to integrate one integral step. The fourth order Runge-Kutta-Blum (RKB) is used to start the process which continues with the Adams-Moulten (AM) method with a variable step-size feature. Starting values for the AM formulas are always obtained using the RKB method whenever the interval size is changed. If, after calculating 4 steps and the last 3 steps are not within the required precision, the step-size will be halved and will start over at the first step. If only steps 2 and 3 are within the limit, the step-size is halved and the new start is initiated at step 5. The author urges G.N.P. users to refer to Ref. (5) for a more detailed description.

DAUX

Equations (2), (3), (4), and (7) will have been solved for one step before exiting this subroutine. **RWINT** requires certain variables be placed first in **CØMMØN**. They are assigned as follows:

NEQ = number of equations, N - L + 2
T(2) = independent variable (distance), Z
T(3) = ΔZ, increment
T(4) = T, temperature
T(5) = ρ, density
T(6) = F_1, species i = 1
T(7) = F_2, species i = 2
⋮
T(NEQ + 3) = F_j, last species (i.e., j = N - L)
T(NEQ + 4) = dT/dZ
T(NEQ + 5) = $d\rho/dZ$
T(NEQ + 6) = dF_1/dZ
T(NEQ + 7) = dF_2/dZ
⋮
T(2NEQ + 3) = dF_j/dZ

On entering **DAUX** the F_i's are set equal to their corresponding T(j), j = 6, NEQ+3 and their derivatives are assigned properly on leaving. After the latter is performed, the Accumulator Overflow is tested. If it is on, a message, --AC HAS ØVERFLØWED – will be printed and the problem will continue; if it is off, the routine continues normally.

At one time it was thought that there could be no solution if any arithmetic calculation produced a number greater than 10^{38}. But a valid solution can sometimes occur. RWINT senses this overflow and will back up a few steps, halve the interval and proceed again. If the overflow message is printed many times between lines of output, more than likely it is not valid and an investigation of the system and initial conditions is warranted.

CMAS

The L elementary species are computed (Eq. 1) based on the constants CØN calculated in CØNSER. This is performed after entering DAUX with a new step. (The new N - L species, temperature and density, were produced by RWINT.)

TABLE

This is a FAP subroutine that contains the tables of the natural logarithms of the equilibrium constants K for temperature every 100 degrees Kelvin from 300 to 3500. (See NTRP11 and ECØE.)

NTRP11

This is a service routine (Ref. 6) written in FAP which linearly interpolates the tables of Temperature vs ln K for a given T-value. It will extrapolate outside the given temperature range.

ECØE

ECØE employs NTRP11 which in turn "looks-up" ln K. Values of ln K are stored in the same order, I^*, as the elementary reactions presented in Appendix A, Table III. Because the temperature will always be found in Fortran location T(4), a value K_m for the m^{th} elementary reaction, E(M), for a specific temperature, T(4), can be obtained from the following statement:

$$E(M) = EXPF(EC0E(M)) \tag{9}$$

AREA

AREA is a function subroutine. For a given distance Z the value for A is calculated.

DAREA

DAREA is also a function subroutine. It computes A^{-1} (dA/dZ) = d ln A/dZ for given Z.

THERM

A polynominal of the form shown in Eq. (10) was chosen (Ref. 7) in order to be consistent with our equilibrium calculations (Refs. 3, 4, 8).

A least squares fit to the tabulated enthalpy $(H - H_{298.15})$ (Ref. 9) was made so that

$$C = a + bX + cX^{-2} \tag{10}$$

and

$$H = H^{\circ} + \int_{3000}^{X} C \, dx \tag{11}$$

$$H^{\circ} = \Delta H_f^{298.15} + \Delta H_{298.15}^{3000.0}$$

H is the total enthalpy; C is the heat capacity; $\Delta H_f^{298.15}$ is the heat of formation; $\Delta H_{298.15}^{3000.0}$ is an integration constant from the standard reference temperature of 3000°K.

a, b, c are fit coefficients and X is temperature in °K.

The fit coefficients (a, b, c) and ($\Delta H_f^{298.15}$ and $\Delta H_{298.15}^{3000.0}$) are shown in Table II.

W0T

A separate subroutine is set aside to control and print titles and answers. For a particular problem, Fortran statements 21 to 22 are left for the programmer to write. FØRMAT 5 is for page title printed at top. FØRMAT 6 is for number fields. JL is the line counter (e.g., JL = JL + 2 implies two lines of information per integration step).

