# STANJAN

## INTERACTIVE COMPUTER PROGRAMS FOR CHEMICAL EQUILIBRIUM ANALYSIS

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## Interactive Computer Programs for Chemical Equilibrium Analysis

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## Abstract

This report describes a flexible and robust program for making chemical equilibrium calculations in an interactive computing setting. The program has proven to be an excellent asset for use in classes in thermodynamics, combustion, propulsion and energy conversion, and should also be very useful in industrial applications. The report describes the operation of the program, the basic underlying science, the key numerical methods employed, the management of the supporting data file, and the procedures one follows to obtain the programs and implement them on the user's own computer. A procedure that one may follow to try out the program by telephone link to the Stanford computer is given.

# Acknowledgments

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# I. OVERVIEW

## 1. Introduction

STANJAN is a set of computer programs developed at Stanford for analysis of chemical equilibrium problems arising in combustion, MHD systems, propulsion and other applications. The set consists of JANAF, an interactive program which makes it very easy to run a stream of problems with different species; JFILE, JPACK, and JALPH, a set of programs used to maintain and update the basic chemical data file; and a set of subroutines that can be called by the user's programs to do chemical equilibrium analysis as part of other thermodynamic process analysis.

The program treats the gas phase as a mixture of ideal gases and condensed phases as separated incompressible solids or liquids. The thermochemical data base is taken from and structured by the JANAF tables--hence the name.

The JANAF program is extremely flexible and is ideal for use either as a teaching tool or in engineering analysis. The user specifies the names of the species involved. If they are on file, the only other information needed is the relative atomic populations and the operating conditions (e.g., temperature and pressure, or enthalpy and pressure, etc.). If they are not on file, the user must read in thermochemical data from the JANAF tables. If calculations are to be made with unfiled substances at more than one or two temperatures, the user can enlarge the data file to include the new substance using the JFILE program. All of these programs are interactive and self-instructing, very robust, and very tolerant of user error.

The equilibrium calculations use a version of the method of element potentials developed by the author. In this method, described in Chapter II, exact equations for the gas-phase mole fractions are derived in terms of Lagrange multipliers associated with the atomic constraints. These Lagrange multipliers (the "element potentials") and the total number of moles are adjusted to meet the constraints and to render the sum of the mole fractions unity. Thus, if one has $c$ species and $a$ atoms, where $c$ can be much larger than $a$, one need only adjust $a+1$ quantities. This is in contrast to most other methods for equilibrium analysis in which all of the unknown mole fractions are adjusted in a massive iteration process. If condensed

phases are present, their populations also must be adjusted to achieve phas equilibrium. However, the condensed-phase species need not be present in th gas phase, and this enables the method to deal with problems in which the ga phase mole fraction of a condensed species is extremely low, as with the formation of carbon particulates.

The element potential is a concept not widely known in the thermodynamics community. However, one can show that, at equilibrium, each atom of eac element contributes exactly the same amount to the Gibbs function of eac species, regardless of what species or phase that atom is in. This provides very useful way to estimate the concentrations of minor species that may no have been included in the calculation. For example, one can consider a mixture of $O_2$ and $CO_2$, with mole fractions determined simply by the C an O atomic populations. From these mole fractions the element potentials ca be calculated, and these potentials used to estimate the mole fractions of O CO, and C in the mixture. If these mole fractions are small, the estimate will be very good and will have been obtained without doing *any* equilibriu calculations. Examples showing the use of element potentials in making suc estimates are given in Chapter III.

These programs are written in a broadly acceptable FORTRAN, and have bee extensively tested on both DEC and IBM systems. The interactive program i mounted on Stanford's DEC-20 system at the LOTS computation facility. Tape of the programs and data files may be obtained from the author; potentia users having telephone-coupled terminals may make arrangements to try th program on the LOTS system before ordering the tape. For more details se Chapter V.

The remainder of this chapter is devoted to several examples that displa the use of the programs. These examples should be more than adequate as primer for the potential user. For the user who wants to dig more deeply int the programs, they have been liberally commented and written in a consisten and structured manner for easy understanding by anyone who understands th basic method described in Chapter II.

## 2. Examples

We shall now present a series of examples. These will illustrate the main features of the JANAF program and should serve as an adequate primer for the user. Additional help will be provided by the program itself when the user encounters difficulty. Each example below is a transcript of an actual run. User inputs are single lines following lines ended with a ? character. All user lines are ended with a carriage return. Blank user lines just involved the carriage return.

For the first example, let's set up a problem involving the dissociation of $CO_2$. We shall allow the mixture to contain $CO_2$, CO, $O_2$, and O, and solid carbon C(s). The program does not require us to include C in the gas, but we if we wanted to we could. We shall set the equilibrium composition at 1 atm and 3000K for a mixture with two atoms of carbon per atom of O. Other equilibrium programs are reported to have difficulty with carbon-rich mixtures of this type, so this will be a good test of the robustness of the program.

The user must first define logical unit 21 as the JANAF package data file (see Section IV.3). The program JANAF will look for the data in this file. Then the JANAF program is called, and the transactions begin:

```
WELCOME TO THE STANFORD CHEMICAL EQUILIBRIUM FINDER.
YOU WILL BE GUIDED IN PREPARING THE INPUT FOR A REACTION
EQUILIBRIUM PROBLEM THAT INVOLVES A MIXTURE OF IDEAL GASES
AND POSSIBLE CONDENSED SPECIES, SUCH AS C(S) OR H2O(L).

ALL ALPHABETIC RESPONSES MUST BE IN CAPITAL LETTERS.
IF POSSIBLE, SET YOUR TERMINAL FOR ALL CAPS.

IF YOU HAVE DIFFICULTY, CALL THE PROGRAM DEVELOPER:
 W. C. REYNOLDS 415-497-4021; M.E. DEPT., STANFORD 94305


WHAT IS YOUR REQUIRED LEVEL OF
INSTRUCTION (MUCH,SOME,NONE)?
MUCH

YOU WILL PUT IN DATA IN RESPONSE TO PROMPTS.
IF YOU MAKE A MISTAKE, CONTINUE RESPONDING WITH THE MINIMUM
RESPONSE UNTIL INVITED TO ABORT THE RUN. YOU CAN ALSO ABORT
BY TYPING   A   WHEN ASKED FOR NUMERICAL DATA.
```

```
FIRST WE WILL MAKE UP THE LIST OF REACTING SPECIES.
THE FOLLOWING SPECIES ARE AVAILABLE IN THIS VERSION:
  A       C       C(S)    CH4     CO      CO2     E-
  H       H2      H2O     H2O(L)  HO      K       K+
  N       N2      NO      NO2     O       O2
YOU MAY SELECT FROM THIS LIST AND/OR ADD OTHERS. HAVE JANAF TABLE
AT HAND TO PUT IN DATA FOR THE NEW SPECIES THAT YOU INTRODUCE.
NAME ONE SPECIES AFTER EACH PROMPT TO INCLUDE.
JUST RETURN WHEN YOU HAVE FINISHED SPECIFYING EACH PHASE.
IF YOU RESPOND  ALL  THE ENTIRE PACKAGE WILL BE INCLUDED.
IF YOU RESPOND  COMB  THE FOLLOWING SET WILL BE INCLUDED:
  CO  CO2 H   H2  HO  H2O N   N2  NO  NO2 O   O2

GAS SPECIES:
 INCLUDE?
CO
  INCLUDE?
CO2
  INCLUDE?
O2
  INCLUDE?
```

Note that the species to be included are specified by their chemical symbols, and that a carriage return indicates the end of the list specification.

```
NEXT YOU MUST SPECIFY ANY CONDENSED SPECIES THAT YOU
WANT TO ALLOW. THE COMPUTION WILL DETERMINE IF THEY FORM.
PRESS RETURN WHEN THE LIST IS COMPLETE.


CONDENSED SPECIES:
 INCLUDE?
C(S)
  INCLUDE?
```

If we did not want to include the C(s), we would just return after the first prompt.

```
NEXT, YOU MUST SPECIFY THE ATOMIC PROPORTIONS.
 RELATIVE ATOMIC POPULATIONS?

C    POP?
2

O    POP?
1
```

The read routine will accept any format. Hence the C and O populations could have been input in any of the following:

2    2.    2EO    .2E1

The read routine also gives the user a second change if a non-numeric symbol is typed, or if a number is out of the range expected for that quantity.

```
 THE ATOMIC MAKEUP IS NOW COMPLETELY SPECIFIED.
WANT TO INSPECT THE ATOMIC SET-UP?
Y

           ATOMS
          C  O
CO        1  1
CO2       1  2
O2        0  2
C(S)      1  0
```

Yes/no questions may be answered Y or N. As JANAF will tell us later, we can also use a carriage return for "no" or for several other common responses. Note that the program has set up the correct atoms in the species involved.

```
THE STATE MUST BE FIXED BY SPECIFYING TWO PROPERTIES.
HERE ARE THE OPTIONS:
    1: T,P SPECIFIED
    2: H,P SPECIFIED
    3: S,P SPECIFIED
    4: P SPECIFIED, S SAME AS LAST RUN
    5: P SPECIFIED, S, X SAME AS LAST RUN
    6: T SPECIFIED, S SAME AS LAST RUN
    7: H AND P SAME AS LAST RUN

OPTION NUMBER?
1
 T, K?
3000
 P, ATM?
1
```

