STUDY OF HIGH TEMPERATURE EQUILIBRIUM BY FREE ENERGY MINIMIZATION METHOD

by

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Submitted in Partial Fulfillment of the Requirements
for the Degree of
Master of Science in Engineering
in the
Materials Science
Program

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YOUNGSTOWN STATE UNIVERSITY
August, 1982

ABSTRACT

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Master Of Science in Engineering
Youngstown State University, 1982

Equilibrium composition of a chemically reactive system can be obtained by free energy minimization method. The mathematical model was first developed in 1958, which was further developed to make it applicable to multiphase systems. A computer program has since been developed to carry out the neumerical manipulations required to obtain the equilibrium composition based on this mathematical model.

This work consists of three parts. First, a review of the mathematical theory has been done. In the second part, the method as applied to the situation has been analyzed. Finally, an analysis of the computer program has been made, and a number of sample data sets have been run in the program to demonstrate the capability of the software.

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LIST OF SYMBOLS

SYMBOL	DEFINITION	UNITS OR REFERENCE
a	no. of atoms	
b	amount of an element	moles
c	constant	
f	chemical potential	Joules
g^o	free energy of a species	Joules/mole
i	species no.	none
j	element no.	none
k	element no.	none
ℓ	total no. of elements	none
m	total no. of species	none
n	mole no. of a species	mole
p	phase no.	none
q	total no. of liquid and solid phases	none
∂	a constant	moles
s	total no. of invarients	none
x	mole no. of a species	mole
y	mole no. of a species	mole
A	activity of a species	Joules/mole
G	free energy	Joules
H	enthalpy	Joules/mole
N	sum of moles of all species	mole
P	total pressure	

LIST OF SYMBOLS

SYMBOL	DEFINITION	UNITS OR REFERENCE
R	gas constant	Joules/mole ^{o}K
T	reaction temperature	^{o}K
x	sum of moles of all species in a phase	mole
y	sum of moles of all species in a phase	mole
λ	Lagrangian multiplier	see Equation 5
Δ	displacement amount	
Σ	summation of the mathematical terms that follow	
a_{pij}	no. of atoms of jth element in ith species of pth phase	see Equation 17
m_p	no. of species in pth phase	see Equation 16
f_{pi}	a mathematical quantity for ith species in pth phase	see Equations 25 and 26
π	a mathematical quantity	see Equation 30

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CHAPTER 1

Introduction

Many industrial processes, such as primary ore reduction, secondary refining of metals, synthesis of organic compounds, and combustion of fuels, all have a common problem. Each of these processes is characterized by a multi-component, multi-phase, chemically reactive system. The problem is to calculate the thermodynamic equilibrium composition of such a system. The traditional attempt at solving this problem involved solving a set of simultaneous equations associated with the chemical reactions thought to occur in the system. There are two shortcomings of this method which limits its use to very simple systems. First, it is sometimes difficult to predict which chemical reactions will occur. More importantly, however, is that the set of equations generated are usually non-linear. In a complex system containing many components and several phases, the traditional method of determining the equilibrium composition usually yields no results even when used with a computer.

Fortunately, a totally different approach is possible to solve this problem. This method is based on the thermodynamic fact that the sum of the chemical potentials of all substances in the system must have a minimum value at equilibrium. The technique, first suggested by White, et al,[1] involves minimizing a free-energy function subject the condition that mass must be conserved in the system. The free-energy function is the summation, over all phases, of the summation of the chemical potentials of the substances in each phase. There are two advantages to this method. First, the final solution requires solving a set of simultaneous linear equations. Second, the free-energy function has been generalized so that it is applicable to all systems, regardless of the number of components and phases existing in the system.

The problem with the method is how to minimize the complex free-energy function. White suggested two techniques; namely, the method of steepest descents and Danzig's Simplex computer routine. Both of these techniques have been used with great success in fuel combustion problems. These problems involve, however, only a single gaseous phase in equilibrium with pure condensed phases. The problem involving equilibrium between variable composition condensed phases has not received a great deal of attention.

A computer program applicable to this last problem has been developed by Eriksson. Eriksson's work is, unfortunately, not well known, and has not been widely used in metallurgical industry.

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[1] W. B. White, S. M. Johnson, and G. B. Danzig, "Chemical Equilibrium in Complex Mixtures," The Journal of Chemical Physics 28, No. 5 (May 1958), pp. 751-755.

The first objective of this work was to understand the numerical method that has been used and the algorithm of the program that utilizes the numerical method. Secondly, to modify the original program to make it compatible with the existing computer system at Youngstown State University, and the final objective was to use the program for a reaction system which has been studied before and see if the results obtained from the computer agrees.

CHAPTER II

Optimization By Method Of Lagrangian Multiplier

The numerical problem is one of optimization of a multivariable objective function with equality constraint equations. The method used is the Lagrangian Multiplier and steepest descent technique.

Lagrangian Multiplier Method

Let the objective function be

$$y = f\ (x_1,\ x_2,\ x_3,\ \ldots.\ x_n) \tag{1}$$

where x_1, x_2, ... x_n are the variables and

$$g_k = f\ (x_1,\ x_2,\ \ldots.\ x_n) = 0 \tag{2}$$

for $k = 1, 2, 3, \ldots. m$ are the equality constraints.

y to be optimum, the first derivative of equation (1) must vanish. Therefore,

$$dy = \sum_{i=1}^{n} \frac{\partial y}{\partial x_i} \partial x_i = 0 \tag{3}$$

for $i = 1, 2, 3 \ldots. n$.

Also, since all displacements in x_i must satisfy equation (2)

$$dg_k = \sum_{i=1}^{n} \frac{\partial g_k}{\partial x_i} \partial x_i = 0 \tag{4}$$

for $i = 1, 2, 3, \ldots. n$

and $k = 1, 2, 3, \ldots. m$

df is now formed such that,

$$df = dy + \sum_{k=1}^{m} \lambda_k dg_k \qquad (5)$$

where λ_k are m multipliers, values of which will be determined later. Equation (5) can be expanded as follows

$$dF = (\frac{\partial y}{\partial x_1} dx_1 \ldots \frac{\partial y}{\partial x_n} dx_n) +$$

$$\lambda_1 (\frac{\partial g_1}{\partial x_1} dx_1 + \frac{\partial g_1}{\partial x_2} dx_2 + \ldots . \frac{\partial g_1}{\partial x_n} dx_n) +$$

$$\ldots \lambda_m (\frac{\partial g_m}{\partial x_1} dx_1 + \frac{\partial g_m}{\partial x_2} dx_2 + \ldots \frac{\partial g_m}{\partial x_n} dx_n) \qquad (6)$$

Equation 6 can be rearranged as

$$dF = (\frac{\partial y}{\partial x_1} dx_1 + \lambda_1 \frac{\partial g_1}{\partial x_1} dn_1 + \ldots$$

$$\lambda_m \frac{\partial g_m}{\partial x_1} dx_1) + \ldots . (\frac{\partial y}{\partial x_n} dx_n + \lambda_1 \frac{\partial g_1}{\partial x_n} + \ldots$$

$$\lambda_m \frac{\partial g_m}{\partial x_n} dx_n)$$

or, $$dF = \sum_{i=1}^{n} (\frac{\partial y}{\partial x_i} + \sum_{k=1}^{m} \lambda_k \frac{\partial g_k}{\partial x_i}) dx_i \quad \ldots \qquad (7)$$

It may be noted that Equation (5) and Equation (7) are the same equation written in different form. Further, in Equation (5) $dF = 0$ as dF is composed of two parts which independently vanish.

Now, to make $dF = 0$ in Equation (7), values are chosen for λ_k for $k = 1, 2, 3 \ldots m$ such that $\frac{\partial y}{\partial x_i} + \sum_{k=1}^{m} \frac{\partial g_k}{\partial x_i}$ is equal to zero, for $i = 1, 2, \ldots m$. It is imperative that since there are m constraints and n variables, $n - m$

displacements can be chosen arbitrarily, therefore

$$\frac{\partial y}{\partial x_i} + \sum_{k=1}^{m} \lambda_k \frac{\partial g_k}{\partial x_i}$$

in Equation (7) is equal to zero for $i = m+1, m+2 \ldots n$. This yields the modified objective function

$$F = y + \sum_{k=1}^{m} \lambda_k g_k \tag{8}$$

where all displacements are independent with respect to F. Therefore, to obtain the stationary point, Equation (8) is optimized subject to Equation (2) and thus obtain

$$\frac{\partial F}{\partial x_i} = 0 \tag{9}$$

for $i = 1, 2, \ldots n$ and

$$g_k = 0 \tag{10}$$

for $k = 1, 2, \ldots m$.

Equation (9) and Equation (10) gives a set of $n+m$ Equations from which m λ_ks and $n-m$ x_is are to be evaluated, which is possible. Then substituting λ_k values, appropriate x_is can be determined.

Method of Steepest Descent

Equation (1) is made use of to explain the method of steepest descent.

Expanding Equation (1) in Taylor's series around an arbitrary point Y gives

$$f(X) = f(Y) + f'(Y)\,\Delta y + \frac{f''(Y)}{2!}\,\Delta y^2 + \frac{f'''(Y)}{3!}\,\Delta y^3 \ldots$$

where $f(x)$ is the value of function at x and Δy is the displacement in the variables. Now a quantity λ is calculated from the equation

$$y_i + \lambda_i\,(x_i - y_i) = 0$$

for each displacement, where x_is are obtained by optimizing $f(X)$

λ is finally created from the expression

$$\lambda = K\lambda_{min}$$

where $K < 1$.

Now all x_is are modified according to the Equation

$$x_i = y_i + \lambda(x_i - y_i)$$

This procedure ensures all x_is are positive valued but at the same time as close to the optimum value as possible. It also ensures that all the displacements are unidirectional. It is evident at optimum point, $f(X) = f(Y)$.

CHAPTER III

MATHEMATICAL MODEL

Objective Function

Free energy of a chemical system having a mixture of n chemical species can be written as

$$G\ (N) = \sum_{i\ =\ 1}^{n} f_i, \tag{11}$$

where, $N = n_1,\ n_2,\ \ldots\ n_n$ the set of **mole** nos.

$f_i = n_i\ (C_i + \ln\ (ni/N))$

$C_i = G^o/RT + \ln P$ for gaseous mixture

P = total pressure.

$N = \sum_{i=1}^{n} n_i$

expanding Equation (11) about arbitrary point Y in Taylor series,

$$O\ (N) = G\ (Y) + \sum \frac{\partial G}{\partial n_i} \Delta_i \Big|_{N\ =\ Y} + \tfrac{1}{2} \sum_{ik}\sum \frac{\partial^2 G}{\partial n_i \partial n_k} \Delta_i \Delta_k \Big|_{N\ =\ Y}$$

It may be noted here,

$$\frac{\partial G(N)}{\partial n_i} = C_i + \ln\ (n_i/N) \tag{12}$$

$$\frac{\partial^2 G(N)}{\partial n_i^2} = \frac{1}{n_i} - \frac{1}{N} \tag{13}$$

$$\frac{\partial^2 G(N)}{\partial n_i \partial n_k} = -\frac{1}{N}\ \text{for}\ i \neq K\ \ldots \tag{14}$$

from Equation (13) and Equation (14) follows that both

$G(N)$ and $Q(N)$ are convex as the second partials for both the functions are positive.