TERM

This routine can control the termination point of the machine calculation. It also can be used for controlling printout. (i.e., if one is printing out every 20th step and wants to see every step after a certain condition is met, set L = 3. To stop the program, set L = 2.)

At present, almost any parameter or combination of parameters can be investigated.

IV. H_2 + AIR EXAMPLE

Consider the equilibrium conditions (Ref. 8) of a H_2 + Air, ER = 1, gas mixture at the throat of a diverging nozzle to be:

$$\left.\begin{array}{llcl}
\text{composition:} & \text{FH2} & = & \text{2.8612E-3}^{2} \\
 & \text{FH2Ø} & = & \text{9.3965E-3} \\
 & \text{FØ2} & = & \text{1.0001E-3} \\
 & \text{FØH} & = & \text{1.9980E-3} \\
 & \text{FH} & = & \text{1.7704E-3} \\
 & \text{FØ} & = & \text{7.4710E-4} \\
 & \text{FN2} & = & \text{2.6601E-2} \\
\text{temperature:} & \text{T(4)} & = & \text{3000.0} \\
\text{density:} & \text{T(5)} & = & \text{9.1544359E-5}
\end{array}\right\} \qquad (12)$$

Since N_2 composition was given no chemical reaction, N = 6 and L = 2. Then

$$\text{NEQ} = 6. \qquad (13)$$

These will undergo some of the reactions listed in Appendix A. Namely,

$$I^{*} = 1, 2, 3, 4, 14, 15, 19, 20.$$

The rate constants k associated with these eight reactions are:

C(1) = 1.0E+15 * EXPF(-2.5E+4/RT)
C(2) = 5.0E+14 * EXPF(-1.8E+4/RT)

---

[2] These expressions are in Fortran code. The first expression, FH2 = 2.8612E-3, means $F_{H_2} = 2.8612 \times 10^{-3}$.

$$\left.\begin{array}{lll} C(3) & = & 7.0E+12 * EXPF(-0.85E+4/RT) \\ C(4) & = & C(2) \\ C(14) & = & 2.0E+18/T(4) \\ C(15) & = & C(14) \\ C(19) & = & 3.0E+19/T(4) \\ C(20) & = & C(14) \end{array}\right\} \quad (14)$$

where

$$RT = 1.9872 * T(4)$$

Only four rate equations of the form (2) are needed with six chemically reacting species and two elements.

$$\left.\begin{array}{lll} H_2: & D(1) & = T(296) * (R(1) - R(3) + R(14)) \\ H_2O: & D(2) & = T(296) * (-R(1) - R(2) + R(19)) \\ O_2: & D(3) & = T(296) * (-R(4) + R(15)) \\ OH: & D(13) & = T(296) * (R(1) + 2.0*R(2) + R(3) + R(4) \\ & & \quad - R(19) + R(20)) \end{array}\right\} \quad (15)$$

where

$$T(296) = B * T(5) * T(5) * AR$$

$$AR = AREA\ (T(2))$$

H and O atom rates can be derived from the element convervation Eqs. (1).

$$\left.\begin{array}{lll} H: & D(10) & = -(2.0 * D(1) + D(2) + D(13)) \\ O: & D(11) & = -(2.0 * D(3) + D(2) + D(13)) \end{array}\right\} \quad (16)$$

The rate quantities $R(I^*)$ which arithmetically make up r_i for each species i are listed in Appendix A.IV.

Consider the nozzle geometry to be a simple conical expansion with 25° total having an inlet radius of 1 cm. Therefore

```
FUNCTIØN AREA (Z)
AREA = (0.22169 * Z + 1.0) ** 2
RETURN
END
```

and

```
FUNCTIØN DAREA (Z)
DAREA = (2.0*0.22169)/(0.22169*Z + 1.0)
RETURN
END
```

Subroutine INPUT will now consist of Fortran expressions (12) and (13).

Fortran location 2 may be

```
2 READ INPUT TAPE 5,1,T(2),T(4),T(5),FH2,FH2Ø,FØ2,FØH,FH,FØ,FN2
1 FØRMAT (6E12.7)
```

This depends on the programmer and his IBM 7090 installation.