The input is now complete. JANAF now gives us a chance to abort, in case we made an error. We could also abort by typing A in response to a request for numerical data.

```
WANT TO ABORT THIS RUN?
N
```

```
DO YOU WANT TO SEE THE DATA FROM JANAF TABLES?
Y

JANAF TABLE DATA:                          FOR T = 3000.00 K
SPECIES      MOL.WT.      ENTH.FORM.      S0           H-H0
             G/MOL        KCAL/MOL     CAL/(MOL*K)   KCAL/MOL
GAS SPECIES
CO          28.01054      -26.420       65.370        22.357
CO2         44.00995      -94.054       79.848        36.535
O2          31.99879        0.000       67.973        23.446
CONDENSED SPECIES
C(S)        12.01100        0.000       12.129        14.412
DENSITY OF C(S)        2.70 G/CC
```

These are the data that JANAF took from the data file and used in the computations.

```
DO YOU WANT TO SEE THE ELEMENT POTENTIALS?
Y

 ATOM        POP      PLANCK POTENTIAL
   C    2.0000E+00         -3.6861
   O    1.0000E+00        -29.8915
```

If the user did not elect to view the element potentials, the terminal display would begin with the following:

```
COMPOSITION AT T =3000.000 K      P =    1.000 ATM.
 SPECIES                MOL. FRACTION   MASS FRACTION    MOL FRACTION
                          IN MIXTURE     IN MIXTURE       IN GAS PHASE
  GAS PHASE
       CO                0.50000E+00     0.69988E+00      0.10000E+01
       CO2               0.59660E-06     0.13121E-05      0.11932E-05
       O2                0.76380E-13     0.12214E-12      0.15276E-12
CONDENSED SPECIES
       C(S)              0.50000E+00     0.30011E+00

MIXTURE PROPERTIES:  GAS MOL. WT. =  28.011 KG/KMOL
   T = 3000.000 K        P =   1.0133E+05 PA      V =  6.1510E+00 M**3
   U =       458.67 KJ/KG  H =     1081.92 KJ/KG  S =      8.1020 KJ/(K

THE LAST ITERATION REQUIRED  24 PASSES
```

Finally, the user may direct that the output for this case be printed:

```
DO YOU WANT PRINTED OUTPUT?
Y

THE OUTPUT WILL BE SENT TO THE PRINTER.
```

For the next example, we shall consider the determination of the adiabatic flame temperature in stoichiometric combustion of methane with oxygen at 1 atm. We shall assume that the user is now experienced and hence needs no instruction.

```
ARE YOU FINISHED?
N

WHAT IS YOUR REQUIRED LEVEL OF
INSTRUCTION (MUCH,SOME,NONE)?


RETURN MAY BE USED FOR NEGATIVE ANSWERS OR  SAME.
```

Note that a carriage return was used to say NONE for instruction level.

```
GAS SPECIES:
 INCLUDE?
CH4
  INCLUDE?
O2
  INCLUDE?


CONDENSED SPECIES:
 INCLUDE?
```

The user first specifies $CH_4$ and $O_2$. This will not require any equilibrium calculations, but will give the user the enthalpy of the reactants $CH_4$ and $O_2$.

```
 RELATIVE ATOMIC POPULATIONS?

C   POP?
1

H   POP?
4

O   POP?
4
```

```
 WANT TO INSPECT THE ATOMIC SET-UP?

      1: T,P SPECIFIED
     2: H,P SPECIFIED
     3: S,P SPECIFIED
     4: P SPECIFIED, S SAME AS LAST RUN
     5: P SPECIFIED, S, X SAME AS LAST RUN
     6: T SPECIFIED, S SAME AS LAST RUN
     7: H AND P SAME AS LAST RUN

OPTION NUMBER?
1
 T, K?
300
 P, ATM?
10

WANT TO ABORT THIS RUN?


DO YOU WANT TO SEE THE DATA FROM JANAF TABLES?


DO YOU WANT TO SEE THE ELEMENT POTENTIALS?


COMPOSITION AT T = 300.000 K      P =   10.000 ATM.
 SPECIES                 MOL. FRACTION   MASS FRACTION    MOL FRACTION
                           IN MIXTURE     IN MIXTURE      IN GAS PHASE
  GAS PHASE
       CH4                0.33333E+00     0.20044E+00     0.33333E+00
       O2                 0.66667E+00     0.79956E+00     0.66667E+00

MIXTURE PROPERTIES:  GAS MOL. WT. =  26.680 KG/KMOL
   T =  300.000 K        P =  1.0133E+06 PA    V =  9.2266E-02 M**
   U =   -1026.73 KJ/KG  H =     -933.24 KJ/KG  S =     6.9369 KJ/(

THE LAST ITERATION REQUIRED   0 PASSES

DO YOU WANT PRINTED OUTPUT?
```

The user (and JANAF) now know the enthalpy of the reactants, so now the user specifies a mixture of combustion products:

```
ARE YOU FINISHED?

 INSTRUCTION (MUCH,SOME,NONE)?
```

```
GAS SPECIES:
 INCLUDE?
COMB
  INCLUDE?


CONDENSED SPECIES:
 INCLUDE?
```

Note that the specification COMB gets the user a set of 12 gas-phase species, namely,

```
CO   CO2   H   H2   HO   H2O   N   N2   NO   NO2   O   O2
```

However, there is no N in the reactants; the user specifies the populations as follows:

```
 RELATIVE ATOMIC POPULATIONS?

C    POP?
1

H    POP?
4

O    POP?
4

N    POP?



 WANT TO INSPECT THE ATOMIC SET-UP?
Y

           ATOMS
           C  H  O
CO         1  0  1
CO2        1  0  2
H          0  1  0
H2         0  2  0
HO         0  1  1
H2O        0  2  1
O          0  0  1
O2         0  0  2
```

Note that JANAF has eliminated the nitrogen-containing species. JANAF now prompts for the state specification mode (with minimal instruction):

```
     1: T,P SPECIFIED
     2: H,P SPECIFIED
     3: S,P SPECIFIED
     4: P SPECIFIED, S SAME AS LAST RUN
     5: P SPECIFIED, S, X SAME AS LAST RUN
     6: T SPECIFIED, S SAME AS LAST RUN
     7: H AND P SAME AS LAST RUN

OPTION NUMBER?
7
 ESTIMATED T, K?
3000

WANT TO ABORT THIS RUN?


DO YOU WANT TO SEE THE DATA FROM JANAF TABLES?


DO YOU WANT TO SEE THE ELEMENT POTENTIALS?


COMPOSITION AT T =3358.612 K      P =  10.000 ATM.
 SPECIES               MOL. FRACTION  MASS FRACTION   MOL FRACTION
                         IN MIXTURE     IN MIXTURE     IN GAS PHASE
  GAS PHASE
       CO                0.15024E+00    0.19039E+00    0.15024E+00
       CO2               0.12591E+00    0.25070E+00    0.12591E+00
       H                 0.33864E-01    0.15443E-02    0.33864E-01
       H2                0.64659E-01    0.58974E-02    0.64659E-01
       HO                0.95489E-01    0.73473E-01    0.95489E-01
       H2O               0.42296E+00    0.34475E+00    0.42296E+00
       O                 0.29660E-01    0.21470E-01    0.29660E-01
       O2                0.77213E-01    0.11178E+00    0.77213E-01

MIXTURE PROPERTIES:  GAS MOL. WT. =  22.104 KG/KMOL
   T = 3358.612 K         P =  1.0133E+06 PA   V =  1.2468E+00 M**3
   U =    -2196.60 KJ/KG  H =     -933.24 KJ/KG S =    12.4931 KJ/(K

THE LAST ITERATION REQUIRED  24 PASSES

DO YOU WANT PRINTED OUTPUT?
```

The user now knows that the adiabatic flame temperature is 3358 K.

For the next example, we shall continue the previous run. The user considers the isentropic expansion of the products of the previous combustion to 1 atm:

```
ARE YOU FINISHED?


 INSTRUCTION (MUCH,SOME,NONE)?

GAS SPECIES:
 INCLUDE?
SAME
```

The user could have used a carrage return instead of typing SAME.

```
 DO YOU WANT TO CHANGE THE ATOMIC POPULATIONS?
```

Note that the carriage return is used to reply no above.

```
      1: T,P SPECIFIED
      2: H,P SPECIFIED
      3: S,P SPECIFIED
      4: P SPECIFIED, S SAME AS LAST RUN
      5: P SPECIFIED, S, X SAME AS LAST RUN
      6: T SPECIFIED, S SAME AS LAST RUN
      7: H AND P SAME AS LAST RUN

OPTION NUMBER?
4
 P, ATM?
1
 ESTIMATED T, K?
2400

WANT TO ABORT THIS RUN?


DO YOU WANT TO SEE THE DATA FROM JANAF TABLES?


DO YOU WANT TO SEE THE ELEMENT POTENTIALS?
```

```
COMPOSITION AT T =2826.955 K        P =    1.000 ATM.
 SPECIES                  MOL. FRACTION    MASS FRACTION    MOL FRACTION
                            IN MIXTURE      IN MIXTURE       IN GAS PHASE
  GAS PHASE
       CO                   0.11661E+00     0.13900E+00      0.11661E+00
       CO2                  0.17696E+00     0.33143E+00      0.17696E+00
       H                    0.19606E-01     0.84100E-03      0.19606E-01
       H2                   0.47687E-01     0.40912E-02      0.47687E-01
       HO                   0.59244E-01     0.42879E-01      0.59244E-01
       H2O                  0.50004E+00     0.38338E+00      0.50004E+00
       O                    0.15222E-01     0.10365E-01      0.15222E-01
       O2                   0.64629E-01     0.88008E-01      0.64629E-01

MIXTURE PROPERTIES:   GAS MOL. WT. =   23.498 KG/KMOL
   T = 2826.955 K        P =  1.0133E+05 PA     V =  9.8718E+00 M**3/
   U =    -4521.71 KJ/KG H =    -3521.46 KJ/KG  S =     12.4931 KJ/(K

THE LAST ITERATION REQUIRED  22 PASSES

DO YOU WANT PRINTED OUTPUT?
```