The free energy for any system can now be generalized[2] as

$$G = \sum_{p=1}^{1} \sum_{i=1}^{m_p} n_{pi} \left(g^o_{pi} + RT\ln \left(\frac{n_{pi}}{N_p} p \right) \right) +$$

$$\sum_{p=2}^{q+1} \sum_{i=1}^{m_p} n_{pi} \left(g^o_{pi} + RT\ln \left(\frac{n_{pi}}{N_p} \right) \right) +$$

$$\sum_{p=q+2}^{q+s+1} \sum_{i=1}^{m_p} n_{pi}\, g^o_{pi} \tag{15}$$

where $N_p = \sum_{i=1}^{m_p} n_{pi}$

where phases are numbered consecutively, from $p = 1$ for gaseous phase, $p = 2$ to $q + 1$ for solid and liquid mixtures, $p = q + 2$ to $q + s + 1$ for invariants dividing Equation (15) by RT, to make the left-hand side dimensionless, we get

$$\frac{G}{RT} = \sum_{p=1}^{1} \sum_{i=1}^{m_p} n_{pi} \left((q^o/RT)_{pi} + \ln P + \ln \left(\frac{n_{pi}}{N_p} \right) \right) +$$

$$\sum_{p=2}^{q+1} \sum_{i=1}^{m_p} n_{pi} \left((g^o/RT)_{pi} + \ln \left(\frac{n_{pi}}{N_p} \right) \right)$$

$$+ \sum_{p=q+2}^{q+s+1} \sum_{i=1}^{m_p} n_{pi} \tag{16}$$

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[2] Gunnar Eriksson and Erik Rosen, "General Eq$^{\underline{n}}$s for the Calculation of Equilibrium in Multiphase Systems," <u>Chemica Scripta</u> 1973, 4, pp. 193-194.

Equation 16 is the objective function which needs to be minimized subject to the constraint equations developed below.

Constraint Equations

The constraint equations are developed from the fact that the total amount of each element present in the system is constant. Therefore, the constraint equations can be expressed as follows,

$$\sum_{p=1}^{q+s+1} \sum_{i=1}^{m_p} a_{pij} n_{pi} = b_j \quad for\ j = 1, 2, \ldots \ell \tag{17}$$

where a_{pij} represents the number of atoms, of the jth element in the i th substance in the p th phase.

b_j = total amount of j th element

Optimization Method

By using the method of Lagrangian method of undetermined coefficient, the following equations can be obtained from Equation (16) and Equation (17),

$$(g^o/RT)_{pi} + \ell n\ P + \ell n\ \left(\frac{n_{pi}}{N_p} \right) - \sum_{j=1}^{\ell} \lambda_j a_{pij} = 0 \tag{18}$$

for $i = 1, 2, \ldots m_p$

and $p = 1$

$$(g^o/RT)_{pi} + \ell n\ \left(\frac{n_{pi}}{N_p} \right) - \sum_{j=1}^{\ell} \lambda_j \tag{19}$$

for $i = 1, 2, \ldots m_p$

$p = 2, 3, \ldots q + 1$

$$(g^{o}/RT)_{pi} - \sum_{j=1}^{\ell} \lambda_j a_{pij} = 0 \tag{20}$$

for $i = 1$

$p = q + 1, q + 2, \ldots q + s + 1$

In Equations (18), (19), and (20) λ_j are the Langrangian multipliers. Expanding Equations (18), (19), and (17) in Taylor series about an arbitrary point Y and neglecting terms of second and higher order, we obtain respectively,

$$(go/RT)_{pi} + \ell n\ P + \ell n\ \left(\frac{y_{pi}}{Y_p} \right) - \sum_{j=1}^{\ell} \lambda_j a_{pij} + \frac{x_{pi}}{y_{pi}} - \frac{X_p}{Y_p} = 0 \tag{21}$$

for $i = 1, 2, \ldots m_p$

and $p = 1$

$$(go/RT)\ pi + \ell n\ \left(\frac{y_{pi}}{Y_p} \right) - \sum_{j=1}^{\ell} \lambda_j a_{pij} + \frac{x_{pi}}{y_{pi}} - \frac{X_p}{Y_p} = 0 \tag{22}$$

for $i = 1, 2, \ldots m_p$

and $p = 2, 3, \ldots q+1$

$$\sum_{p=1}^{q+s+1} \sum_{i=1}^{m_p} a_{pij} y_{pi} - b_j +$$

$$\sum_{p=1}^{q+s+1} a_{pij} (x_{pi} - y_{pi}) = 0 \tag{23}$$

for $j = 1, 2, \ldots \ell$

In Equations (21), (22), and (23),

$$Xp = \sum_{i=1}^{m_p} x_{pi} \text{ and } Yp = \sum_{i=1}^{m_p} y_{pi}$$

from Equation (11), we get

$$x_{pi} = - f_{pi} + y_{pi} \quad ((X_p / Y_p) + \sum_{j=1}^{\ell} \lambda_j a_{pij}) \tag{24}$$

for $i = 1, 2, m_p$

$p = 1$

where $f_{pi} = y_{pi} ((g^0/RT)_{pi} + \ell n\, P + \ell n\, (y_{pi}/Yp))$ (25)

for $i = 1, 2, \ldots m_p$

$p = 1$

from Equation (22) we get

$$x_{pi} = - f_{pi} + y_{pi} ((Xp/Yp) + \sum_{j=1}^{\ell} \lambda_j a_{pij}) \tag{26}$$

for $i = 1, 2, \ldots m_p$

$p = 2, 3, \ldots q + 1$

where $f_{pi} = y_{pi} \quad ((g^0/RT)_{pi} + \ell n\, (y_{pi}/Y_p))$ (27)

for $i = 1, 2, 3, \ldots m_p$

$p = 2, 3, \ldots q + 1$

Summing Equation 24 over $i = 1, 2, \ldots m_p$ we get

$$\sum_{i=1}^{m_p} f_{pi} = \sum_{j=1}^{\ell} \lambda_j \sum_{i=1}^{m_p} y_{pi} a_{pij} \tag{28}$$

Summing Equation (26) over $i = 1, 2, \ldots mp$ for $p = 2, 3, \ldots q + 1$ would also result in Equation (18). Substituting Equation (28) and 1f in Equation (23) and reanalizing we get,

$$\sum_{p=1}^{q+1} \sum_{k=1}^{\ell} \lambda_k r_{pjk} + \sum_{p=1}^{q+1} ((Xp/Yp) - 1) \sum_{i=1}^{m_p} a_{pij} y_{pi} + \sum_{p=q+1}^{q+s+1} \sum_{i=1}^{m_p} a_{pij} x_{pi} = \sum_{p=1}^{q+1} \sum_{i=1}^{m_p} a_{pij} (f_{pi} - y_{pi}) + b_j \tag{29}$$

for $j = 1, 2, \ldots \ell$

where f_{pi} is defined as per Equations (25) and (27)

and $r_{pjk} = \sum_{i=1}^{m_p} (a_{pij} a_{pik}) \, y_{pi}$

$for\ j, k, = 1, 2, \ldots \ell$

Now Equations (29), (28), and (20) constitute a system of ℓ + q + s + 1 equations with the same number of unknowns as follows:

Unknown	No
λ_k	ℓ
$Xp/Yp-1$	$q+1$
x_{pi}	s

For $i=1$, and $p=q+2, q+3, \ldots q+s+1$

By solving this linear system of equations, the amount of pure compounds can be directly obtained.

To obtain x_{pi}'s for p = 1, i.e. for the gas phase, Equation (14) is used where λ_j's and corresponding X_p/Y_{p-1} are substituted.

To obtain x_{pi}'s for $p = 2$ to $q+1$ Equation (16) is used where again λ_j's and corresponding X_p/Y_{p-1} are substituted.

After obtaining all the x_{pi}'s, they have to be modified to satisfy the final restriction that x_{pi}'s must be non-negative.

This is accomplished by using the method of steepest descent.

A quantity π is calculated according to

$$y_{pi} = \pi(y_{pi} - x_{pi}) \quad \text{for } i = 1, 2, \dots m_p \qquad p = 1, 2, \dots q + s + 1 \tag{30}$$

Now from Equation (20) π_{min} which is the smallest π is used to calculate a quantity λ such that $\lambda = k\pi_{min}$ where $k<1$ usually equal to 0.99.

The x_{pi}'s are then modified according to $x_{pi} = x_{pi} + \lambda(x_{pi} - y_{pi})$.

These x_{pi}'s are now used as y_{pi}'s to obtain the next approximation. This process is continued until difference between y_{pi}'s and x_{pi}'s are negligible. The final x_{pi}'s are the desired optimum values.

CHAPTER IV

PROGRAM ANALYSIS

The computer program is composed of a main routine, six subroutines, and three function subprograms. The basic control transfer between the different subroutines and the main program is shown in Figure 1.

Minimization of free energy by solving equations is accomplished in the subroutine GASOL, after the necessary data have been generated in the main routine.

Input information can be read into the main program as well as subroutine HETTA, which depend on the nature of information available. Output is generated by both the main program and HETTA, which again depends on the required output.

The subroutine SPEQUA has been provided to generate information related to the equilibrium composition of the system as required by the user. The user must provide not only his own functions in SPEQUA, but also his own output formats.

Main Program

The main program does very little computation work. Its main purposes are to read-in all the necessary information, and to print-out the results as calculated in the subroutines.

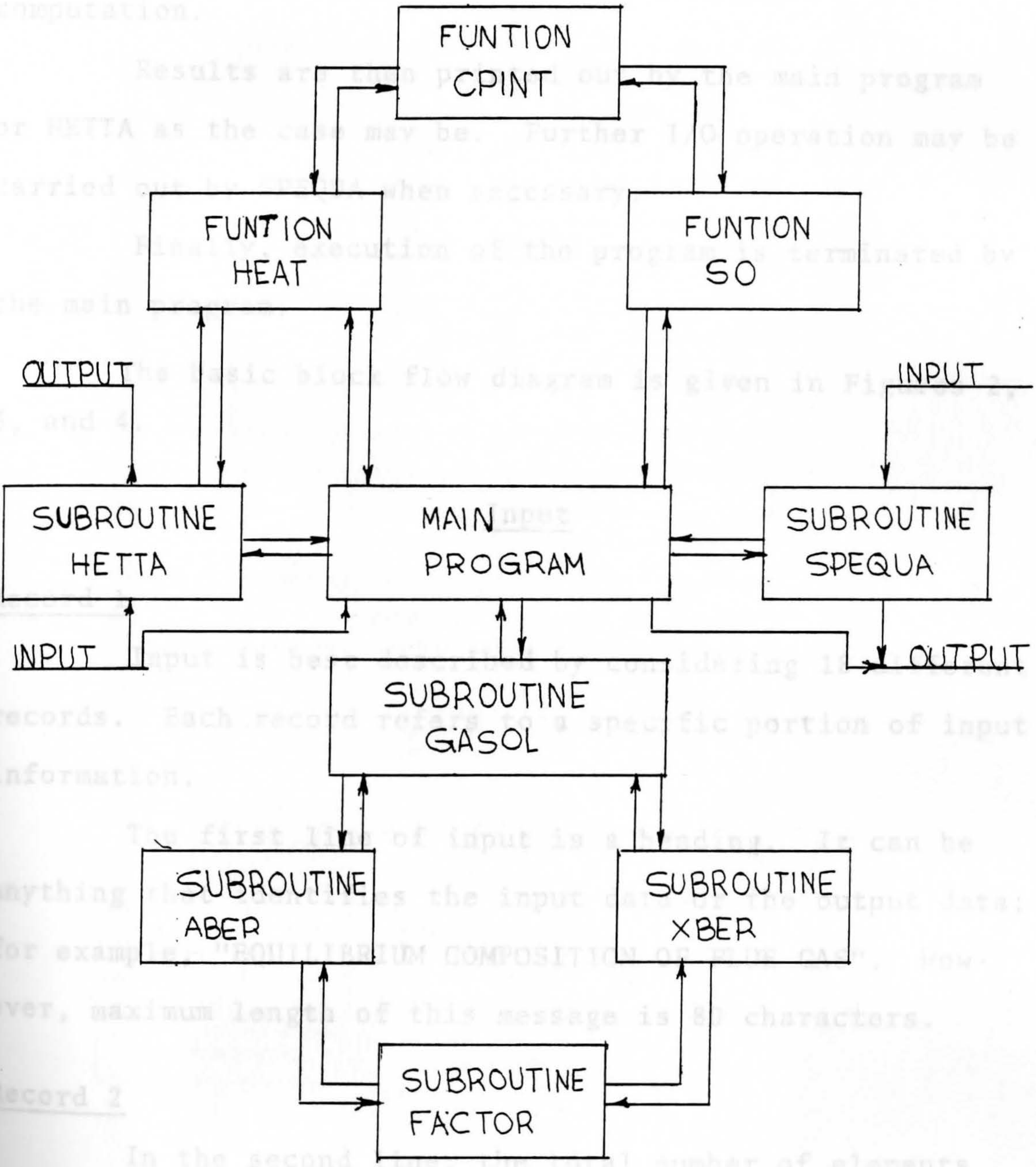

Figure 1. Transfer diagram. Flow between the various subroutines and the main program of SOLGASMIX is shown in the diagram.