In subroutine DAUX the first assignment starts at location 40. It will read as follows:

```
40 FH2   =  T(6)
   FH2Ø  =  T(7)
   FØ2   =  T(8)
   FØH   =  T(9)
```

After the CMAS is called to get FH and FØ, ΣF_i is calculated and placed in T(300).

```
T(300)  =  FH2 + FH2Ø + FØ2 + FØH + FH + FØ + FN2
```

Then the equilibrium constants, K_I*, are obtained:

```
E(1)   =  EXPF(ECØE (1))
E(2)   =  EXPF(ECØE (2))
E(3)   =  EXPF(ECØE (3))
E(4)   =  EXPF(ECØE (4))
E(14)  =  EXPF(ECØE (14))
E(15)  =  EXPF(ECØE (15))
E(19)  =  EXPF(ECØE (19))
E(20)  =  EXPF(ECØE (20))
```

The rate constants, expression (14), and the rate quantities $R(I^*)$ are computed.

The derivatives of the species, expressions (15) and (16), are calculated in DERSP and then the value of

$-(\sum_i F_i)^{-1} \sum_i (dF_i/dZ)$ is written as

```
T(297) = -(D(1) + D(2) + D(3) + D(10) + D(11) + D(13))/T(300)
```

DTEMP and DRHØ are expressed generally. These equations can be easily altered.

Now assign the proper locations to enter RWINT starting at location 9

```
9 T(6)   =  FH2
  T(7)   =  FH2Ø
  T(8)   =  FØ2
  T(9)   =  FØH
  T(10)  =  DTEMP
  T(11)  =  DRHØ
  T(12)  =  D(1)
```

```
T(13)  =  D(2)
T(14)  =  D(3)
T(15)  =  D(13)
```

"What to print," "when to stop," and the data deck are now left.

If the plan is to stop integrating when **AR** ≥ 80 and to see every step past **AR** ≥ 50, then subroutine Term will be

```
      AAA  =  AREA(T(2))
      IF (50.0-AAA) 30,30,10
   30 IF (L - 2) 20,10,10
   20 L  =  3
   10 IF (80.0-AAA) 1,2,2
    1 L  =  2
    2 RETURN
      END
```

For printing, assume two lines per step.

The first line will have

Z,T,RHØ,FH2,FH2Ø,FØ2,FØH,FH,PRESSURE

and the second

$$\text{AREA},\ \frac{dT}{dZ},\ \frac{dRHØ}{dZ},\ \frac{dFH2}{dZ},\ \frac{dFH2Ø}{dZ},\ \frac{dFØ2}{dZ},\ \frac{dFØH}{dZ},\ \text{FØ},\ \text{VELOCITY}\ .$$

The idea is to squeeze in as much as possible.

(Pressure in atms and velocity in cm/sec are obtained from Eqs. (5) and (6), respectively.)

To do this the following Fortran statements in subroutine WØT will be

```
  5   FØRMAT(5X8HZ / AREA8X1HT11X3HRHØ11X2HH210X3HH2Ø
   1     8X5HH / Ø8X5HP / V)
  6   FORMAT (1PE15.7,E14.6,7E13.5/1X,OPF13.8,1X,
   1          1PE14.6,7E13.5)
 21   PR = T(4)*T(5)*T(300)*82.057
      AR = AREA(T(2))
       V = 1.0/(AR*B*T(5))
      WRITE ØUTPUT TAPE 6,6,T(2),T(4),T(5),FH2,FH2Ø,
  1                         FØ2,FØH,FH,PR,AR,T(10),T(11),
  2                         D(1),D(2),D(3),D(13),FØ,V
      JL = JL + 2
 22   RETURN
```

The value of B must be established for the Data Deck. As part of the initial conditions assume that this gas has a flow velocity of 5×10^5 cm/sec. From Eq. (6) and

$$\frac{A_o}{\dot{m}} = B = W^{-1} ,$$

and therefore

$$B = \frac{1}{\rho v AR},$$

and our throat conditions are at zero, AR = 1,

$$B = \frac{1}{9.1544359\times10^{-5} \times 5.0 \times 10^{+5}} = 2.1847332 \times 10^{-2}.$$

Card 1:

Col. 1-8: 12/31/62

Card 2:

Col. 3: 1
Col. 20: 1
Col. 39: 1
all other columns are blank

Card 3:

Col. 1-12: 2.1847332E-2
Col. 13-24: 1.0E-8
Col. 25-36: 1.0E-6
Col. 40-41: 25
Col. 45-46: 10

Card 4:

Columns 1-30 are all one's.