For our last example we shall consider a case where the user must add thermochemical data. This example represents an MHD combustion problem involving the ionization of potassium.

```
ARE YOU FINISHED?

 INSTRUCTION (MUCH,SOME,NONE)?


GAS SPECIES:
 INCLUDE?
COMB
  INCLUDE?
K
  INCLUDE?
K+
  INCLUDE?
E-
  INCLUDE?
HKO
  INCLUDE?


CONDENSED SPECIES:
 INCLUDE?
```

Since the Species HKO is not on file, JANAF asks the user for its atomic description:

```
MOLECULE:HKO
 ATOM?
H
   NUMBER? (MAX 9)
1
  ATOM?
K
   NUMBER? (MAX 9)
1
  ATOM?
O
   NUMBER? (MAX 9)
1
  ATOM?
```

The run continues as before:

```
  RELATIVE ATOMIC POPULATIONS?

C    POP?
1

H    POP?
4

O    POP?
4

K    POP?
0.05

N    POP?
0
 WANT TO INSPECT THE ATOMIC SET-UP?
Y
                ATOMS
              C  H  O  E-  K
CO            1  0  1  0   0
CO2           1  0  2  0   0
H             0  1  0  0   0
H2            0  2  0  0   0
HO            0  1  1  0   0
H2O           0  2  1  0   0
O             0  0  1  0   0
O2            0  0  2  0   0
K             0  0  0  0   1
K+            0  0  0 -1   1
E-            0  0  0  1   0
HKO           0  1  1  0   1
```

The number of E- particles (electrons) assigned to an ion is the surplus over the electrically neutral atoms. Hence, the K+ ion is treated as having -1 E- particles. The run continues:

```
     1: T,P SPECIFIED
     2: H,P SPECIFIED
     3: S,P SPECIFIED
     4: P SPECIFIED, S SAME AS LAST RUN
     5: P SPECIFIED, S, X SAME AS LAST RUN
     6: T SPECIFIED, S SAME AS LAST RUN
     7: H AND P SAME AS LAST RUN

OPTION NUMBER?
1
 T, K?
3500
 P, ATM?
10

WANT TO ABORT THIS RUN?
```

Since the species HKO was not in the data file, the user must input its thermochemical data. With the JANAF tables in hand, he responds to JANAF's prompts:

```
HKO
    MOL.WT.,G/MOL?
56.01937
     ENTH.FORM. 298.15K, KCAL/MOL?
-55.4
   AT T = 3500.0 K:
    ENTROPY (1ATM) , CAL/(MOL*K)?
87.137
     ENTHALPY ABOVE 298.15K, KCAL/MOL?
39.861
```

This is all the JANAF table input that is required. Here is what follows:

```
DO YOU WANT TO SEE THE DATA FROM JANAF TABLES?
Y
```

```
JANAF TABLE DATA:                              FOR T = 3500.00 K
SPECIES      MOL.WT.       ENTH.FORM.        S0           H-H0
             G/MOL         KCAL/MOL      CAL/(MOL*K)    KCAL/MOL
GAS SPECIES
CO           28.01054       -26.420        66.746        26.822
CO2          44.00995       -94.054        82.151        44.006
H             1.00797        52.100        39.628        15.907
H2            2.01600         0.000        49.850        25.703
HO           17.00740         9.432        62.721        25.841
H2O          18.01601       -57.798        70.496        36.936
O            16.00000        59.559        50.870        16.033
O2           31.99879         0.000        69.461        28.276
K            39.10000        21.310        50.743        16.536
K+           39.10000       122.896        49.155        15.907
E-            0.00055         0.000        17.224        15.907
HKO          56.01937       -55.400        87.137        39.861

DO YOU WANT TO SEE THE ELEMENT POTENTIALS?
Y

 ATOM        POP      PLANCK POTENTIAL
   C    1.0000E+00        -17.4892
   H    4.0000E+00        -10.8264
   O    4.0000E+00        -15.5446
   E-   0.0000E+00        -12.1398
   K    5.0000E-02        -22.6783

COMPOSITION AT T =3500.000 K       P =   10.000 ATM.
 SPECIES                 MOL. FRACTION    MASS FRACTION     MOL FRACTION
                           IN MIXTURE       IN MIXTURE      IN GAS PHASE
  GAS PHASE
       CO                  0.16437E+00     0.21573E+00     0.16437E+00
       CO2                 0.95918E-01     0.19779E+00     0.95918E-01
       H                   0.51558E-01     0.24350E-02     0.51558E-01
       H2                  0.76922E-01     0.72661E-02     0.76922E-01
       HO                  0.11281E+00     0.89898E-01     0.11281E+00
       H2O                 0.35889E+00     0.30296E+00     0.35889E+00
       O                   0.44313E-01     0.33221E-01     0.44313E-01
       O2                  0.81887E-01     0.12277E+00     0.81887E-01
       K                   0.75439E-02     0.13821E-01     0.75439E-02
       K+                  0.31533E-03     0.57770E-03     0.31533E-03
       E-                  0.31533E-03     0.81078E-08     0.31533E-03
       HKO                 0.51552E-02     0.13531E-01     0.51552E-02

MIXTURE PROPERTIES:  GAS MOL. WT. =  21.342 KG/KMOL
   T = 3500.000 K        P =   1.0133E+06 PA     V =   1.3457E+00 M**3/KG
   U =      -743.92 KJ/KG H =       619.58 KJ/KG  S =      12.7615 KJ/(KG*K)

THE LAST ITERATION REQUIRED  13 PASSES
```

The user who desired to do a number of calculations of this type could use the JFILE program to add HKO to the master data file and then use the JPACK program to make up a package data file that contained all of the species of interest and no others. He would then define this package file as logical 21, and then when prompted to INCLUDE? for gas species would respond simply ALL to incorporate all species in the package.

This concludes the examples. In the next chapters the theory and methods of solution of the equilibrium problem are detailed, and the procedures that users must follow to implement the system computers and to manage the data file are given.

## II. METHODS OF SOLUTION

### 1. Theoretical Formulation

The equilibrium composition at fixed T and P is the composition that minimizes the Gibbs function of the mixture. Denoting mole numbers by $\eta$ and molar Gibbs function by g,

$$G = \sum_{j=1}^{c} \eta_j g_j(T,P_j) + \sum_{j*=1}^{c*} \eta_{j*} g_{j*}(T,P) \quad (1.1)$$

Here j denotes a gas species at partial pressure $P_j$, and j* denotes a condensed phase species at the mixture pressure P and temperature T. We assume that the gas species are perfect, and hence

$$g_j(T,P_j) = g_j(T,P) + RT \ln x_j \quad (1.2)$$

where R is the universal gas constant and $x_j$ is the gas-phase mole fraction of j.

It is convenient to set the problem with specified numbers of moles of each type of atom. If $p_k$ is the population of k atoms (in moles),

$$p_k = \sum_{j=1}^{c} n_{kj}\eta_j + \sum_{j*=1}^{c*} n_{kj}\eta_{j*} \quad (1.3)$$

where $n_{kj}$ is the number of k atoms in a j molecule. Equation (1.3) must be satisfied for k = 1, 2, ... , a ; these are constraints on the minimizing of G.