After all information has been read, the main program transfers control to GASOL, which does the required computation.

Results are then printed out by the main program or HETTA as the case may be. Further I/O operation may be carried out by SPEQUA when necessary.

Finally, execution of the program is terminated by the main program.

The basic block flow diagram is given in Figures 2, 3, and 4.

Input

Record 1

Input is best described by considering 18 different records. Each record refers to a specific portion of input information.

The first line of input is a heading. It can be anything that identifies the input data or the output data; for example, "EQUILIBRIUM COMPOSITION OF FLUE GAS". However, maximum length of this message is 80 characters.

Record 2

In the second line, the total number of elements (L), the total number of mixtures (MP), the total number of invarients (MSOL), and the number of species in each mixture are listed. Format for this line is 4012. Maximum number of species that can be considered is 80, maximum number of

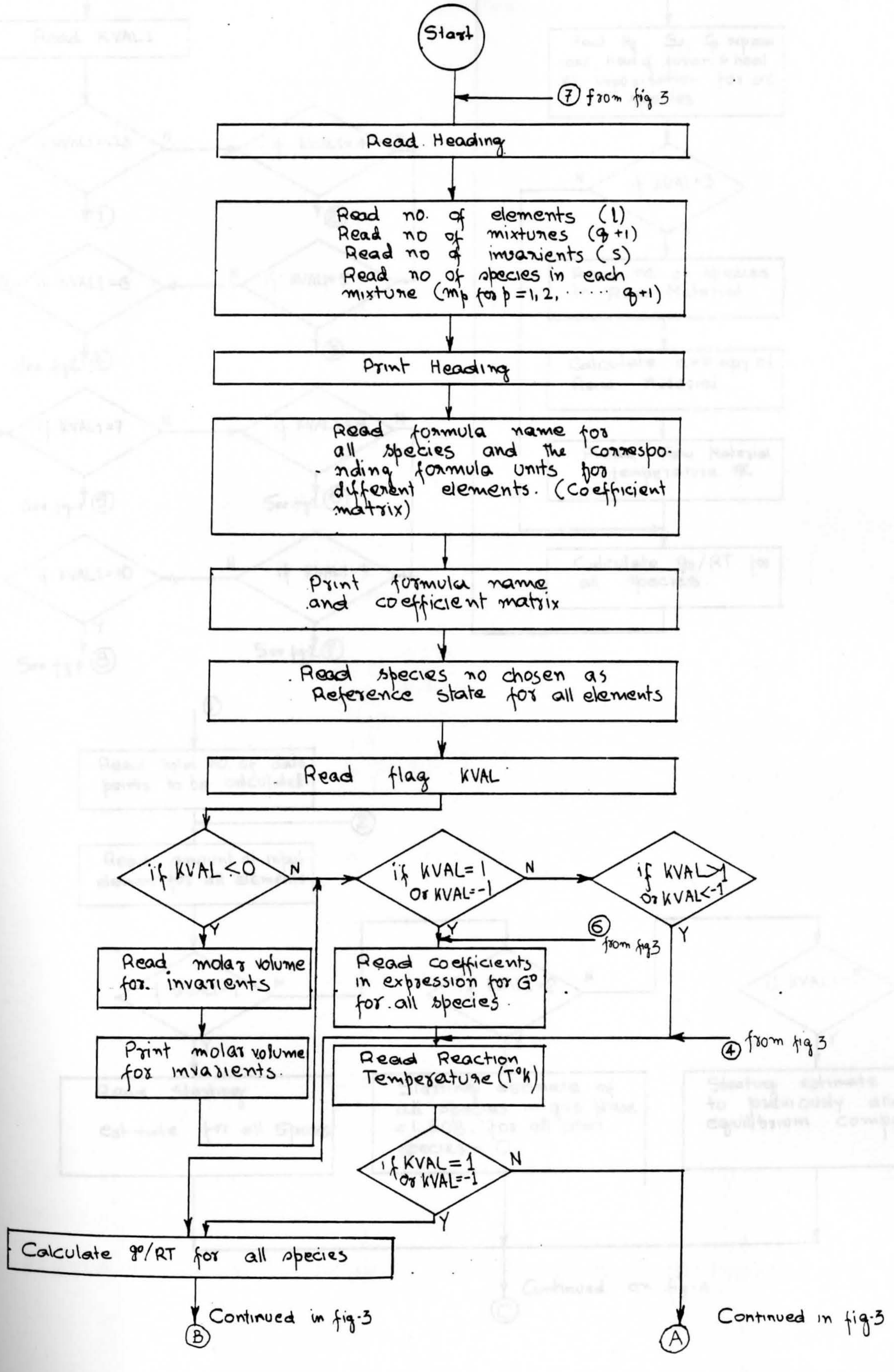

Figure 2. Flow Diagram of Main Program.

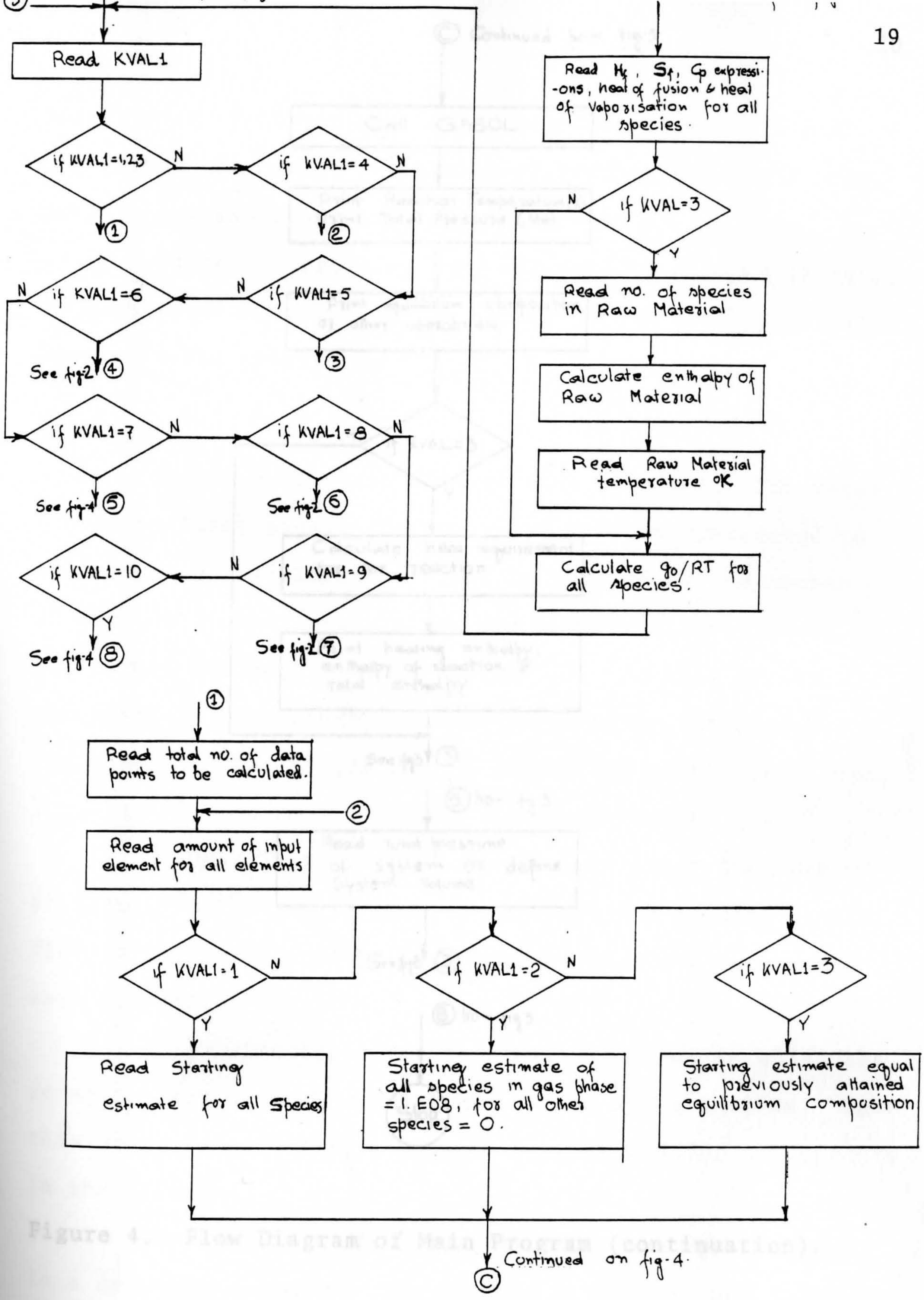

Figure 3. Flow Diagram of Main Program (continuation).

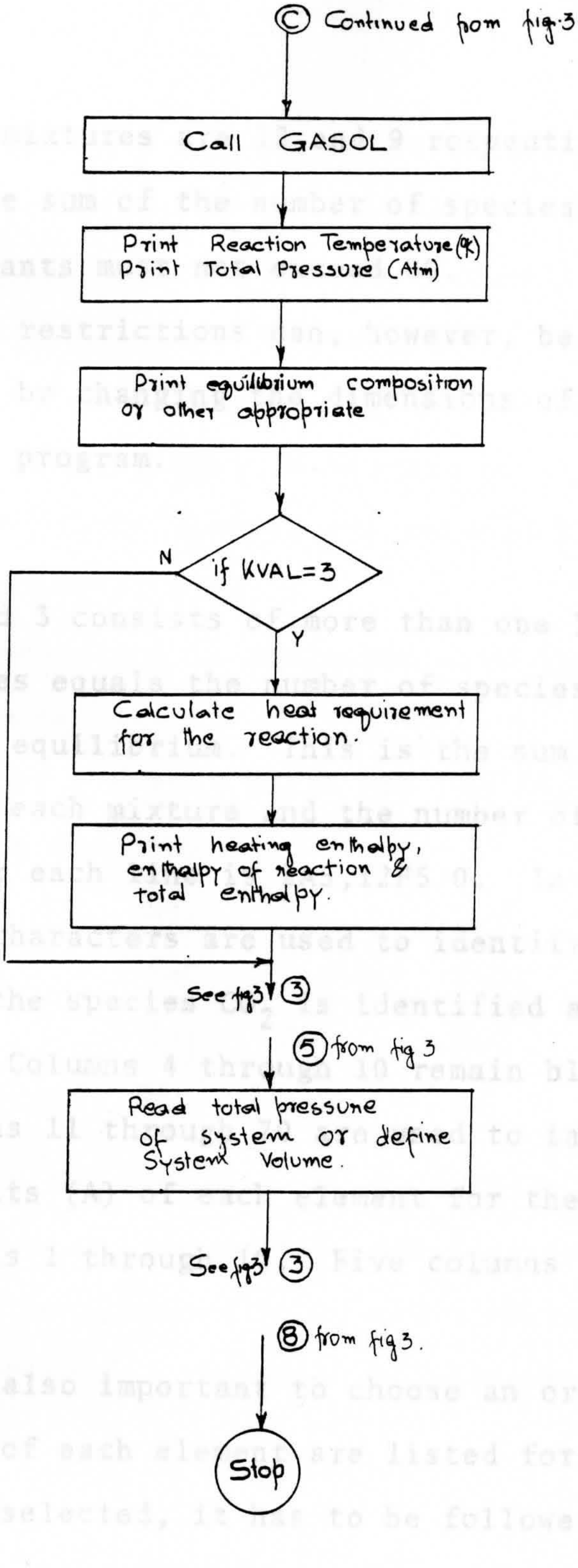

Figure 4. Flow Diagram of Main Program (continuation).

elements and mixtures are 12 and 9 respectively. This implies that the sum of the number of species and total number of invariants must not exceed 80.