If a Frozen Flow is desired showing every step, then

Card 5:

Col. 3: 1
Col. 13: 1
all other columns are blank

Card 6:

Col. 1-12: 2.1847332E-2
Col. 13-24: 1.0E-8
Col. 25-36: 1.0E-6
Col. 40-41: 25

Card 7:

blank card

A detailed description of the input-output formulas is given in Appendix B.

V. CONCLUSION

This IBM-7090 computer program has proven to be useful in one-dimensional flow studies. Programming the problem in Fortran makes it adaptable for special insertions and revisions. The versatility of the integrating routine allows the solution of other systems of differential equations either separately or with the ones described in this report. For example, the H_2-Air problem was run with the restriction that velocity and pressure remain constant. The conversion from the original equations was handled speedily and with ease.

APPENDIX A

AVAILABLE INFORMATION IN G.N.P.

I. Composition: Space for 20 species was made. A sample list of species and their assigned order is below:

1. H_2
2. H_2O
3. O_2
4. N_2
5. NO
6. NO_2
7. CO
8. CO_2
9. CH_4
10. H
11. O
12. N
13. OH
14. CH_3

15-20. Not presently used

II. Thermodynamic data for individual chemical species were calculated by an auxiliary IBM program from the U. S. Naval Ordnance Test Station (Refs. 7 and 8) which produced the coefficients a, b, c, and $\Delta H_{298.15}^{3000.0}$. The coefficients found in subroutine THERM in G.N.P. are as follows:

Table II

Thermodynamic Data

Order	Species	$\Delta H_f^{298.15}$ cal/mole	$\Delta H_{298.15}^{3000.0}$ $\times 10^4$	a	$b \times 10^{+4}$	$c \times 10^{-4}$
1	H_2	0.0	2.12345	6.42855	8.64880	-2.50591
2	H_2O	-57797.9	3.02728	9.18719	15.4169	-69.2461
3	O_2	0.0	2.34447	8.12927	4.85368	-27.5743
4	N_2	0.0	2.21820	7.97126	3.49537	-42.8312
5	NO	21652.0	2.27519	8.01039	3.77348	-15.4347
6	NO_2	8060.0	3.82491	10.5130	23.8926	-27.9960
7	CO	-26416.0	2.23754	8.13878	3.02427	-44.1544
8	CO_2	-94052.0	3.65606	13.6291	5.04544	-104.589
9	CH_4	-17889.0	5.36247	19.9055	19.9409	-496.670
10	H	52102.0	1.34219	4.96913	-0.00714522	-0.0282708
11	O	59559.0	1.35186	4.95165	0.100159	+3.51743
12	N	113054.0	1.34344	4.94684	0.122082	+0.665158
13	OH	9330.0	2.14857	6.80978	7.42330	-14.3735
14	CH_3	32000.0	4.29528	11.5620	32.8539	-127.486

III. Elementary Reactions

The elementary reactions (Table III) are in the same order as the equilibrium constants K_I^* are stored in subroutine TABLE. They are defined as reactants (on left) divided by products (on right). The specific rate constants are forward (e.g., k_I^*) and reverse (k_{-I}^*) steps which are related by $K_I^* = k_{-I}^*/k_I^*$. Following this same order, for example, k_I^* is calculated and stored in $C(I^*)$. The data used to obtain these constants (K_I^*) are from Ref. (9).

Table III

Elementary Reactions

1. $H_2O + H \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} H_2 + OH$
2. $H_2O + O \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} OH + OH$
3. $H_2 + O \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} OH + H$
4. $O_2 + H \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} OH + O$
5. $O_2 + N \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} NO + O$
6. $N_2 + O \underset{k_{-6}}{\overset{k_6}{\rightleftarrows}} NO + N$

7. $NO_2 + O \overset{k_7}{\underset{k_{-7}}{\rightleftarrows}} NO + O_2$

8. $NO_2 + H \overset{k_8}{\underset{k_{-8}}{\rightleftarrows}} NO + OH$

9. $NO_2 + N \overset{k_9}{\underset{k_{-9}}{\rightleftarrows}} NO + NO$

10. $CO + OH \overset{k_{10}}{\underset{k_{-10}}{\rightleftarrows}} CO_2 + H$

11. $CH_4 + H \overset{k_{11}}{\underset{k_{-11}}{\rightleftarrows}} CH_3 + H_2$

12. $CH_4 + O \overset{k_{12}}{\underset{k_{-12}}{\rightleftarrows}} CH_3 + OH$

13. $CH_4 + {}^{\cdot}OH \overset{k_{13}}{\underset{k_{-13}}{\rightleftarrows}} CH_3 + H_2O$