To minimize G subject to (1.3), we use the method of Lagrange multipliers, and set

$$\delta\left(\frac{G}{RT} - \sum_{k=1}^{a} \lambda_k p_k\right) = 0 \quad (1.4)$$

where G/RT is given by (here $\tilde{g}$ denotes g/RT):

$$\frac{G}{RT} = \sum_{j=1}^{c} \eta_j \left(\tilde{g}_j(T,P) + \ln x_j\right) + \sum_{j*=1}^{c*} \eta_{j*}\tilde{g}_{j*}(T,P) \quad (1.5)$$

and $p_k$ is taken from (1.3). The $\lambda$ are Lagrange multipliers; they play a key role in the analysis and have an important physical interpretation. Note that here the Gibbs functions $\tilde{g}_j$ and $\tilde{g}_{j*}$ are both evaluated at T, P. Henceforth the arguments (T,P) will be omitted. Taking the variation (1.4) with respect to arbitrary variations $\delta\eta_j$ and $\delta\eta_{j*}$, and denoting the total number of gas moles by $\eta$, one finds

$$\sum_{j=1}^{c} \delta\eta_j \left(\tilde{g}_j + \ln x_j\right) + \sum_{j=1}^{c} \eta_j \left(\frac{\delta\eta_j}{\eta_j} - \frac{1}{\eta} \sum_{\ell=1}^{c} \delta\eta_\ell\right)$$

$$+ \sum_{j*=1}^{c*} \tilde{g}_{j*}\delta\eta_{j*} - \sum_{k=1}^{a} \lambda_k \left(\sum_{j=1}^{c} n_{kj}\delta\eta_j + \sum_{j*=1}^{c*} n_{kj*}\delta\eta_{j*}\right) = 0 \tag{1.6}$$

Note that the second term in (1.6) is zero. Setting the coefficient of $\delta\eta_j$ = 0, one has

$$\tilde{g}_j + \ln x_j - \sum_{k=1}^{a} \lambda_k n_{kj} = 0$$

so the gas phase mole fraction must be of the form

$$x_j = \exp\left(- \tilde{g}_j + \sum_{k=1}^{a} \lambda_k n_{kj}\right) \tag{1.7}$$

Note that specification of only a values of $\lambda_k$ will determine all of the c values of $x_j$. Setting the coefficient of $\delta\eta_{j*} = 0$ in (1.6), one finds

$$\tilde{g}_{j*} - \sum_{k=1}^{a} \lambda_k n_{kj*} = 0 \tag{1.8}$$

This is the condition for phase equilibrium. Note that, if gas species j is the same as condensed species j*, then, since $n_{kj} = n_{kj*}$,

$$\tilde{g}_j(T,P_j) = \tilde{g}_j + \ln x_j = \sum_{k=1}^{a} \lambda_k n_{kj} = \tilde{g}_{j*} \tag{1.9}$$

as expected for phase equilibrium of j and j*.

At this point the physical significance of the Lagrange multipliers $\lambda_k$ can be seen. Since

$$\tilde{g}_j(T,P_j) = \sum_{k=1}^{a} \lambda_k n_{kj} \tag{1.10a}$$

and

$$\tilde{g}_{j*}(T,P) = \sum_{k=1}^{a} \lambda_k n_{kj*} \tag{1.10b}$$

we see that $\lambda_k$ represents the Gibbs function/RT per mole of k atoms. For this reason $\lambda_k RT$ is called the "element potential" for element k. Note that at equilibrium the contribution of each k atom to the Gibbs function of a species is the same, regardless of the molecule or phase in which the atom is located. This fact allows the population of minor species to be estimated quite simply from known populations of major species. See Chapter III for examples.

The author searched the literature seeking a suitable name for $\lambda$. Tribus (1961) defined the quantity $-\tilde{g}$ as the "Planck potential." We shall adopt this terminology (with a change in sign consistent with the term "potential") and call $\lambda_k$ the <u>element Planck potential of k atoms</u>.

The Lagrange multipliers (Planck potentials) are determined by the atomic constraints. Using (1.7) in (1.3),

$$p_k = \eta \sum_{j=1}^{c} n_{kj} \exp\left(-\tilde{g}_j + \sum_{\ell=1}^{a} \lambda_\ell n_{\ell j}\right) + \sum_{j*=1}^{c*} n_{kj*}\eta_{j*} \tag{1.11}$$

$$k = 1, 2, \ldots, a$$

Also, since

$$\sum_{j=1}^{c} x_j = 1 \tag{1.12a}$$

we have the additional condition

$$\sum_{j=1}^{c} \exp\left(-\tilde{g}_j + \sum_{k=1}^{a} \lambda_k n_{kj}\right) = 1 \tag{1.12b}$$

Finally, if species j* is present in the condensed phase, we have, from (1.8),

$$\phi_{j*} = -\tilde{g}_{j*} + \sum_{k=1}^{a} \lambda_k n_{kj*} = 0 \qquad (1.13)$$

Equations (1.11)-(1.13) form a set of $a + 1 + c^*$ equations for the $a$ $\lambda_k$, $\eta$, and the $c^*$ $\eta_{j*}$. In the next section we shall see how they can be solved simultaneously.

The condensed species might not be present. Suppose that gas species $j$ and condensed species $j^*$ are the same. Then, with all other mole numbers fixed, the variations in $j$ and $j^*$ produce

$$dG = \tilde{g}_j(T,P_j)\, d\eta_j + \tilde{g}_{j*}(T,P)\, d\eta_{j*} \leq 0 \qquad (1.14)$$

But $d\eta_{j*} = -d\eta_j$, and hence (1.14) gives

$$\left[\tilde{g}_{j*}(T,P) - \tilde{g}_j(T,P_j)\right] d\eta_{j*} \leq 0 \qquad (1.15)$$

Using the fact that $n_{ij*} = n_{ij}$, if (1.7) is satisfied it follows from (1.9) that

$$\phi_{j*} = -\tilde{g}_{j*}(T,P) + \tilde{g}_j(T,P_j) \qquad (1.16)$$

Hence, (1.15) becomes

$$\phi_{j*} d\eta_{j*} \geq 0 \qquad (1.17)$$

Therefore,

$$\left.\begin{array}{l} \text{a) if } \phi_{j*} > 0, \text{ then } d\eta_{j*} > 0; \\ \text{b) if } \phi_{j*} < 0 \text{ and } \eta_{j*} > 0, \text{ then } d\eta_{j*} < 0; \\ \text{c) if } \phi_{j*} < 0 \text{ and } \eta_{j*} = 0, \text{ then no } j^* \text{ forms.} \end{array}\right\} \qquad (1.18)$$

We remark that the solution based on this theory requires adjustment of a small number of Lagrange multipliers $\lambda_k$, which in turn determine a large number of mole fractions $x_j$. This is in contrast to other methods for equilibrium composition analysis, which require adjustment of a large number of unknown mole fractions.

## 2. Relationship to Other Methods

The analysis developed above is very similar to what has come to be called the "method of element potentials," summarized by Van Zeggeren and Storey (1970). This term was introduced by Powell (see Powell et al. (1959)), who recognized that (1.10) indicates that each atom of a given element contributes the same amount to the total system Gibbs function, regardless of the species or phase in which that atom resides; the element potential $RT\lambda_i$ is this contribution. White (1967) also noticed this fact and suggested ways in which it would be useful in calculations. The RAND method for equilibrium calculation described by Clasen (1965) is essentially a method for iterative determination of the element potentials. Bigelow (1970) extends the nonlinear programming theory of this method.

The present author developed all of this theory and computation system before becoming aware of the earlier work. The new contributions of the present work appear to lie in the special algorithms that have been developed for solution, and in the creation of a very flexible, robust, and easy-to-use implementation of the method of element potentials.

## 3. Algorithm for Solution

A convergent algorithm exists for solution of (1.11)-(1.13). We define

$$W = \eta \sum_{j=1}^{c} x_j + \sum_{k=1}^{a} \lambda_k \left( \sum_{j*=1}^{c*} n_{kj*} \eta_{j*} - p_k \right) \tag{3.1}$$

and

$$H_k = \eta \sum_{j=1}^{c} n_{kj} x_j + \sum_{j*=1}^{c*} n_{kj*} \eta_{j*} - p_k \tag{3.2}$$

where $x_j$ is given by (1.7). Then,

$$\left. \frac{\partial W}{\partial \lambda_k} \right|_{\lambda_\ell, \eta, \eta_{j*}} = H_k \tag{3.3}$$

In general, since $W = W(\lambda_k, \eta, \eta_{j*})$,

$$dW = \sum_{k=1}^{a} \frac{\partial W}{\partial \lambda_k} d\lambda_k + \frac{\partial W}{\partial \eta} d\eta + \sum_{j*=1}^{c*} \frac{\partial W}{\partial \eta_{j*}} d\eta_{j*} \tag{3.4}$$

We denote

$$Z = \sum_{j=1}^{c} x_j \tag{3.5}$$

Then

$$dW = \sum_{k=1}^{a} H_k d\lambda_k + Z d\eta + \sum_{j*=1}^{c*} \left(\frac{\partial W}{\partial n_{j*}}\right)_{\eta,\lambda} dn_{j*} \tag{3.6}$$

Also, denoting

$$D_k = \sum_{j=1}^{c} n_{kj} x_j \tag{3.7}$$

it follows that

$$dZ = \sum_{k=1}^{a} D_k d\lambda_k \tag{3.8}$$

Now we define

$$Q_{k\ell} = \sum_{j=1}^{c} n_{kj} n_{\ell j} x_j \tag{3.9}$$

and then

$$dH_k = \eta \sum_{\ell=1}^{a} Q_{k\ell} d\lambda_\ell + D_k d\eta + \sum_{j*=1}^{c*} n_{kj*} dn_{j*} \tag{3.10}$$

We note that $H_k = 0$ when the $k^{th}$ atomic constraint (1.11) is satisfied. Therefore, $W$ is stationary with respect to arbitrary variations in the $\lambda_k$ when the atomic constraints are satisfied. Moreover,

$$\frac{\partial^2 W}{\partial \lambda_k \partial \lambda_\ell} = \frac{\partial H_k}{\partial \lambda_\ell} = \eta Q_{k\ell} \tag{3.11}$$

Since $Q_{kk} > 0$, $W$ is a <u>minimum</u> at the extremum and $W$ is a concave function of the $\lambda_k$. This means that the minimum point can always be found by the method of steepest descent.