These restrictions can, however, be changed (increased or decreased) by changing the dimensions of the appropriate arrays in the program.

Record 3

Record 3 consists of more than one line. The total number of lines equals the number of species considered to be present at equilibrium. This is the sum of the number of species in each mixture and the number of invariants. The format for each line is 2A5,12F5.0. In this format, the first 10 characters are used to identify the species. For example, the species CO_2 is identified as CO_2 in Columns 1, 2, and 3. Columns 4 through 10 remain blank.

Columns 11 through 70 are used to input the number of formula units (A) of each element for the species identified in Columns 1 through 10. Five columns are reserved for each element.

It is also important to choose an order in which the formula units of each element are listed for a species. Once this order is selected, it has to be followed for all species in the system.

The species in different mixtures are to be listed in a definite sequence. The species in Mixture One is input first. Then comes Mixture Two and so on. For example, it can not be input as 1-2-4-3-5 if there are five mixtures in the system considered. The order has to be 1-2-3-4-5. However, the species within a mixture can be in any order. If a species exists in more than one mixture, it has to be listed separately for each mixture. Another restriction is that the gas phase mixture must be Mixture No. 1.

The invariant species are entered last after all the mixtures have been entered.

This procedure is explained with the help of the following example.

Consider a system which has the following combination of species and phases:

GAS	SO_2	N_2	O_2	S_2
SLAG	FeO	Fe_304	SiO_2	FeS
MATTE	Cu_2S	Cu	FeO	S
INVARIENTS	Cu	Cu_2S	Fe	Si

This system has six elements (S, N, O, Fe, Cu, and Si), three mixtures (gas, slag, and matte), and four invariants (Cu, Cu_2S, Fe, and Si). The mixtures 1, 2, and 3 contain 4, 4, and 4 species respectively. The order of elements can be as follows:

1. S
2. N
3. O.
4. Fe
5. Cu
6. Si

Input is shown in Figure 5.

Record 4

Record 4 has a format 40I2. The species number which is considered to be the reference state for each element is input here (IEL). The order of the elements is the same as listed in Record 3. The species number is calculated from the third record, No. 1 being the first species in the record.

In the example of Figure 5, reference state for the first element, which is S, is species No. 4; for N it is No. 2 and so on. So the input record for Record 4 would look as follows:

b4b2b3151316*

Number 10 could be used rather than 12 as the reference state of Cu.

These reference states are also important in the output. For example, if there were 10 moles of S in the system, the program will print 0.5000E01 under X/Mole, against species S_2. But if we chose species No. 12 as the reference for S, the print-out against S_2 would be 0.0000E00 but against S it would print 0.1000E02.

Record 5

Record 5 is a number which acts as a switch in the

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*b = blank in column.

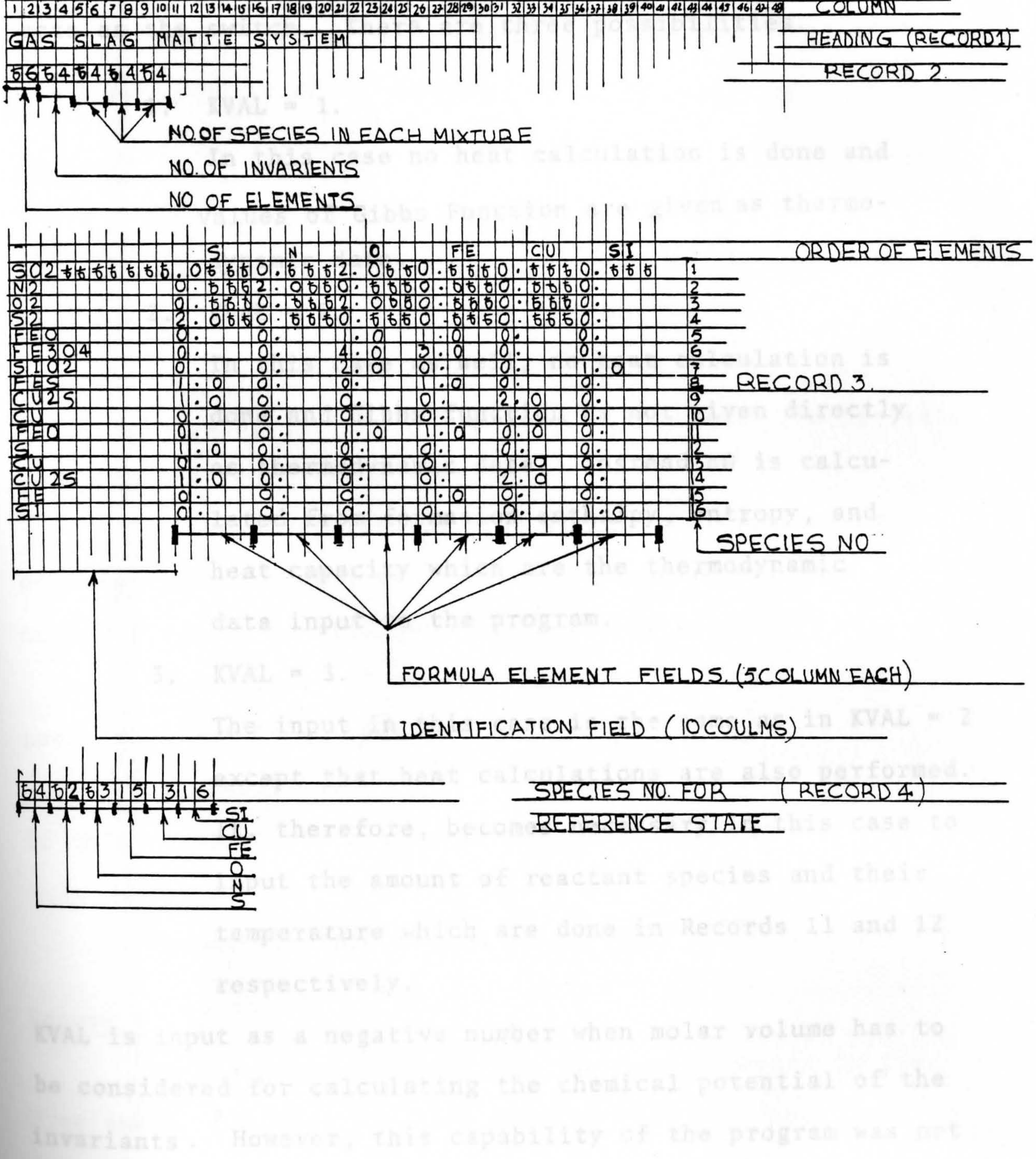

Figure 5. An Explanation of the Input Format.

flow of the program. The name of the variable is KVAL, which acts as the switch. There are three possibilities.

1. KVAL = 1.

   In this case no heat calculation is done and values of Gibbs Function are given as thermodynamic data.
2. KVAL = 2.

   In this case as well, no heat calculation is done and Gibbs function is not given directly as thermodynamic data. Instead ΔG is calculated from formation enthalpy, entropy, and heat capacity which are the thermodynamic data input to the program.
3. KVAL = 3.

   The input in this case is the same as in KVAL = 2 except that heat calculations are also performed. It, therefore, becomes necessary in this case to input the amount of reactant species and their temperature which are done in Records 11 and 12 respectively.

KVAL is input as a negative number when molar volume has to be considered for calculating the chemical potential of the invariants. However, this capability of the program was not investigated in this work.

Record 5 is therefore simply a number input in Column 2 which is 1, 2, or 3. Again, the input format is 40I2.

Record 6

Record 6 is where the molar volumes for invariants are input, and is not discussed.

Record 7

This input is made if KVAL is equal to 1.

The input in this record is used to calculate the free energy of a species from the expression

$$G = A/T+B+CT+DT^2+ET^3+FT^4+GT^5+HALOG(T)$$

where A,B,C,D,E,F,G, and H are the thermodynamic coefficients and T is the reaction temperature.

In the first line of this record the total number of co-efficients (MGT) that are used is input and then a number for each co-efficient is input (IGT).

For example, if co-efficients A, B, D, and F are used, then the input will be

b4b1b2b4b6

If only co-efficient B is used the input will be

b1b2

Format for this record is 40I2.

Record 8

In this record values for the co-efficients in the free energy function for each species (GE) are input, one line for each species, and the order of species is the same as that in Record 3.

Format for this input is 8E10.0.

Records 7 and 8 are skipped if KVAL = 2 or 3.

Record 9

Reaction temperature is input in this record, which has the format 8E10.0.

Records 10 through 12 are needed when KVAL = 3. Only Record 10 is input when KVAL = 2.

Record 10

Record 10 supplies formation enthalpy at 298°K, entropy at 298°K, the specific heat expressions, heat of fusion and heat of vaporization for each species in the order of species. More than one specific heat expression becomes necessary when phase transformation takes place between 298°K and the reaction temperature. The input format can be followed from the input guide given in Appendix A.

Records 11 and 12 are needed when an enthalpy calculation has to be done.

Record 11

This input record consists of one line which has the format 40I2. Total number of species in the raw material (MIN) and then the species number for each of these species (IIN) listed in the sequence of Record 3 are input.

Record 12

This supplies the temperature of the raw material (TO) in °K and the format for this input is 8E10.0.

Record 13 will not be discussed for the reason given for not explaining Record 6.

Record 14

Record 14 is another switch similar to KVAL introduced in Record 5.

The purpose of this variable called KVAL 1 is to facilitate the user to change a part of the input information after the equilibrium composition has been attained without disturbing the rest of the information, and then calculate a new equilibrium composition. For the first run KVAL1 is either 1 or 2. If it is 1, the computer generates the initial values for the equilibrium composition, and if it is 2, the initial values are read in as per Record 18.

For example, if one has to recalculate the equilibrium composition at a different temperature, 6 is input in Record 14, and the control goes to 'Read Record 9' mode, where new temperature is input. After the computation is complete, the control returns to 'Read Record 14' mode again. If at this time no new computation is required, 10 is entered for KVAL 1 and this causes execution to stop.

The program flow is shown in Figure 3.

In each computation cycle up to 25 sets of equilibrium compositions can be calculated based on variation in the raw material input amounts, or the amount of each element present in the system.

Record 15

This record supplies the number of sets of computations (NPKT) that have to be done in a cycle.

Record 16

This record is an index (KH) which indicates how the amount of each raw material or element present in the system varies from one computation to another. Index (KH) for each of the elements or the raw materials are input separately in one line in the sequence already established before. The index works as follows:

1. Variation is irregular from group to group.
2. No variation.
3. Varies by a constant increment.

Format for this input is 40I2.

Record 17

17A is used when KH = 1. In this case the amount of an element or raw material species is input one after another for each group, according to the format 8EI0.0. Again the species or the elements are input in the sequence established before.

When KH = 3, which implies the variation is regular, the amount need not be entered separately for each group. The initial amount and the constant increment (STEPX) is sufficient. This is done as per Record 17C.

Record 17B is used when KH = 2, or when the amount remains constant between groups.

Format for Record 17B and 17C is also 8EI0.0.

Record 18

Record 18 is used when the initial estimate is supplied by the user, which is the situation when KVAL = 1.