14. $H + H + M \overset{k_{14}}{\underset{k_{-14}}{\rightleftarrows}} H_2 + M$

15. $O + O + M \overset{k_{15}}{\underset{k_{-15}}{\rightleftarrows}} O_2 + M$

16. $N + N + M \overset{k_{16}}{\underset{k_{-16}}{\rightleftarrows}} N_2 + M$

17. $\mathrm{N + O + M} \underset{k_{-17}}{\overset{k_{17}}{\rightleftarrows}} \mathrm{NO + M}$

18. $\mathrm{O + NO + M} \underset{k_{-18}}{\overset{k_{18}}{\rightleftarrows}} \mathrm{NO_2 + M}$

19. $\mathrm{H + OH + M} \underset{k_{-19}}{\overset{k_{19}}{\rightleftarrows}} \mathrm{H_2O + M}$

20. $\mathrm{H + O + M} \underset{k_{-20}}{\overset{k_{20}}{\rightleftarrows}} \mathrm{OH + M}$

IV. Rate quantities $R(I^*)$ are defined as follows:

$$R(1) = k_1 \left(F_{H_2O}F_H - K_1 F_{H_2} F_{OH}\right).$$

But in the Fortran language, using the above notation, they are

```
R(1)  = C(1)  * (FH2Ø * FH - E(1)  * FH2 * FØH)
R(2)  = C(2)  * (FH2Ø * FØ - E(2)  * FØH * FØH)
R(3)  = C(3)  * (FH2 * FØ - E(3)  * FØH * FØ)
R(4)  = C(4)  * (FØ2 * FH - E(4)  * FØH * FØ)
R(5)  = C(5)  * (FØ2 * FN - E(5)  * FNØ * FØ)
R(6)  = C(6)  * (FN2 * FØ - E(6)  * FNØ * FN)
R(7)  = C(7)  * (FNØ2 * FØ - E(7)  * FNØ * FØ2)
R(8)  = C(8)  * (FNØ2 * FH - E(8)  * FNØ * FØH)
R(9)  = C(9)  * (FNØ2 * FN - E(9)  * FNØ * FNØ)
R(10)= C(10) * (FCØ * FØH - E(10) * FCØ2 * FH)
R(11)= C(11) * (FCH4 * FH - E(11) * FH2 * FCH3)
R(12)= C(12) * (FCH4 * FØ - E(12) * FØH * FCH3)
```

```
R(13) = C(13) * (FCH4 * F0H - E(13) * FH20 * FCH3)
R(14) = C(14) * (T(5) * FH * FH - E(14) * FH2/RT) * T(300)
R(15) = C(15) * (T(5) * F0 * F0 - E(15) * F02/RT) * T(300)
R(16) = C(16) * (T(5) * FN * FN - E(16) * FN2/RT) * T(300)
R(17) = C(17) * (T(5) * F0 * FN - E(17) * FN0/RT) * T(300)
R(18) = C(18) * (T(5) * FN0 * F0 - E(18) * FN02/RT) * T(300)
R(19) = C(19) * (T(5) * FH * F0H - E(19) * FH20/RT) * T(300)
R(20) = C(20) * (T(5) * FH * F0 - E(20) * F0H/RT) * T(300)
```

$$RT = 82.057 \left(\frac{cm^3 \ atm}{mole \ {}^\circ K}\right) \ x \ T(4)$$

T(4) = value of Temperature (°K)

T(5) = value of Density (gm/cm^3)

$T(300) = \sum_i F_i$

$$V. \quad D(I) = \frac{dF_i}{dZ} = AR \left(\frac{A_o}{\dot{m}}\right) \rho^2 \left(\sum_{\ell_i} R(I^*) \ (-1)^{m_i} \right), \ i = I$$

where ℓ_i are those rate quantities necessary for species i to express their net rate of change. $(-1)^{m_i}$ is the direction of the rate for species i.

$\left(\frac{A_o}{\dot{m}}\right) \left(\frac{cm^2 sec}{gm}\right)$ is actual area at Z = 0 and $\dot{m}$ $(\frac{gm}{sec})$ is the mass flow rate.

APPENDIX B

INPUT - OUTPUT - DATA CARDS AND PRINTOUT

I. Input Deck

The first card, the date, was originally just a luxury, but has since proven quite useful. The next card, 2, is the Control Card to any problem.