At fixed $\eta$ and $n_{j*}$, we have, from (3.4) and (3.3),

$$dW = \sum_{k=1}^{a} H_k d\lambda_k \tag{3.12}$$

If a descent path in $\lambda_k$ space has length ds, then

$$d\lambda_k = f_k ds \tag{3.13a}$$

$$\sum_{k=1}^{a} f_k f_k = 1 \tag{3.13b}$$

where $f_k$ are the direction cosines for the path of descent in $\lambda_k$ space. To find the path of steepest descent, we set

$$\delta \left\{ \frac{dW}{ds} - \frac{\beta}{2} \sum_{k=1}^{a} f_k f_k \right\} = 0$$

or

$$\delta \left\{ \sum_{k=1}^{a} \left( H_k f_k - \frac{\beta}{2} f_k f_k \right) \right\} = 0 \tag{3.14}$$

where $\beta$ is a Lagrange multiplier for the normalizing constraint (3.13b). Varying the $f_k$, we find

$$\sum_{k=1}^{a} (H_k - \beta f_k)\, \delta f_k = 0$$

Since this must hold for arbitrary $\delta f_k$, the direction cosines for steepest descent are given by

$$f_k = H_k / \beta \tag{3.15}$$

Then (3.13b) gives

$$\sum_{k=1}^{a} H_k H_k = \beta^2 \tag{3.16}$$

But then

$$\frac{dW}{ds} = \sum_{k=1}^{a} H_k H_k / \beta = \beta$$

which must be negative for descent. Hence,

$$\beta = -\sqrt{\sum_{k=1}^{a} H_k H_k} \tag{3.17}$$

For a given set of $\lambda_k$, we get a set of $H_k$. Then (3.15) and (3.17) allow us to calculate directions in which $\lambda_k$ should be changed to reduce $W$ as rapidly as possible. The distance $\Delta s$ that we should go along the path of steepest descent is estimated using a Taylor series expansion of $dW/ds$,

$$\frac{dW}{ds} = \left.\frac{dW}{ds}\right|_0 + \left.\frac{d^2W}{ds^2}\right|_0 \Delta s + \ldots = 0$$

or

$$0 = \beta + \sum_{\ell=1}^{a} \frac{\partial}{\partial\lambda_\ell}\left(\frac{\partial W}{\partial s}\right)\frac{\partial\lambda_\ell}{\partial s}\Delta s = \beta + \sum_{\ell=1}^{a}\sum_{k=1}^{a} \frac{\partial^2 W}{\partial\lambda_k\partial\lambda_\ell} f_k f_\ell \Delta s$$

So

$$\Delta s = \frac{-\beta}{\eta \sum_{k=1}^{a}\sum_{\ell=1}^{a} Q_{k\ell} f_k f_\ell} \tag{3.18}$$

The matrix $Q_{k\ell}$ is determined by the current values of the $\lambda$. Hence the desired $\Delta s$ is readily determined. This process defines the method of steepest descent, denoted by mode 1 in the program.

An alternative method, which may be faster when the $\lambda$ are very close to the extremizing values, is to use Newton-Raphson adjustment of the $\lambda$ to force the $H_k$ all to zero. Taylor series expansions give

$$H_k^{\text{new}} = H_k + \sum_{\ell=1}^{a} \frac{\partial H_k}{\partial\lambda_\ell}\Delta\lambda_\ell + \ldots$$

Using (3.3) and (3.10) and setting $H_k^{\text{new}} = 0$,

$$0 = H_k + \eta \sum_{\ell=1}^{a} Q_{k\ell}\Delta\lambda_\ell + \ldots$$

So we have the simultaneous set of equations for the changes $\Delta\lambda_\ell$,

$$\sum_{\ell=1}^{a} Q_{k\ell}\Delta\lambda_\ell = -H_k/\eta \tag{3.19}$$

Since $Q_{k\ell}$ is strongly diagonal, these equations are easily solved by elimination. This process for adjusting the $\lambda$ is designated as mode 2 in the program.

After we have adjusted the $\lambda$ to make all of the $H$ acceptably small at fixed $\eta$ and $\eta_{j*}$, we must next adjust $\eta$ until (1.12) is satisfied. A slight change in $d\eta$ will lead to new values of the $\lambda_k$ for zero $H_k$ (or minimum $W$). This will correspond to a $Z$ change (see (3.8)).

$$dZ = \sum_{k=1}^{a} D_k d\lambda_k \tag{3.20}$$

The $D_k$ are easily calculated for any set of $\lambda$. We need now to relate the $d\lambda_k$ to $d\eta$ for two nearby W-minimum states. Since (1.3) is satisfied at both states, between two W-minimum states with the same $\eta_{j*}$ (3.10) gives

$$dH_k = 0 = \eta \sum_{\ell=1}^{c} Q_{k\ell} d\lambda_\ell + D_k d\eta$$

So

$$\sum_{\ell=1}^{c} Q_{k\ell} d\lambda_\ell = - D_k d(\ell n\ \eta) \tag{3.21}$$

We define a vector $E_\ell$ such that

$$\sum_{\ell=1}^{c} Q_{k\ell} E_\ell = - D_k \tag{3.22}$$

Then (3.21) gives, between two W-minimum states with the same $\eta_{j*}$,

$$d\lambda_\ell = E_\ell d(\ell n\ \eta) \tag{3.23}$$

Then, if we define

$$\alpha = \sum_{k=1}^{a} D_k E_k \tag{3.24}$$

we have, from (3.8) and (3.23), for two nearby W-minimum states

$$dZ = \alpha d(\ell n\ \eta) \tag{3.25}$$

We are trying to adjust $\eta$ to bring $Z$ to 1; a Taylor series for $Z$ gives

$$1 = Z + \alpha\Delta(\ell n\ \eta) + \ldots$$

or

$$\Delta(\ell n\ \eta) = (1-Z)/\alpha \tag{3.26}$$

This is used to adjust $\eta$ (at fixed $\eta_{j*}$) in order to bring $Z = 1$. The new $\eta$ is found from

$$\ell n(\eta_{new}) = \ell n(\eta) + \Delta(\ell n\ \eta)$$

or

$$\eta_{new} = \eta \exp[\Delta(\ell n\ \eta)] \tag{3.27}$$

The process of $\eta$ adjustment described above will have difficulty if $Z$ is not a monotone function of $\eta$. But, at fixed $\eta_{j*}$, (3.10) becomes

$$dW = \sum_{k=1}^{a} H_k d\lambda_k + Z d\eta \tag{3.28}$$

Since the $H_k$ all vanish at points of minimum $W$,

$$dW_{min} = Z d\eta \tag{3.29}$$

Since $Z > 0$, $W_{min}$ is a monotone-increasing function of $\eta$. Now, from (3.25),

$$\frac{dZ}{d(\ell n\ \eta)} = \alpha \tag{3.30}$$

From (3.24),

$$\alpha = -\sum_{\ell=1}^{c} Q_{k\ell} E_k E_\ell = -\sum_{j=1}^{c} \sum_{\ell=1}^{a} \sum_{k=1}^{a} n_{kj} n_{\ell j} E_k E_\ell x_j \tag{3.31}$$

So

$$\alpha = -\sum_{j=1}^{c} \left( \sum_{k=1}^{a} n_{kj} E_k \right)^2 x_j < 0 \tag{3.32}$$

Hence we see that $Z$ at the minima of $W$ is indeed a monotone-decreasing function of $\eta$, as desired for stable iteration.

When all the $H_k$ are small and $Z$ is close to 1, a Newton-Raphson procedure can be used to adjust the $\lambda$ and $\eta$ simultaneously (at fixed $\eta_{j*}$). Between any two states of neighboring $\lambda_k$ and $\eta$ having the same $\eta_{j*}$, from (3.10)

$$\frac{1}{\eta}\, dH_k = \sum_{\ell=1}^{a} Q_{k\ell} d\lambda_\ell + D_k d(\ell n\ \eta) \tag{3.33a}$$

Repeating (3.8),

$$dZ = \sum_{\ell=1}^{a} D_\ell d\lambda_\ell \tag{3.33b}$$

Equations (3.33) form a set that can be solved simultaneously for the changes $\Delta\lambda_\ell$ and $\Delta(\ell n\ \eta)$ required to bring $Z$ to 1 and all $H_k$ to zero. This process is denoted as mode 3 in the program.

What remains is to establish a procedure for adjusting the condensed phase moles $\eta_{j*}$ to bring the $\phi_{j*}$ to zero (or to bring $\eta_{j*}$ to zero with a negative $\phi_{j*}$). Between two adjacent states for which all $H_k$ are zero, from (3.10),

$$\sum_{\ell=1}^{a} Q_{k\ell} d\lambda_\ell = - D_k d(\ell n\ \eta) - \frac{1}{\eta} \sum_{j*=1}^{c*} n_{kj*} d\eta_{j*} \tag{3.34}$$

for each $j*$ that can appear in the condensed phase. We define a matrix $F_{\ell j*}$ such that

$$\sum_{\ell=1}^{a} Q_{k\ell} F_{\ell j*} = - \frac{1}{\eta}\, n_{kj*} \tag{3.35}$$

Then, using (3.22) and (3.35) in (3.34),

$$d\lambda_k = E_k d(\ell n\ \eta) + \sum_{j*=1}^{c*} F_{kj*} d\eta_{j*} \tag{3.36}$$

Between two states for which $Z = 1$, from (3.8),

$$0 = \sum_{k=1}^{a} D_k d\lambda_k \tag{3.37}$$

Substituting (3.36) into (3.37) and using (3.24),

$$0 = \alpha d(\ln \eta) + \sum_{k=1}^{a} \sum_{j^*=1}^{c^*} D_k F_{kj^*} d\eta_{j^*} \tag{3.38}$$

Defining

$$V_{j^*} = -\frac{1}{\alpha} \sum_{k=1}^{a} D_k F_{kj^*} \tag{3.39}$$

we see that, between two states for which all $H_k$ are zero and $Z = 1$,

$$d(\ln \eta) = \sum_{j^*=1}^{c^*} V_{j^*} d\eta_{j^*} \tag{3.40}$$

This allows us to estimate $\eta$ changes associated with $\eta_{j^*}$ changes (at $H_k = 0$ and $Z = 1$). Then (3.36) gives

$$d\lambda_k = \sum_{j^*=1}^{c^*} A_{kj^*} d\eta_{j^*} \tag{3.41}$$

where

$$A_{kj^*} = E_k V_{j^*} + F_{kj^*} \tag{3.42}$$

This allows us to estimate $\lambda_k$ changes associated with the $\eta_{j^*}$ changes.