Computation

As mentioned earlier, very little computation is carried out in the main program.

The major computation done in the main program is evaluating the quantity $(g^o/RT)pi$ in Equation 16 for all species.

g^o is calculated either from the information input in Records 7, 8, and 9 from the expression

$$g^o = A/T+B+CT+DT^2+ET^3+FT^4+GT^5+HT\log T \qquad (31)$$

or from information input in Records 9 and 10 from the expression

$$\Delta g^o = \Delta H - T\Delta S. \qquad (32)$$

However, in this case ΔH is computed in function subprogram HEAT and ΔS is calculated in function subprogram SO. Both these subprograms again use function subprogram CPINT to obtain the Cp/T integral.

The main program then calls the subroutine GASOL, which does most of the computation.

Output

The first line of output is the heading as input in Record 1.

The species and the corresponding formula unit are then printed.

The free energy co-efficients are printed in the species order when KVAL = 1. But if KVAL = 2 or 3, the co-efficients for the Cp expressions for each species is printed instead in the species order.

Standard heat of formation and entropy for each species are then printed using one line for each species. Heat of fusion and heat of vaporization are also included when phase transformation takes place.

The reaction temperature and total pressure are then printed.

The contents of the following columns can be identified from the respective headings.

Initial amount of species are printed under X/MOLE. Equilibrium composition (Y/MOLE) are listed in the next column. In the third column for gas phase species, partial pressure (P/ATM) and mole fraction for species in the condensed mixture (MOLE FRACTION) are printed. For invariants this column remains blank. In the last column activity (ACTIVITY) for all species are printed.

Subroutine GASOL

Most of the computation is done in this subroutine. The subroutine is written in a manner such that final composition is reached within the shortest time possible. To do that, during the iteration process, when amount of a species become less than 10^{-10}, it is made equal to zero. When all the species in a mixture become zero, that mixture is dropped all together.

However, when iteration is complete, following checks are necessary.

Note, free energy of the system can in addition to Equation 16 be expressed by

$$G/RT = \sum_{j=1}^{\ell} \lambda_j b_j \qquad (33)$$

Equation 33 is obtained by substituting Equations 18, 19, and 20 in Equation 16. Now comparing Equation 33 and 19, we can say for any mixture which was not included in previous phase continuation, if the sum of the mole fractions for that mixture is greater than 1, has to be included.[3]

For invariants, according to Equation 20, for any non-included species if $(g^o/RT)_{pi}$ is less than $\sum_{j=1}^{\ell} \lambda_j a_{pij}$ the species must be included in the phase combination.[4]

---

[3] Gunnar Eriksson, "SOLGASMIX, A Computer Program for Calculation of Equilibrium Compositions in Multiphase Systems," Chemica Scripta 1975, 8, pp. 100-103.

[4] Gunnar Eriksson, "SOLGAS, A Computer Program for Calculating the Composition and Heat Condition of an Equilibrium Mixture," Acta Chemica Scandinavica 1971, 25, pp. 2651-2658.

When these conditions arise, for non-included mixtures, the one which has the highest sum of mole fractions is considered in the next iteration.

If none of the above conditions arise, the equilibrium composition has been obtained.

Computation Steps

From the input information the total number of phase combinations that are possible is calculated, and each combination is assigned a number.

The same thing is done for the invariants .

A phase combination is then chosen which has not been considered before.

f_{pi} is calculated as per Equation 24 for $p = 1$ and as per Equation 27 for $p = 2, 3, \ldots q + 1$

r_{pjk} is calculated as per

$$r_{pjk} = \sum_{i=1}^{m_p} (a_{pij} a_{pik}) y_{pi} \quad \text{for } j, k = 1, 2, \ldots \ell$$

A linear system of equations as per Equations 29, 28, and 30 is set up .

It may be noted here that since during computation procedure the constraint conditions must be satisfied at all times, initial estimate of the species must be carefully chosen so that they satisfy Equation 17.

However, this condition can be avoided by using a correction factor C in Equation 17 such that

$$\sum_{p=1}^{q+s+1} \sum_{i=1}^{m_p} a_{pij} - b_j = C_j \quad for\ j = 1,\ 2,\ \ldots \ell$$

Substituting this in Equation 29, the objective function is modified as

$$\sum_{p=1}^{q+1} \sum_{k=1}^{\ell} \lambda_k\, r_{pjk} + \sum_{p=1}^{q+1} ((X_p/Y_p)-1) \sum_{i=1}^{m_p} a_{pij} y_{pi}$$

$$= \sum_{p=1}^{q+1} \sum_{i=1}^{m_p} a_{pig} (f_{pi} - y_{pi}) - C_j \quad for\ j = 1,\ 2,\ \ldots \ell$$

Now initial estimate need not satisfy constraint equations. The system is solved by Gaussian elimination method.

The next step is to check if any non-included mixture would lower the free energy of the system. To do that hypothetical mole-fraction for the species of a non-included mixture is calculated as follows.

Activity of a species can be written as

$$\ell n A_{pi} = -(g^o/RT)_{pi} + \sum_{j=1}^{\ell} \lambda_j a_{pij} \tag{34}$$

and mole fraction

$x_{pi} = A_{pi}/f_{pi}$ where f_{pi} = activity co-efficient for species i of pth phase.

Now if $\sum_{i=1}^{m_p} x_{pi} > 1$, the mixture has to be considered. If the condition exists for a number of mixtures, the phase for which the quantity is maximum is included in the next iteration cycle. A new set of $\lambda_j s$ are again calculated and the same check is made. The process is continued until the satisfactory mixture combination is obtained.

The non-included invariants are then checked to see if inclusion of any of those would reduce the free energy. This is accomplished by checking if $(g^{o}/RT)_{pi}$ is less than $\sum_{j=1}^{\ell} \lambda_j a_{pij}$ for that particular invariant. If the condition exists, the process of calculating a new set of λ_j's is restarted.

The calculated amounts are then checked for negative amounts. If negative amounts exist, the method of steepest descent is used to make them all positive.

After this, if the amount of any species appears to be less than 1E-10, it is removed and the amounts thus arrived at are used as the starting estimate for the next cycle of calculation.

The computation is complete when subsequent iteration does not produce significant change in λ_j values. The equilibrium composition has been obtained.

Subroutine ABER

This is a short subroutine, which calculates activity A_{pi} from the expression

$$A_{pi} = x_{pi} f_{pi}.$$

Where f_{pi} is the activity co-efficients, f_{pi} is assumed to be unity if not otherwise specified. When f_{pi} is not unity a suitable f_{pi} expression is introduced in the subroutine FACTOR by the user, which is called by ABER when calculating A_{pi}.

Subroutine ABER is called by GASOL whenever necessary.

Subroutine XBER

The main purpose of this subroutine is to check if a non-included mixture would lower the free energy. To do that it first calculates the hypothetical activity from Equation 34. Then evaluate X_{pi}s from which it can be checked if $\sum_{i=1}^{m_p} x_{pi} > 1$.

Here again, Factor is called if activity co-efficients are not unity.

Subroutine FACTOR

As explained, this subroutine calculates f_{pi} from user-supplied expressions, where f_{pi} are the activity co-efficients.

Subroutine SPEQUA

This is a user's subroutine, which can perform calculations discernible from the equilibrium composition already compiled.

The whole program has been included in Appendix B as produced from an actual computer printout.

The program is stored on YSU System as RUN OSJOB. Another copy is stored as TEST OSJOB. The original program as procured is also preserved as SOLGAS OSJOB.

CHAPTER V

PROGRAM EXECUTION

Program Modification

A program was obtained on a tape which was directly loaded on the YSU computer system. Even though it was a form of FORTRAN, the software was not suitable for execution on the YSU system. The following modification had to be made.

Variables

All variables were changed to DOUBLE PRECISION type. This was accomplished by declaring this at the beginning of each routine.

The argument type for the built-in subprograms was then changed. For example, ALOG had to be changed to DLOG.

This was done by trying to execute the program with a sample input, and whereever an ERROR MESSAGE appeared, the change was made.

However, it must be mentioned here that since all the capabilities of the program were not investigated, which means all the statements were not executed, there still may be a few arguments which are not correct. These can be corrected during further investigation, and is a very minor and easily correctable situation.

DO LOOP Parameters

YSU System does not accept any DO LOOP parameters except simple integers. Therefore, wherever other types of DO LOOP parameter were encountered, they were changed. For example,

```
DO M(I), N (K)
```

was changed to

```
MI = M (I)
NK = N (K)
DO MI, NK
```

Statement Number Sequence

The statement numbers appearing in Columns 1 through 5 in the original program were not sequential. This posed a serious problem in following the program, since too many GO TO statements have been used.

Therefore, all the statement numbers were changed to make them sequential.

FORMAT Statements

In the original program the FORMAT statements were put immediately after the READ/WRITE statement. All FORMAT statements were grouped and put sequentially immediately before the RETURN or END statements of the respective routines.

Program Execution

Eight different runs were made. The data files were

DATA FILE 2

DATA FILE 3

DATA FILE 4

DATA FILE 7

DATA FILE 8

DATA FILE 2 and DATA FILE 4 are the same system containing 10 species in total, with one gas phase containing 9 species and one invariant.

Gas phase species are CH_4, C_2H_6, C_2H_2, CO_2, CO, O_2, H_2, H_2O, and C_2H_6.

The only invariant considered was C.

2 moles of C, 4 moles of O and 14 moles of H were considered to be present in the system, which is equivalent to one mole of Ethane and four moles of water.

Equilibrium temperature or reaction temperature was assumed to be 1000^oK.

The difference between the two sets of data is whereas in DATA FILE 2 the computer generated the initial estimate, in DATA FILE 4 the initial estimate was supplied as input.

It was found that computation was faster when initial estimate was supplied, rather than generated by the computer.

In both the cases output was the same and agreed with available reference.[5]

DATA FILE 3 is a system containing CO, H_2O, CO_2, H_2 and O_2 in the gas phase. C was the only invariant considered.

In this case again the initial estimate was supplied as input data.

DATA FILE 7 is a system containing 4 elements, S, O, N, and Cu, gas phase containing 15 species and there are 5 invariants.

This computation took longer time, but can be considered very fast, considering the large number of species considered present in the system.

This file was also used as a test file during modification of the program. This data file, along with a corresponding output, was supplied along with the program when it was originally procured.

Every time a further modification in the program was made, this sample file was run to make sure the modification was proper.

DATA FILE 8 constitutes the same system as in DATA FILE 2 and DATA FILE 4, but in this case five different points were considered by varying the input amount of H and O but keeping the amount of C constant. The data points represent

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[5] Richard E. Balzhiser, Michael R. Samuels, and John D. Eliassen, Chemical Engineering Thermodynamics Prentice-Hall, Inc. (Englewood Cliffs, New Jersey, 1972), pp. 513-527.

reactions between one mole of Ethane and 4, 3, 2, 5, and 6 moles of water.

All data files and the corresponding outputs as computer printouts have been reproduced sequentially in Appendix C.

The file names used are the actual names of data files in which the data are stored in the YSU computer system.

CHAPTER VI

SUMMARY

Findings

A computer program for solving Equations 20, 28, and 29 has been developed by G. Eriksson of the University of Umeå, Umea Sweden. Eriksson's work required approximately 10 years to complete, and resulted in a program he called SOLGASMIX. A copy of SOLGASMIX was purchased by Youngstown State University through a research grant awarded to R. W. Jones of the Department of Chemical and Metallurgical Engineering by the Research Council.

The major effort of the work presented here concerned an analysis of SOLGASMIX and a subsequent modification in order that the program be compatible with the YSU computer system.

To check if the modification of the program was proper, a number of data files were run and the result obtained agreed totally with available reference.

It was also found that the program was very fast and therefore could be used at a very low cost, as computer time requirements are small.