Card 1: example 12/31/62
Col. 1-2: month (numbered)
Col. 3: / (slash)
Col. 4-5: day (numbered)
Col. 6: / (slash)
Col. 7-8: year (minus 1900)

This card is used only once in stacking problems.

Card 2: Control Card

Col.		
1	if = 1	Read in new initial conditions. Overlook values stored in INPUT. (The programmer may request all or any values read in. Same problems may use the same initial composition but only change Temperature. (See paragraph II.)
2	blank	Not used.

Col.		
3	must = 1	If this number is zero, data output described under Initial Conditions will be printed out every time DAUX is called.
4-6	blank	Partial use of output in Initial Conditions.
5-12	blank	Not used.
13	if = 1	Will yield Frozen Flow only. (i.e., $dF_i/dZ = 0$ for all Z)
14-19	blank	Not used.
20	must = 1	If and only if $M > 1$. (M is the frequency of output found on data card 3.)
21-24	blank	Not used.
25	if = 1	Read in the values of the initial derivatives. (See paragraph II.)
26-38	blank	Not used.
39	if = 1	Will print out C_i and H_i for the first step only. If Col. 3 is zero, all steps will be printed out. (See paragraph III.)
40-70	blank	Not used.
71-72	blank	Used by the program.

Card 3: Format (3E12.8, 2I5)

Col.	
1-12	value of $\frac{A_o}{\dot{m}} = B$
13-24	ΔZ, starting increment, either positive or negative.

Col.	
25-36	Precision. This cell contains the upper bound for the truncation error test done in the predictor-corrector mode. This value can range between 10^{-8} and 10^{-3}.
37-41	Number of pages of output.
42-46	$M \geq 1$ is the frequency of output. (All steps of integration will be printed until the first page is filled; then only every Mth step is printed. If desired, as explained in subroutine **TERM**, every step can be printed once more.)

Card 4: Under ordinary conditions columns 1 through 30 of this card will each be punched with a "1." This is used to set certain parts of the rate quantities equal to zero, i.e., for the expression

$$R(1) = k_1 \left(F_{H_2O} F_H - K_1 F_{H_2} F_{OH}\right) .$$

It is easy to set $K_1 = 0$ or to another value, but at times it would be interesting to see the effect of setting $F_{H_2O}F_H$ to zero without making these compositions void. Therefore, one will find in subroutine DAUX

```
R(1) = C(1)*(P(1)*FH2Ø*FH - E(1)*FH2*FØH).
```

The same is true for all rate quantity expressions.

If column 1 of card 4 is zero, then P(1) = 0 and

$$R(1) = k_1(-\ K_1\ F_{H_2}\ F_{OH})$$

and so forth.

To run a second problem follow same rule as cards 2, 3, and 4.

II. Auxiliary Input

A "1" punched in column one of the control card indicates to subroutine INPUT that data is to be read in under the control of its READ statement 2. The data to be supplied and its format is left to the programmer. This data will follow card 4.

A "1" punched in column 25 of the control card implies that the initial derivatives should be read in and no initial execution is performed in subroutine DAUX. The information to be read in is ordered as follows:

Location 2 in subroutine DAUX:

```
Read input tape 5, 3, DTEMP, DRHØ, D
```

Location 3 Format (6E12.8)

where

DTEMP = dT/dZ
DRHØ = $d\rho/dZ$

D is dimensioned (20). D's are the derivatives of the composition in I order and calculated in subroutine DERSP. Again, the programmer has the choice to change it.

III. Output

The general output is controlled by the programmer in subroutine **WØT**. A general title is printed by way of Format numbers 38 and 40 where 40 is printed for a frozen case. Format 5 is for specific title under numbers following the form given in Format 6.

But for the first initial step, many items are printed out under the heading **INITIAL CONDITIONS**. Much of this output is controlled by the Control Card in the Input data. Subroutine **INCØN** will automatically printout the constants for the element conservation equations. The initial temperature, T_o, and specific heat, C_i, and enthalpy, H_i in the proper order will be printed next if column 39 of the control card is not blank or zero. This output is done by subroutine **THERM**. The rest of this output, found in DAUX, was used to debug but still may be useful. This output will be printed for every integration step unless column 3 is "1."

These locations will again be printed out before terminating any problem, whether by maximum page number or by **TERM**; thus the problem can be continued at that point.

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