All we need now is a method for selecting the $\eta_{j^*}$ changes. One possibility would be to do a steepest descent on the total Gibbs function. However, a simpler approach is to pick $\eta_{j^*}$ changes that will seek to minimize

$$Y = \frac{1}{2} \sum_{j^*=1}^{c^*} \phi_{j^*} \phi_{j^*} \tag{3.43}$$

The minimum will of course be zero, for which all of the condensed phase constraints (1.13) will be satisfied. Note that condensed species for which $\eta_{j^*} = 0$ and $\phi_{j^*} < 0$ must not be included in this summation, since these species will be absent from the condensed phase.

We define direction cosines $f_{j^*}$ for the $\eta_{j^*}$ changes by

$$d\eta_{j^*} = f_{j^*} ds^* \tag{3.44a}$$

$$\sum_{j^*=1}^{c^*} f_{j^*} f_{j^*} = 1 \tag{3.44b}$$

Here $ds^*$ is the step along the descent path in $\eta_{j^*}$ space. Then, using (1.13) and (3.41),

$$dY = \sum_{j^*=1}^{c^*} \phi_{j^*} d\phi_{j^*} = \sum_{j^*=1}^{c^*} \sum_{k=1}^{a} \sum_{j^{*\prime}=1}^{c^*} \phi_{j^*} n_{kj^*} A_{kj^{*\prime}} d\eta_{j^{*\prime}} \tag{3.45}$$

Denoting

$$T_{j^{*\prime}} = \sum_{k=1}^{a} \sum_{j^*=1}^{c^*} \phi_{j^*} n_{kj^*} A_{kj^{*\prime}} \tag{3.46}$$

(3.45) gives

$$\frac{dY}{ds} = \sum_{j^*=1}^{c^*} T_{j^*} f_{j^*} \tag{3.47}$$

To select the path of steepest descent, we want to minimize (3.47) subject to (3.44b). We take a variation

$$\delta \left\{ \sum_{j^*=1}^{c^*} T_{j^*} f_{j^*} - \frac{\gamma}{2} \sum_{j^*=1}^{c^*} f_{j^*} f_{j^*} \right\} = 0 \tag{3.48}$$

where $\gamma$ is a Lagrange multiplier for the constraint (3.44b). For (3.48) to vanish for arbitrary variations in $f_{j^*}$,

$$f_{j^*} = \frac{1}{\gamma} T_{j^*} \tag{3.49a}$$

Then (3.44b) gives

$$\gamma = - \sqrt{\sum_{j^*=1}^{c^*} T_{j^*} T_{j^*}} \tag{3.49b}$$

where the negative sign is chosen to assure descent.

Equations (3.49) give us the direction of $\eta_{j^*}$ change. The step $\Delta s^*$ will be selected to bring a weighted $\phi_{j^*}$ error to zero. We define

$$R_{j^*} = \sum_{k=1}^{a} \sum_{j^{*\prime}=1}^{c^*} n_{kj^*} A_{kj^{*\prime}} f_{j^{*\prime}} \tag{3.50}$$

Then, from (1.13),

$$\Delta\phi_{j*} = \sum_{k=1}^{a} n_{kj*}\Delta\lambda_k = R_{j*}\Delta s* \tag{3.51}$$

We shall choose $\Delta s*$ such that the weighted sum of (3.51) vanishes,

$$\sum_{j*=1}^{c*} \phi_{j*}(\Delta\phi_{j*} - R_{j*}\Delta s*) = 0 \tag{3.52}$$

Since $\Delta\phi_{j*} = -\phi_{j*}$ is desired to bring $\phi_{j*}$ to zero,

$$\Delta s* = -\sum_{j*=1}^{c*} \phi_{j*}\phi_{j*} \Big/ \sum_{j*=1}^{c*} \phi_{j*}R_{j*} \tag{3.53}$$

Under this procedure, the condensed species with the greatest residual error dominates in the choice of $\Delta s*$.

Care must be taken to be sure that the new $\eta_{j*}$ are feasible. They must not be negative and must not consume all of any species. Provisions to protect against such problems are incorporated in the program.

## 4. Initialization

The method described above requires initial estimates for the Lagrange multipliers $\lambda_i$, the total number of mols $\eta$, and the number of moles in each condensed phase $\eta_{j*}$. The rapidity and success of the convergence depend significantly on the accuracy of these estimates, and hence a considerable effort has been spent in developing an initialization procedure that can handle the broad range of problems that a general purpose program like this will encounter.

The initialization method is based on the idea that in any mixture there are certain species that are the dominant ones for each atom. Given an assignment of the number of moles of each atom, the task is then to identify these dominant or sink species, and then assign the atoms to them. This provides the initial estimates for $\eta$ and the $\eta_{j*}$; and, through the estimates of the mole fractions of the gas-phase sink species obtained in this process, one can readily calculate the estimated $\lambda_i$ using (1.7).

From the user's point of view, the number of moles of each species is a relative thing; what is really of interest is the relative populations or mole fractions. However, from the program point of view it is very convenient to work with moles in the initialization process. Therefore, the user inputs relative atomic populations, and internally they are regarded as mole specifications. At the completion of the calculation the mole fractions are determined, and only these are reported to the user.

The initializer first selects a possible sink species for each atom. The best choice is a molecule containing only that atom, with the species having the most atoms chosen (e.g., $N_2$ instead of N). If the mixture does not contain a species having only that atom, the species is selected that has the highest ratio of that atom to other atoms (e.g., $CO_2$ is chosen over CO as the initial sink for C in a mixture of CO, $CO_2$, and $O_2$). The atoms are then assigned to these sink species, and all other species are assigned zero moles. This produces an initial composition that is feasible in that it is consistent with the atomic constraints. However, it may be far from the equilibrium composition, so further adjustment is required. We shall discuss this momentarily.

In some cases there will be fewer species than atoms (e.g., if the user specifies a mixture of $CH_4$ and $O_2$). In cases like this, each species serves as the sink for only one atom, and there are some atoms that do not have assigned sinks. The atoms that do have sinks are assigned to their sink species to form a feasible mixture, and then the atomic constraints are checked to be sure that the user has specified atomic populations consistent with the available species.

The next step in the initialization is to rearrange the mole assignments to bring the composition closer to that in actual equilibrium. This is accomplished by neglecting the log term in the gas-phase Gibbs function (see (1.5)) and minimizing this modified Gibbs function of the mixture. This has proven to be a very good way to shift the atoms from the initial sink species to the thermodynamically preferred species that are the dominant species in the equilibrium mixture. It gives us a classic problem in linear programming and is solved by the simplex method.

We seek

$$\frac{G^*}{RT} = \sum_{j=1}^{C} n_j \tilde{g}_j(T,P) = \min \tag{4.1a}$$

subject to

$$\sum_{j=1}^{C} n_{ij}\eta_j = p_i \quad , \quad i = 1, \ldots a \tag{4.1.b}$$

$$\eta_j \leq 0 \tag{4.1.c}$$

Here, C is the total number of species (gas phase plus condensed phases). In the simplex method one has a set of basis variables (the sink species) equal in number to the number of constraints (atom types). Changes in assignments of the variables (moles) are made in a stepwise manner that at each step replaces one basis variable with another, making the old basis variable zero (zero moles) and changing all of the other basis variables (mole assignments) in a manner consistent with the constraints. This amounts to a transfer of the atoms in a selected current sink species to a new set of sink species. The objective function $(G^*/RT)$ is reduced at each step in the process, until it can be reduced no further. At the end of this process, all of the atoms are in the set of sink species that minimize (4.1a), and all the constraints (4.1b) and (4.1c) are satisfied.

The simplex method accomplishes this through the simultaneous solution of the original minimization problem (4.1) and an associated dual problem; in our notation the dual problem is

$$\sum_{k=1}^{a} \lambda_k p_k = \max \tag{5.1a}$$

subject to

$$\sum_{k=1}^{a} \lambda_k n_{kj} \leq \tilde{g}_j \tag{5.1.b}$$

Here the $\lambda_k$ are called "simplex multipliers." They are Lagrange multipliers associated with the atomic constraints, and play exactly the same role as the $\lambda_k$ in the previous developments. For a lucid discussion of the simplex method and proofs of the associated theorems, see Veinott (1970).