Conclusion

Even though SOLGASMIX has not yet been very widely utilized, it appears to be a very versatile software, capable of making thermodynamic analyzing of complex multicomponent, multi-phase, chemically reactive system.

The program would be most suitable for high temperature, low pressure systems where equilibrium is reached very quickly.

When the system behaves non-ideally, reliability of the results will totally depend on the accuracy of the thermodynamic data available for the system being investigated.

Recommendations

It is recommended that since the program has been modified and set up on the YSU computer system, further work be directed towards using it for non-ideal systems.

An interactive version of the program is also available. It would also be very useful to set up the interactive version of the program on the YSU system.

Since a reasonably advanced knowledge of programming is necessary, it would be a good idea to carry out further work jointly by the Departments of Computer Science and Chemical Metallurgical Engineering Departments.

APPENDIX A

Data Input Guide

DATA INPUT GUIDE

```
C     PROGRAM SGMXBA
C         ****************************************
C         *  SOLGASMIX (BATCH VERSION)           *
C         ****************************************
C         *  YOUNGSTOWN STATE UNIVERSITY         *
C         *  CHEMICAL ENGINEERING DEPARTMENT     *
C         *  YOUNGSTOWN OHIO 44555               *
C         *  TELEPHONE 216 742 3020              *
C         ****************************************
C
C I N P U T   G U I D E
C ------------------------------------------------------------------------------
C RECORD 1 (80A1)
C ITEXT    HEADING.
C ------------------------------------------------------------------------------
C RECORD 2 (40I2)
C L        THE TOTAL NUMBER OF ELEMENTS (<=12).
C MP       THE TOTAL NUMBER OF MIXTURES (<=9).
C MSOL     THE TOTAL NUMBER OF INVARIANTS (= CONDENSED PHASES OF INVARIANT STOI-
C          CHIOMETRY).
C MN(1)    THE TOTAL NUMBER OF SPECIES IN MIXTURE 1 (GASEOUS),
C MN(2)    THE TOTAL NUMBER OF SPECIES IN MIXTURE 2 (CONDENSED),
C ETC.
C NOTE- THE TOTAL NUMBER OF SPECIES MUST BE <=80. THE TOTAL NUMBER OF MIXTURES
C    PLUS INVARIANTS MUST BE <=(MPOT - 1) IF THE INTEGER VALUE RANGE EXTENDS
C    TO (2**MPOT - 1) (DEFAULT MPOT VALUE = 48). THE REAL VALUE RANGE IS DE-
C    FAULTED TO EXP(POTM) WHERE POTM = 500.
C ------------------------------------------------------------------------------
C RECORD 3 (2A5,12F5.0)
C IDENT    IDENTIFICATION FOR SPECIES I.
C A(I,1)   THE TOTAL NUMBER OF FORMULA UNITS OF ELEMENT 1 IN SPECIES I,
C A(I,2)   THE TOTAL NUMBER OF FORMULA UNITS OF ELEMENT 2 IN SPECIES I,
C ETC.
C NOTE- THERE IS ONE LINE PER SPECIES IN SPECIES ORDER. SPECIES IN MIXTURE 1
C    MUST BE GIVEN THE LOWEST NUMBERS, ETC, AND THE INVARIANTS FOLLOW LAST.
C    THE FORMATION OF A SPECIES WILL BE SUPPRESSED IF THE IDENTIFICATION CON-
C    TAINS THE CHARACTER '*' IN COLUMN 10. EQUILIBRIUM ACTIVITIES FOR ALL IN-
C    VARIANTS AND EQUILIBRIUM MOLE FRACTIONS FOR ALL SPECIES IN THE CONDENSED
C    MIXTURES, SUPPRESSED OR NONSUPPRESSED, WILL BE GIVEN IN THE OUTPUT. IF
C    THE EQUILIBRIUM ACTIVITY FOR A SPECIES WILL BE SPECIFIED, THIS SPECIES
C    HAS TO BE REGARDED AS AN ELEMENT IN ITS CHOSEN REFERENCE STATE.
C ------------------------------------------------------------------------------
C RECORD 4 (40I2)
C IEL(1)   THE SPECIES NUMBER FOR ELEMENT 1 IN ITS CHOSEN REFERENCE STATE,
C IEL(2)   THE SPECIES NUMBER FOR ELEMENT 2 IN ITS CHOSEN REFERENCE STATE,
C ETC.
C ------------------------------------------------------------------------------
C RECORD 5 (40I2)
C KVAL      = 1 NO HEAT CALCULATIONS AND VALUES OF GIBBS FUNCTION AS THERMODYNA-
C               MIC DATA.
C           = 2 NO HEAT CALCULATIONS AND VALUES OF FORMATION ENTHALPY, ENTROPY,
C               AND HEAT CAPACITY AS THERMODYNAMIC DATA.
C           = 3 HEAT CALCULATIONS AND VALUES OF FORMATION ENTHALPY, ENTROPY, AND
C               HEAT CAPACITY AS THERMODYNAMIC DATA.
C NOTE- PUT KVAL NEGATIVE IF MOLAR VOLUMES WILL BE CONSIDERED IN THE CALCULATION
```

DATA INPUT GUIDE (continued)

```
C     OF THE CHEMICAL POTENTIALS FOR THE INVARIANTS.
C ----------------------------------------------------------------------------
C CONTINUE WITH RECORD 7 IF KVAL = 1 AND WITH RECORD 9 IF KVAL = 2 OR 3.
C ----------------------------------------------------------------------------
C RECORD 6 (8E10.0)
C VO(M1)      MOLAR VOLUME/CM3 FOR INVARIANT 1,
C VO(M1+1) MOLAR VOLUME/CM3 FOR INVARIANT 2,
C ETC.
C NOTE- THE MOLAR VOLUMES ARE ASSUMED INDEPENDENT OF TEMPERATURE AND PRESSURE.
C ----------------------------------------------------------------------------
C CONTINUE WITH RECORD 9 IF KVAL = -2 OR -3.
C ----------------------------------------------------------------------------
C RECORD 7 (40I2)
C MGT         THE TOTAL NUMBER OF COEFFICIENTS IN THE GIBBS FUNCTION EXPRESSION
C             WHICH CAN BE DIFFERENT FROM ZERO (G/J.MOL-1 = A/T + B + C*T + D*T*T +
C             + E*T**3 + F*T**4 + G*T**5 + H*T*ALOG(T)).
C IGT(1)      THE NUMBER FOR ONE OF THESE COEFFICIENTS,
C IGT(2)      THE NUMBER FOR ANOTHER OF THESE COEFFICIENTS,
C ETC.
C NOTE- A IS COEFFICIENT 1, B IS COEFFICIENT 2, ETC.
C ----------------------------------------------------------------------------
C RECORD 8 (8E10.0)
C GE(I,1)   THE VALUE OF COEFFICIENT IGT(1) FOR SPECIES I,
C GE(I,2)   THE VALUE OF COEFFICIENT IGT(2) FOR SPECIES I,
C ETC.
C NOTE- THERE IS ONE LINE PER SPECIES IN SPECIES ORDER.
C ----------------------------------------------------------------------------
C RECORD 9 (8E10.0)
C T           THE REACTION TEMPERATURE/K.
C ----------------------------------------------------------------------------
C CONTINUE WITH RECORD 14 IF KVAL = -1 OR 1 OR IF KVAL1 < 9 (DEFAULT VALUE = 9).
C ----------------------------------------------------------------------------
C RECORD 10 (2E10.0,I2/8E10.0)
C HF(I)       FORMATION ENTHALPY AT 298 K/J.MOL-1 FOR SPECIES I.
C S(I)        ENTROPY AT 298 K/J.K-1MOL-1 FOR SPECIES I.
C NOM(I)      THE TOTAL NUMBER OF HEAT CAPACITY EXPRESSIONS FOR SPECIES I (<=6).
C
C C(I,J,1) THE VALUE OF A IN CP EXPRESSION J FOR SPECIES I.
C C(I,J,2) THE VALUE OF B IN CP EXPRESSION J FOR SPECIES I.
C C(I,J,3) THE VALUE OF C IN CP EXPRESSION J FOR SPECIES I.
C C(I,J,4) THE VALUE OF D IN CP EXPRESSION J FOR SPECIES I.
C C(I,J,5) THE VALUE OF E IN CP EXPRESSION J FOR SPECIES I.
C C(I,J,6) THE VALUE OF F IN CP EXPRESSION J FOR SPECIES I.
C TOM(I,J) TRANSFORMATION TEMPERATURE J/K FOR SPECIES I.
C HOM(I,J) TRANSFORMATION ENTHALPY J/J.MOL-1 FOR SPECIES I.
C NOTE- THERE ARE (NOM(I) + 1) LINES PER SPECIES IN SPECIES ORDER. THE HEAT CA-
C       PACITY EXPRESSIONS MUST BE VALID FROM 298 K UP TO THE REACTION TEMPERA-
C       TURE (CP/J.K-1MOL-1 = A + B*T + C/T**2 + D*T*T + E/T**3 + F/SQRT(T)).
C       THE TRANSFORMATION TEMPERATURE AND ENTHALPY ARE GIVEN ONLY IF THERE IS A
C       CP EXPRESSION (J + 1).
C ----------------------------------------------------------------------------
C CONTINUE WITH RECORD 14 IF KVAL = -2 OR 2.
C ----------------------------------------------------------------------------
C RECORD 11 (40I2)
C MIN         THE TOTAL NUMBER OF SPECIES IN THE RAW MATERIAL (<=25).
```

DATA INPUT GUIDE (continued)

```
C IIN(1)     THE NUMBER FOR ONE OF THESE SPECIES,
C IIN(2)     THE NUMBER FOR ANOTHER OF THESE SPECIES,
C ETC.
C -----------------------------------------------------------------------------
C RECORD 12 (8E10.0)
C TO         THE TEMPERATURE OF THE RAW MATERIAL/K.
C -----------------------------------------------------------------------------
C CONTINUE WITH RECORD 14.
C -----------------------------------------------------------------------------
C RECORD 13 (8E10.0)
C PTOT       THE TOTAL PRESSURE/ATM OR THE NEGATIVE SYSTEM VOLUME/DM3.
C NOTE- THE SYSTEM VOLUME IS GIVEN WITH A MINUS SIGN IF THE CALCULATIONS WILL BE
C       PERFORMED AT CONSTANT VOLUME.
C -----------------------------------------------------------------------------
C RECORD 14 (40I2)
C KVAL1      = 1 CALCULATE A GROUP OF POINTS WITH NEW VALUES OF THE VARIABLES IN
C                THE RECORDS 15-17 AND THE STARTING ESTIMATE ACCORDING TO RECORD
C                18. CONTINUE WITH RECORD 15.
C            = 2 THE SAME AS FOR KVAL1 = 1 BUT THE STARTING ESTIMATE WILL BE GENE-
C                RATED BY THE PROGRAM. CONTINUE WITH RECORD 15.
C            = 3 THE SAME AS FOR KVAL1 = 1 BUT THE LAST CALCULATED POINT WILL BE
C                USED AS STARTING ESTIMATE. CONTINUE WITH RECORD 15.
C            = 4 CALCULATE A GROUP OF POINTS WITH NEW VALUES OF THE VARIABLES IN
C                RECORD 17 AND UNCHANGED VALUES OF THE VARIABLES IN THE RECORDS
C                15-16. CONTINUE WITH RECORD 17.
C            = 5 CALCULATE A GROUP OF POINTS WITH UNCHANGED VALUES OF THE VARIA-
C                BLES IN THE RECORDS 15-17. CONTINUE WITH RECORD 14.
C            = 6 CHANGE THE REACTION TEMPERATURE. CONTINUE WITH RECORD 9.
C            = 7 CHANGE THE TOTAL PRESSURE (DEFAULT VALUE = 1 ATM) OR DEFINE OR
C                CHANGE THE SYSTEM VOLUME. CONTINUE WITH RECORD 13.
C            = 8 CHANGE THE G EXPRESSIONS. CONTINUE WITH RECORD 8.
C            = 9 CHANGE SYSTEM. CONTINUE WITH RECORD 1.
C            =10 FINISH THE CALCULATIONS.
C -----------------------------------------------------------------------------
C RECORD 15 (40I2)
C NPKT       THE TOTAL NUMBER OF POINTS IN THE GROUP (<=25).
C NOTE- THE VARIATION IN N OR LOG A BETWEEN THE POINTS IN THE GROUP WILL BE DE-
C       FINED FOR EACH ELEMENT OR FOR EACH SPECIES IN THE RAW MATERIAL (N = TO-
C       TAL AMOUNT, A = EQUILIBRIUM ACTIVITY).
C -----------------------------------------------------------------------------
C RECORD 16 (40I2)
C KH(1)      THE VARIATION IN N OR LOG A FOR ELEMENT 1 (KVAL = -1, 1, -2, OR 2) OR
C            IN N FOR SPECIES IIN(1) (KVAL = -3 OR 3),
C KH(2)      THE VARIATION IN N OR LOG A FOR ELEMENT 2 (KVAL = -1, 1, -2, OR 2) OR
C            IN N FOR SPECIES IIN(2) (KVAL = -3 OR 3),
C ETC.
C NOTE- KH = 1 N VARIES IRREGULARLY BETWEEN THE POINTS IN THE GROUP,
C       KH = 2 N IS CONSTANT,
C       KH = 3 N VARIES BY A CONSTANT INCREMENT,
C       KH = 4 LOG A VARIES IRREGULARLY BETWEEN THE POINTS IN THE GROUP,
C       KH = 5 LOG A IS CONSTANT,
C       KH = 6 LOG A VARIES BY A CONSTANT INCREMENT.
C -----------------------------------------------------------------------------
C RECORD 17A (8E10.0)
C B(J,1)     N/MOL FOR ELEMENT J OR SPECIES IIN(J) (KH = 1) OR LOG A FOR ELEMENT J
```