On each simplex path, the first step is to determine the simplex multipliers by solving

$$\sum_{k=1}^{a} n_{kj}\lambda_k = \tilde{g}_j \tag{4.3}$$

where (4.3) applies only for the species (j) that are current bases. Then, for each of the species that are not currently basis species (and hence have been assigned zero mols) we calculate

$$s_j^* = \sum_{k=1}^{a} n_{kj}\lambda_k - \tilde{g}_j \tag{4.4}$$

We then determine the species for which $s^*$ is largest; it will become a basis species, replacing one member of the old basis set. This determines the direction of change in the space of mole numbers. The amount of change is fixed by the first point along this path at which one of the old basis species drops to zero moles. The changes are made, and then we have a new basis set and a new feasible set of mole numbers with lower modified Gibbs functions $G^*$.

The simplex process ends when it is no longer possible to reduce $G^*$. If at this point some of the sink species are condensed species, more work is necessary, because to estimate the $\lambda_k$ we need a non-zero mole fraction for a basis set of <u>gas</u> species. the obvious step is to transfer some of each condensed phase back to the gas phase, the amount transferred being detemined by the phase equilibrium condition. However, if the gas-phase mole fraction of this species is very small, as for example with carbon, this will not produce a satisfactory initialization. So, in the case where the gas-phase species will have a very small mole fraction, some of the condensate is transferred back to the gas phase, along with some of all other condensates, and the simplex process is continued with the condensed species frozen in mole numbers. Thus, for example, the C returned to the gas phase reacts to form CO or $CO_2$; C resides in the gas phase, as desired, but in the species where it is more likely to be in the equilibrium composition.

Another problem arises in stoichiometric reactions, where a basis species in the gas phase may have zero moles (e.g., $CO_2$ and $H_2O$ as basis species for C, O, and H in a mixture formed from $CH_4 + 2O_2$). Since we must have a non-zero mole fraction for each basis species to initialize the $\lambda_k$, the prescribed populations are perturbed slightly (just for the initialization) to remove the singularity. This is done by increasing the number of moles of the zero-moles sink species slightly, and continuing the simplex process to conclusion.

Finally, for those condensed species that are allowed in the gas phase, some of each condensed species is transferred back to the gas phase to force the new composition to satisfy the true phase equilibrium conditions.

At the completion of this process, we have a set of mole numbers that satisfies the phase equilibrium conditions and all of the atomic constraints. In the gas phase there will be one basis (sink) species for each atom, and hence we can use a set of $a$ equations (1.7) to estimate the $a$ values of the $\lambda_k$.

Although the simplex process does not require us to do so, it is helpful to identify a correspondence between basis species and atoms. These identifications are clear for the first set of sinks that start the simplex process, and may change during the process (e.g., $H_2O$ may shift from being the sink for H to serving as the sink for O).

This initialization process can handle problems in which the composition is completely determined by the atomic composition and no minimization is necessary. This enables a user to calculate the thermodynamic properties of non-dissociated mixtures using the program, which proves very useful in adiabatic flame-temperature calculations.

This complicated initialization process is not necessary when doing a problem with the same species list and nearly the same temperature as the previous run. In such cases the dominant (sink) mole fractions from the previous run are used to estimate the $\lambda_k$ for the new run.

## 5. Matrix Conditioning

We have mentioned that there will be a dominant or sink species in the gas phase for each type of atom. In many interesting situations the mole fractions of the sink species differ by many orders of magnitude, in which case the $Q_{k\ell}$ matrix in (3.19), (3.22), and (3.35) is nearly singular. Hence, a treatment that considers the nearly singular nature of $Q_{k\ell}$ is important to the program. This "matrix conditioning" process will now be described.

We want to solve equations of the form

$$\sum_{\ell=1}^{a} Q_{k\ell}X_\ell = Y_k \tag{5.1}$$

Using the definition (3.9), this is equivalent to

$$\sum_{\ell=1}^{a} \sum_{j=1}^{c} n_{kj} n_{\ell j} x_j X_\ell = Y_k \tag{5.2}$$

The idea of "conditioning" is to replace (5.2) by other linear combinations of the same equation. This is equivalent to multiplying (5.2) by a "conditioning matrix" $C_{mk}$;

$$\sum_{\ell=1}^{a} \sum_{j=1}^{c} \sum_{k=1}^{a} C_{mk} n_{kj} n_{\ell j} x_j X_\ell = \sum_{k=1}^{a} C_{mk} Y_k \tag{5.3}$$

Now, for the $m^{th}$ equation, corresponding to $m$ atoms, we select $C_{mk}$ such that the sink species for all other atoms will drop out of the equation. This requires

$$\sum_{k=1}^{a} C_{mk} n_{kj} = \begin{cases} 0 & \text{if } j \text{ is a sink for atoms other than } m \\ 1 & \text{if } j \text{ is the sink for } m \text{ atoms} \end{cases} \tag{5.4}$$

For a given molecular set-up, the conditioning matrix $C_{mk}$ is calculated using (5.4). Then, instead of solving (5.1), we solve

$$\sum_{\ell=1}^{a} \overline{Q}_{m\ell} X_\ell = \overline{Y}_m \tag{5.5}$$

where

$$\overline{Q}_{m\ell} = \sum_{k=1}^{a} C_{mk} Q_{k\ell} \tag{5.6a}$$

$$\overline{Y}_m = \sum_{k=1}^{a} C_{mk} Y_k \tag{5.6b}$$

The program forms the elements of $\overline{Q}_{m\ell}$ directly, and the contributions to $\overline{Q}_{m\ell}$ from sink species other than the sink for $m$ are set to exactly zero. In this way, the $\overline{Q}_{m\ell}$ matrix remains well-conditioned, even in situations where rows of the $Q_{k\ell}$ matrix differ by as little as one part in $10^{20}$. This conditioning process is a very important contributor to the robustness of the program.

# III. USING THE ELEMENT POTENTIALS

## 1. Introduction

The $\lambda_i$, which we have called the element Planck potentials, are crucial to the calculation method. As we shall show by example below, the element potentials can be used to make mixture composition estimates by hand, without detailed equilibrium calculations, in cases where a sub-set of species dominates the composition. Because the element potential concept does not seem to be widely known in the combustion community, this special chapter has been devoted to the concept in order to bring it to the attention of colleagues in the field.

## 2. Post-Calculation Estimates

The element potentials calculated by the program may be used to make post-calculation estimates of the mole fractions of minor gas species that were not included in the initial run. We shall illustrate this using the results from the first example in Section I.2, where a carbon-rich C-O mixture at 3000 K and 1 atmosphere was found to have the following element Planck potentials:

| Atom | $\lambda$ |
|---|---|
| C | -3.6861 |
| O | -29.8915 |

We did not include the molecules C, O, or $O_3$ in the mixture. Let's estimate their mole fractions using (1.7). We first use JANAF table data to calculate $\tilde{g}$ for each species. In the notation of the JANAF tables,

$$\tilde{g} = \left\{ \Delta H^o_{f298.15} + (H^o - H^o_{298}) - T\left(S^o - R\,\ell n(P/P^o)\right)\right\} \Big/ RT$$

Note we have $P = P^o = 1$ atm in this example; also,

$$RT = 1.987165 \times 3000 = 5962 \text{ cal/mol.}$$

For C:

$$\tilde{g} = \left[(170.89 + 13.550) \times 1000 - 3000 \times 49.287\right] / 5962 = 6.1359$$

For O:

$$\tilde{g} = \left[(59.559 + 13.522) \times 1000 - 3000 \times 50.096\right] / 5962 = 12.9509$$

For $O_3$:

$$\tilde{g} = \left[(57.080 + 36.023) \times 1000 - 3000 \times 86.092\right] / 5962 = -27.7066$$

Now, we use (1.7):

$$x_C = \exp\left[-(6.1359) + 1 \times (-3.6861)\right] = 5.42 \times 10^{-5}$$

$$x_O = \exp\left[-(12.9509) + 1 \times (-29.8915)\right] = 2.48 \times 10^{-19}$$

$$x_{O_3} = \left[\exp -(-27.7066) + 3 \times (-29.8915)\right] = 1.22 \times 10^{-27}$$

Note that the mole fraction of the neglected C is greater than that of the included $O_2$. We should have included gaseous C in the calculation. However, the mole fractions of both O and $O_3$ are extremely small, and hence they need not have been included.

## 3. Complete Estimations by Hand

Let's show how this particular calculation might have been done by hand without any computation. We expect that at 3000 K the gas will be predominantly CO. So, for the 2:1 specification for C:O, the composition would be 1 mole of C(s) per mole of CO. Again using JANAF table data,

$$\tilde{g}_{C(s)} = \left[(0 + 14.412) \times 1000 - 3000 \times 12.129\right] /5962 = -3.6862$$

$$\tilde{g}_{CO} = \left[(-26.420 + 22.357) \times 1000 - 3000 \times 65.370\right] /5962 = -33.5777$$

Now, from (1.9), we calculate the element Planck potential for C:

$$-3.6862 = \lambda_C \times 1$$

$$\lambda_C = -3.6862$$

And, from (1.7), we calculate the element Planck potential for O:

$$1 = \exp\left[-(-33.5777) + \lambda_C + \lambda_O\right]$$

$$\lambda_O = -29.8915$$

Note that these are almost exactly the Planck potentials obtained by the program. Having the Planck potentials, we now could make very good estimates of the mole fractions of minor species; for $CO_2$,

$$\begin{aligned}\tilde{g}_{CO_2} &= \left[(-94.054 + 36.535) - 3000 \times 79.848\right]/5962 = -49.8303 \\ x_{CO_2} &= \exp\left[-(-49.8303) + 1 \times (-3.6862) + 2 \times (-29.8915)\right] \\ &= 0.11932 \times 10^{-5}\end{aligned}$$

<u>exactly</u> as calculated by the program.