DATA INPUT GUIDE (continued)

```
C          (KH = 4) AT THE FIRST POINT,
C B(J,2)   N OR LOG A AT THE SECOND POINT,
C ETC.
C
C RECORD 17B (8E10.0)
C B(J,1)   THE CONSTANT VALUE OF N/MOL FOR ELEMENT J OR SPECIES IIN(J) (KH = 2)
C          OR LOG A FOR ELEMENT J (KH = 5).
C
C RECORD 17C (8E10.0)
C B(J,1)   THE INITIAL VALUE OF N/MOL FOR ELEMENT J OR SPECIES IIN(J) (KH = 3)
C          OR LOG A FOR ELEMENT J (KH = 6).
C STEPX    THE CONSTANT INCREMENT IN N OR LOG A.
C NOTE- THERE IS ONE LINE PER ELEMENT (SPECIES IN THE RAW MATERIAL) IN ELEMENT
C       (SPECIES) ORDER. RECORD 17A IS USED IF KH = 1 OR 4, RECORD 17B IS USED
C       IF KH = 2 OR 5, AND RECORD 17C IS USED IF KH = 3 OR 6. VALUES OF N <
C       1.E-8 ARE TREATED AS BEING EQUAL TO ZERO.
C -----------------------------------------------------------------------------
C CONTINUE WITH RECORD 14 IF KVAL1 > 1.
C -----------------------------------------------------------------------------
C RECORD 18 (8E10.0)
C Y(1)     STARTING ESTIMATE/MOL OF THE EQUILIBRIUM AMOUNT FOR SPECIES 1,
C Y(2)     STARTING ESTIMATE/MOL OF THE EQUILIBRIUM AMOUNT FOR SPECIES 2,
C ETC.
C -----------------------------------------------------------------------------
C CONTINUE WITH RECORD 14.
C -----------------------------------------------------------------------------
```