This process is essentially what is done in the program. First, the initializer estimates the populations of the major species, from which a trial value of the element potentials is calculated. Then, the Newton-Raphson iterations, or steepest descent if this fails, are used to adjust the Planck potentials. With a good initial guess, the Newton-Raphson iteration is rapidly successful, and only a few iterations are needed.

## 4. Summary

In summary, the element potentials provide an exceptionally convenient tool for estimating populations when the major species are known. The author believes that the concept of the element potential deserves wider appreciation in the combustion community.

# IV. DATA-FILE MANAGEMENT

## 1. File Content

There are two types of data files associated with these programs. The master data file contains the data on all species thus far input at any installation. This set is limited in length only by the size of the storage device, and with disks or tapes it is essentially infinite. The package data file is a subset of species from the master data file that has been assembled by a particular user for a given set of problems. This set is limited by the dimensioning of arrays in the JANAF program. In the present version at Stanford this limit is 20 species; users may redimension the program for larger or smaller packages.

The structure of these two files is slightly different. In each case the first card contains information on the number of species in the file. In the master file this is followed by a set of records, one for each species, giving its name and the reference date for the data; these are omitted in the package file. Both files contain the data for the species, in alphabetical order, with 13 records per species. The first record provides the chemical name and reference date, the molecular weight, enthalpy of formation at 298.15K, the density (condensed species; 0 for gas species), followed by the atomic composition data (number and names of each atom in the species). The next six records hold the absolute entropy at 1 atm for the JANAF table temperature entries 200, 298.15, 300, 3000, ... , 6000K. The final six records hold the enthalpy above 298.15K at the same temperatures (and at 1 atm in the case of condensed species). The formatting of these files is given in the program comments in the file management programs JFILE and JPACK, respectively.

The author had a choice of holding all of the JANAF file data in tables or approximating it with curves. The choice to use the basic data was made so that students who worked problems by hand using the JANAF tables and associated equilibrium constants would get exactly the same results as yielded by the program.

## 2. Updating the File

The interactive program JFILE allows a user to add a species to the master file. To do this, the user will need to have the JANAF tables in hand for this update.

If the species are not in the JANAF tables, the user will have to first create the required information (see above). For condensed species it is important to have continuous data that do not permit erroneous condensation above the critical temperature. The approach used by the author in constructing a data set for liquid $H_2O$ was to use the actual saturation data to set the properties below 600K (critical T = 647K) and to extend the vapor dome to infinite temperature above 600K. This was done by assuming that $P_{sat} = C_1T^a$ and $h_{fg} = C_2/T^b$, where $C_1$, $C_2$, a, and b are constants determined by matching the values and slopes of the extrapolations and actual behavior at 600K.

To update the master file, the user must define logical unit 22 as the master file and unit 23 as a scratch file of similar capacity, and then call the JFILE program. JFILE will prompt for the required information, provide an opportunity for checking and correction, and then place the updated file in unit 21. The wise user will first save a backup of the old master file in case the system fails during the update.

## 3. Creating a Package File

To prepare a package file, the user must define logical unit 22 as the master file and unit 23 as the package file, and then call the JPACK program. JPACK will present the list of species in the master file, from which the package subset can be selected. The package file, in the form needed for JANAF, is then placed in unit 23.

The JANAF program reads the package file from logical unit 21. Therefore, after checking that the package file is as desired, the user can transfer it to the file identified as unit 21 in the JANAF program, or else define unit 21 as the new package file before calling JANAF.

# V. OBTAINING AND INSTALLING STANJAN

## 1. Availability

The programs and data files needed to implement STANJAN are supplied on magnetic tape, which may be purchased from the Department of Mechanical Engineering at Stanford University. For details on costs and arrangements, see the Appendix. The purchase price covers the tape and shipment. Proceeds are used to support graduate student training through research in the Thermosciences Division.

## 2. Prepurchase Trial

If you would like to experiment with the program before deciding to place an order for a tape and have access to a terminal with telephone coupler, you can make limited use of the program on Stanford's LOTS computer system. To do so, first call the author's office, (415)-497-4021, to obtain the current password and account name for a special account that has been set up for external STANJAN trials. Under this account you will be able to execute STANJAN but will have no data-storage space and no access to the source programs or data files. Then set your coupler for full-duplex communication at 300 Baud, even parity, and dial LOTS at (415)-497-2803. To get the attention of LOTS or to terminate execution while running the program, use control-C. LOTS will respond with its EXEC prompt character @. Type the account code in triangular brackets followed by a space and the password:

```
@<account code> password
```

If you are accepted, you will be invited to read various messages, which you can skip by control-C. LOTS will give you another @ prompt, at which you respond:

```
@DEFINE 21:<R.REY>
```

This gets you a package data file. If you have not already done so, set your terminal for all caps (TTY lock), as all of the input to the interactive programs must be in capital letters. Then, to the next @ prompt, respond

```
@<R.REY>JANAF
```

This will place you in execution with the program JANAF. When you are finished executing, you may return to the EXEC by responding Y to the ARE YOU

FINISHED? query by JANAF, or by control-C. Log off by responding K to an @ prompt.

## 3. The Program Tape

The STANJAN program tape consists of six files:

File 1: the current master data file at Stanford,

File 2: a package data file suitable for combustion problems,

File 3: JALPH program,

File 4: JFILE program,

File 5: JPACK program,

FIle 6: JANAF program.

Each file consists of 80-character records (card format), with a block size of 8000 bytes in ASCII coding. The program files contain FORTRAN source programs, liberally commented.

## 4. Checking and Compiling

The first step will be to load these files into suitable storage on your system and print listings of the programs. Review these programs for incompatibilities with the FORTRAN on your machine. They are fully compatible with most FORTRAN implementations used on both DEC and IBM systems. The tape is supplied in ASCII coding, and must be converted when read by IBM equipment.

Note that these programs are written with the following identification of the logical units:

| Unit | Function |
|---|---|
| 3 | Printer |
| 5 | Terminal input or batch input |
| 6 | Terminal output or batch output |
| 21 | Data file |
| 22 | Data file |
| 23 | Data file |

If you wish to alter these definitions to suit your system, and have a text editor, note that all READ and WRITE statements have the form

READ (unit     or     WRITE (unit

so they can be changed easily with your editor. Alternatively, you may prefer to use job control language to define these files in an appropriate way for your system.

If you want to handle more than 20 species containing more than eight atoms, you will have to redimension arrays in JPACK and JANAF. Read the program listings to see what is required.

Next, compile the programs. Save a load module of the JANAF program to avoid linking on each call.

## 5. Alphabetizing the Master File

BEFORE YOU UPDATE THE DATA FILE ON YOUR SYSTEM, YOU MUST RE-ALPHABETIZE THE MASTER FILE. The reason for this is that different systems use different codings for the letters and special characters that appear in species and atom names, and the update program JFILE will not function properly if the list is not alphabetically in order in the coding system of your computer. As delivered, the tape will have a file alphabetized for the DEC system-20; it is not properly alphabetized for IBM equipment.

To re-alphabetize the master file, define the master file as logical unit 21 and units 22 and 23 as files of comparable capacity. Then call program JALPH. The re-alphabetized file will be delivered to unit 22; unit 23 is a scratch file. Note: JALPH is not an interactive program, and hence this step can be carried out in the batch mode. Compare the original and re-alphabetized files, and if everything is satisfactory, the original master file may be discarded.

## 6. The Package File

The JANAF program must have a package data file in logical unit 21. One package file is supplied on the tape. The fact that this version may not be in alphabetical order on your machine is not of consequence. If you wish to construct other package files, see Chapter IV.

## 7. Program Checkout

Check out your STANJAN implementation by running the sample programs given in Chapter I. If you have problems, call the author at (415)-497-4021.

## 8. In Case of Difficulty

You may challenge the program with a tough problem that will not work. If you do, please contact the author (see above), and we will try to help you solve the problem. Note that the JANAF program will provide diagnostic output if you type MON in response to the last query before execution, "DO YOU WANT TO ABORT THIS RUN?" If you do have difficulty, run the problem with this diagnostic, which will help the author or another person familiar with the program find the source of difficulty and implement a fix.

# References

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## Appendix

## TO ORDER A TAPE

Tapes are standard half-inch magnetic tapes written with nine tracks at 1600 BPI, and are unlabeled. The record length is fixed at 80 characters, and the records are blocked at 8000 bytes/block. The coding is ASCII.

The purchase price for a complete tape is $100. The purchase of a tape implies an agreement not to release the tape or the material thereon to any person outside of your own organization.

Purchasers of the tape will be advised of updates or additions as they arise, at no further cost.

To obtain a tape, send a check made payable to Stanford University or an institutional purchase order to:

W. C. Reynolds
Department of Mechanical Engineering
Stanford University
Stanford, CA 94305

Request one STANJAN magnetic tape.