APPENDIX B

The Computer Program SOLGASMIX

SOLGASMIX PROGRAM (BATCH VERSION)

```
//E0000777 JOB ($$ROUTE3),
// FR105001.JONES,CLASS=H
// EXEC WATFIV
//SYSIN DD *
$JOB
C $OPTIONS NOLIST
      DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
      COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
     *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
      DOUBLE PRECISION POTM,RINV,V,YTOT
      COMMON /SGAX/ MA, MB, NO(80), POTM, RINV, V, YTOT(9)
      DOUBLE PRECISION ASUM,VO
      COMMON /SGGA/ ASUM(80),IPOT(48),IS,IVARJ,KH(25),MG,MX,M1,NG,VO(80)
      DOUBLE PRECISION HF,S,XI
      COMMON /SGHE/ HF(80),IIN(25),IN,IOUT,KVAL1,KVAL2,MIN,S(80),XI(80)
      COMMON /TEXT/ IDENT(80,2)
      DIMENSION BIN(12,25), GE(80,8), IGT(8), MN(10)
      CHARACTER*1 ICHAR, INST, ITEXT(80)
      CHARACTER*5 IDENT
      DATA INST/'*'/
      IPOT(1) = 1
      KVAL1 = 9
      MF(1) = 1
      POTM = 500.
      RINV = 1./8.31433
    5 PTOT = 1.
      V = 0.
      DO 10 J = 1, 24
   10 KH(J) = 0
      READ (5,900) ITEXT
      READ (5,910) L, MP, MSOL, (MN(M), M = 1, MP)
      ML(1) = MN(1)
      MV = MP + 1
      MN(MV) = MSOL
      DO 20 M = 2, MV
      MF(M) = ML(M-1) + 1
   20 ML(M) = ML(M-1) + MN(M)
      MM = ML(1)
      MH = MM + 1
      MG = ML(MP) - MP
      M1 = MF(MV)
      MS = ML(MV)
      N100 = MSOL + MV
      DO 30 M = 2, N100
   30 IPOT(M) = 2*IPOT(M-1)
      MX = IPOT(MSOL+MV)
      WRITE (6,920) ITEXT
      DO 40 I = 1, MS
      XI(I) = 0.
      READ (5,930) (IDENT(I,J), J = 1, 2), (A(I,J), J = 1, L)
      NO(I) = 1
      READ (IDENT(I,2),900) (ICHAR, N = 1, 5)
      IF (ICHAR .EQ. INST) NO(I) = -1
      WRITE (6,940) (IDENT(I,J), J = 1, 2), (A(I,J), J = 1, L)
      DO 40 J = 1, L
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
 40 AO(I,J) = A(I,J)
    IF (MS .LT. M1) GO TO 51
    DO 50 I = M1, MS
    ASUM(I) = 0.
    VO(I) = 0.
    DO 50 J = 1, L
 50 ASUM(I) = ASUM(I) +DABS(A(I,J))
 51 READ (5,910) (IEL(J), J = 1, L)
    READ (5,910) KVAL
    KVAL2 = IABS(KVAL)
    IF (KVAL2 .LT. 3) MIN = L
    IF (KVAL - 1) 52,53,65
 52 READ (5,950) (VO(I), I = M1, MS)
    WRITE (6,960) ((IDENT(I,J), J = 1, 2), VO(I), I = M1, MS)
    IF (KVAL2 - 2) 53,65,65
 53 READ (5,910) MGT, (IGT(N), N = 1, MGT)
 54 WRITE (6,970) (IGT(N), N = 1, MGT)
    DO 60 I = 1, MS
    READ (5,950) (GE(I,N), N = 1, MGT)
 60 WRITE (6,980) (IDENT(I,J), J = 1, 2), (GE(I,N), N = 1, MGT)
 65 READ (5,950) T
    IF (KVAL2 .EQ. 1) GO TO 75
    CALL HETTA
    TEMP = RINV/T
    DO 70 I = 1, MS
    ITEMP = I
 70 G(I) = TEMP*(HF(I) + HEAT(ITEMP,T) - T*(S(I) + SO(ITEMP,T)))
    GO TO 92
 75 DO 80 I = 1, MS
 80 G(I) = 0.
    DO 90 N = 1, MGT
    IF (IGT(N) .LT. 8) TEMP = RINV*T**(IGT(N) - 3)
    IF (IGT(N) .EQ. 8) TEMP = RINV*ALOG(T)
    DO 90 I = 1, MS
 90 G(I) = G(I) + GE(I,N)*TEMP
    GO TO 92
 91 READ (5,950) PTOT
    V = AMAX1(-PTOT,0.)
 92 READ (5,910) KVAL1
    GO TO (93,93,93,94,151,65,91,54,5,205), KVAL1
 93 READ (5,910) NPKT
    READ (5,910) (KH(J), J = 1, MIN)
 94 DO 120 J = 1, MIN
    N101 = KH(J)
    GO TO (95,96,105,95,96,105), N101
 95 READ (5,950) (B(J,N), N = 1, NPKT)
    GO TO 120
 96 READ (5,950) BC
    DO 100 N = 1, NPKT
100 B(J,N) = BC
    GO TO 120
105 READ (5,950) B(J,1), STEPX
    DO 110 N = 2, NPKT
110 B(J,N) = B(J,N-1) + STEPX
120 CONTINUE
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
    IF (KVAL1 - 2) 121,122,145
121 READ (5,950) (Y(I), I = 1, MS)
    GO TO 145
122 DO 130 I = 1, MM
130 Y(I) = 1.E8
    IF (MV .EQ. 1) GO TO 145
    DO 140 I = MH, MS
140 Y(I) = 0.
145 IF (KVAL2 .LT. 3) GO TO 151
    DO 150 N = 1, NPKT
    DO 150 J = 1, MIN
150 BIN(J,N) = B(J,N)
151 NP = 0
155 NP = NP + 1
    IF (KVAL2 .LT. 3) GO TO 172
    DO 160 J = 1, L
160 B(J,NP) = 0.
    DO 170 N = 1, MIN
    I = IIN(N)
    XI(I) = BIN(N,NP)
    DO 170 J = 1, L
170 B(J,NP) = B(J,NP) + A(I,J)*XI(I)
172 CALL GASOL
    WRITE (6,990) T, PTOT
    IF (V .GT. 0.) WRITE (6,1000) V
    IF (IS .LE. MX .AND. NG .LT. 1000) GO TO 175
    WRITE (6,1010)
    IF (IS .GT. MX) WRITE (6,1020)
    IF (NG .EQ. 1000) WRITE (6,1030)
    IF (NP - NPKT) 155,92,92
175 IF (IVARJ .EQ. 15) WRITE (6,1040)
    IF (KVAL2 .EQ. 3) GO TO 195
    DO 190 J = 1, L
    K = IEL(J)
    IF (KH(J) .LT. 4) GO TO 185
    XI(K) = 0.
    DO 180 I = 1, MS
180 XI(K) = XI(K) + AO(I,J)/AO(K,J)*Y(I)
    GO TO 190
185 XI(K) = B(J,NP)/AO(K,J)
190 CONTINUE
195 WRITE (6,1050)
    DO 200 M = 1, MP
    IF (M .GT. 1) WRITE (6,1060)
    N102 = MF(M)
    N103 = ML(M)
    DO 200 I = N102, N103
200 WRITE (6,1070) (IDENT(I,J),J=1,2),XI(I),Y(I),YF(I),AKT(I)
    IF (MS .GE. M1) WRITE (6,1080) ((IDENT(I,J), J = 1, 2), XI(I),
   *Y(I), AKT(I), I = M1, MS)
    IF (KVAL2 .EQ. 3) CALL HETTA
    CALL SPEQUA
    IF (NP - NPKT) 155,92,92
205 STOP
900 FORMAT(80A1)
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
 910 FORMAT(40I2)
 920 FORMAT('1',80A1// ' FORMULA UNITS')
 930 FORMAT(2A5,12F5.0)
 940 FORMAT(1X, 2A5, 12F5.1)
 950 FORMAT(8E10.0)
 960 FORMAT(/14X, 'MOLAR VOLUME'/ (1X, 2A5, F12.3))
 970 FORMAT(/10X, 8('     COEFF', I2))
 980 FORMAT(1X, 2A5, 8(1X, E11.4))
 990 FORMAT('1T =', F8.2, ' K'/ ' P =', 1PE10.3, ' ATM')
1000 FORMAT(' V =', 1PE10.3, ' ATM')
1010 FORMAT(/' THE EQUILIBRIUM COMPOSITION HAS NOT BEEN OBTAINED')
1020 FORMAT(' ALL POSSIBLE PHASE COMPOSITIONS HAS BEEN CONSIDERED')
1030 FORMAT(' 999 DIFFERENT PHASE COMBINATIONS HAVE BEEN CONSIDERED')
1040 FORMAT(/' THE SOLUTION IS NUMERICALLY UNSTABLE')
1050 FORMAT(/18X, 'X*/MOL', 9X, 'Y/MOL', 10X, 'P/ATM', 9X, 'ACTIVITY')
1060 FORMAT(44X, 'MOLE FRACTION')
1070 FORMAT(1X, 2A5, 4(3X, E12.5))
1080 FORMAT(/(1X, 2A5, 2(3X, E12.5), 18X, E12.5))
     END
     SUBROUTINE GASOL
     DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
     COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
    *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
     DOUBLE PRECISION POTM,RINV,V,YTOT
     COMMON /SGAX/ MA, MB, NO(80), POTM, RINV, V, YTOT(9)
     DOUBLE PRECISION ASUM,VO
     COMMON /SGGA/ ASUM(80),IPOT(48),IS,IVARJ,KH(25),MG,MX,M1,NG,VO(80)
     DOUBLE PRECISION ALN,BO,F,GV,OPI,R,YFTOT,YMAX,TEMP
     DIMENSION ALN(80),BO(12),F(80),GV(80),IFAS(9),INR(80),ISOL(46),
    *MNR(80),NRI(80),NSUM(999),OPI(12),R(24,25),YFTOT(9),YMAX(80)
     LOGICAL IDEAL, IGEN, LIVARJ, LX(80), LYFTOT, NON
     IGEN = .FALSE.
     LYFTOT = .FALSE.
     NON = .FALSE.
     SLAM = 0.
     BMAX = 0.
     LO = L
     IF (MS .GE. M1) RTI = 1.E-3*101.325*RINV*(PTOT - 1.)/T
     DO 10 I = 1, MS
  10 IF (MOD(NO(I),2) .EQ. 0) NO(I) = NO(I) + 1
     DO 60 J = 1, L
     BO(J) = B(J,NP)
     IF (KH(J) .LT. 4) GO TO 20
     I = IEL(J)
     TEMP = ALOG(10.)*BO(J)
     BO(J) = EXP(TEMP)
     PI(J) = (G(I) + TEMP)/A(I,J)
     IF (I .GE. M1) PI(J) = PI(J) + RTI*VO(I)/A(I,J)
     GO TO 50
  20 IF (ABS(BO(J)) .GE. 1.E-8) GO TO 60
     K = IEL(J)
     DO 30 I = 1, MS
     IF (A(I,J)*A(K,J)) 60,30,30
  30 CONTINUE
     BO(J) = 0.
```

```
      DO 40 I = 1, MS
   40 IF (A(I,J) .NE. 0. .AND. MOD(NO(I),2) .NE. 0) NO(I) = NO(I) - 1
   50 LO = LO - 1
   60 IF (ABS(BO(J)) .GT. BMAX) BMAX = ABS(BO(J))
      IF (MS .LT. M1) GO TO 90
      DO 80 I = M1, MS
      INR(I) = I
      IF (MOD(NO(I),2) .EQ. 0) GO TO 80
      GV(I) = G(I) + RTI*VO(I)
      DO 70 J = 1, L
      IF (KH(J) .LT. 4 .AND. A(I,J) .NE. 0.) GO TO 80
   70 CONTINUE
      NO(I) = NO(I) - 1
   80 CONTINUE
   90 DO 120 I = 1, MS
      IF (NO(I) .EQ. 1) GO TO 100
      AKT(I) = 0.
      Y(I) = 0.
      YF(I) = 0.
      GO TO 120
  100 YMAX(I) = BMAX
      DO 110 J = 1, L
      IF (KH(J) .GT. 3 .OR. A(I,J) .EQ. 0. .OR. BO(J) .EQ. 0.) GO TO 110
      TEMP = DABS(BO(J)/A(I,J))
      IF (TEMP .LT. YMAX(I)) YMAX(I) = TEMP
  110 CONTINUE
  120 CONTINUE
      MPC = MP + 1
      DO 150 M = 1, MP
      YTOT(M) = 1.
      I = ML(M)
  130 IF (Y(I) .GT. 0.) GO TO 150
      I = I - 1
      IF (I .GE. MF(M)) GO TO 130
      YTOT(M) = 0.
  140 I = I + 1
      IF (NO(I) .EQ. 1) GO TO 150
      IF (I .LT. ML(M)) GO TO 140
      MPC = MPC - 1
      IFAS(MPC) = M
      YTOT(M) = -1.
  150 CONTINUE
      N104 = ML(MP)
      DO 160 I = 1, N104
      AKTF(I) = 1.
  160 DAKTF(I) = 0.
  170 IS = -1
      NG = 0
      GO TO 210
  180 IF (NEG) 260,260,200
  190 NEG = ISOL(K)
  200 Y(NEG) = 0.
C
C         CALCULATION OF A NUMBER SPECIFYING THE PHASE COMBINATION
C         (GAS PHASE = 1, MIX 2 = 2, MIX 3 = 4, MIX 4 = 8, ETC.)
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
C
  210 ISUM = 0
      MSA = 0
      IF (MS .LT. M1) GO TO 230
      DO 220 K = M1, MS
      IF (Y(INR(K)) .EQ. 0.) GO TO 220
      MSA = MSA + 1
      ISOL(MSA) = INR(K)
      ISUM = ISUM + IPOT(K-MG)
  220 CONTINUE
  230 MPA = 0
      NG = NG + 1
      IF (NG .EQ. 1000) RETURN
      NSUM(NG) = ISUM
      DO 240 M = 1, MP
      IF (YTOT(M) .LE. 0.) GO TO 240
      MPA = MPA + 1
      NSUM(NG) = NSUM(NG) + IPOT(M)
  240 CONTINUE
      IF (NSUM(NG) .LT. IS) GO TO 250
      IF (MPA + MSA .LE. LO) GO TO 440
      IF (MSA .EQ. 0) GO TO 250
      NG = NG - 1
      Y(ISOL(1)) = 0.
      GO TO 210
  250 NG = NG - 1
C
C       RANKING THE INVARIANTS AND CHOOSING A PHASE COMBINATION WHICH
C       HASN'T BEEN CONSIDERED PREVIOUSLY
C
  260 IF (.NOT. IGEN .OR. MS .LE. M1) GO TO 340
      DO 270 K = M1, MS
  270 MNR(K) = INR(K)
  280 IGEN = .FALSE.
      N105 = MS-1
      DO 290 K = M1, N105
      N = K + 1
      IF (ALN(K) .GE. ALN(N)) GO TO 290
      IGEN = .TRUE.
      TEMP = ALN(K)
      ALN(K) = ALN(N)
      ALN(N) = TEMP
      ITEMP = INR(K)
      INR(K) = INR(N)
      INR(N) = ITEMP
  290 CONTINUE
      IF (IGEN) GO TO 280
      DO 300 K = M1, MS
  300 NRI(INR(K)) = K - MG
      DO 330 N = 1, NG
      ITEMP = IABS(NSUM(N))
      NSUM(N) = 0
  310 M = 1
  320 M = M + 1
      IF (IPOT(M) .LE. ITEMP) GO TO 320
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      M = M - 1
      K = M + MG
      IF (K .LT. M1) GO TO 330
      NSUM(N) = NSUM(N) + IPOT(NRI(MNR(K)))
      ITEMP = ITEMP - IPOT(M)
      GO TO 310
  330 NSUM(N) = NSUM(N) + ITEMP
      IS = -1
  340 IS = IS + 2
      IF (IS .GT. MX) RETURN
      DO 350 M = 1, MP
  350 IF (YTOT(M) .GT. 0.) YTOT(M) = 0.
      ISUM = 0
      MPA = 1
      IF (MSA .EQ. 0) GO TO 370
      DO 360 N= 1, MSA
  360 Y(ISOL(N)) = 0.
      MSA = 0
  370 IF (IS .EQ. 1) GO TO 430
      ITEMP = IS
  380 M= 1
  390 M= M+ 1
      IF (IPOT(M) .LE. ITEMP) GO TO 390
      M= M-1
      IF (M .GT. MP) GO TO 410
      IF (YTOT(M) .EQ. -1.) GO TO 340
      MPA = MPA + 1
      YTOT(M) = 1.
      N106 = MF(M)
      N107 = ML(M)
      DO 400 I =N106, N107
  400 IF (NO(I) .EQ. 1) Y(I) = YMAX(I)
      GO TO 420
  410 I = INR(M+MG)
      IF (NO(I) .LT. 1) GO TO 340
      MSA = MSA + 1
      ISOL(MSA) = I
      ISUM = ISUM + IPOT(M)
      Y(I) = YMAX(I)
  420 ITEMP = ITEMP - IPOT(M)
      IF (ITEMP .GT. 1) GO TO 380
      IF (MPA+ MSA - LO) 430,430,340
  430 NG = NG + 1
      IF (NG .EQ. 1000) RETURN
      NSUM(NG) = IS
      IF (NG .GT. 1) NSUM(NG-1) = IABS(NSUM(NG-1))
      YTOT(1) = 1.
  440 IF (NG .EQ. 1) GO TO 460
      N108 = NG-1
      DO 450 N = 1, N108
      IF (NSUM(NG) - NSUM(N)) 450,250,450
  450 CONTINUE
      IF (NG .EQ. 2) GO TO 460
      ITEMP= -NSUM(NG-2)
      IF (ITEMP.LT.0.OR.NSUM(NG).EQ.ITEMP.AND.NSUM(NG-1).LT.0) GO TO 460
```

```
      NSUM(NG-2) = ITEMP
      IF (NSUM(NG) - ITEMP) 460,250,460
  460 MPB = MPA + 1
      MPC = MPA
      MPA = 0
      IDEAL = .TRUE.
      DO 520 M = 1, MP
      IF (YTOT(M)) 520,470,490
  470 MPC = MPC + 1
      IFAS(MPC) = M
      N109 = MF(M)
      N110 = ML(M)
      DO 480 I = N109, N110
  480 Y(I) = 0.
      GO TO 520
  490 MPA = MPA + 1
      IFAS(MPA) = M
      MA = MF(M)
      MB = ML(M)
      DO 500 I = MA, MB
      IF (NO(I) .LT. 1) GO TO 500
      IF (Y(I) .GT. YMAX(I)) Y(I) = YMAX(I)
      IF (Y(I) .LT. 1.E-8) Y(I) = 1.E-8
  500 LX(I) = .FALSE.
      ITEMP = M
      CALL ABER(ITEMP)
      IF (.NOT. IDEAL .OR. M .EQ. 1 .OR. MPB + MSA .LT. 4) GO TO 520
      DO 510 I = MA, MB
      IF (AKTF(I) .EQ. 1.) GO TO 510
      IDEAL = .FALSE.
      GO TO 520
  510 CONTINUE
  520 CONTINUE
      FLAM = -0.09
      LIVARJ = .FALSE.
      LS1 = L + MPA + MSA
      LS = LS1 - 1
      LS2 = LS + 2
      GO TO 550
  530 Y(I) = YTOT(M)*YF(I)
  540 IF (Y(I) .GT. YMAX(I)) Y(I) = YMAX(I)
      LX(I) = .TRUE.
      CALL ABER(M)
  550 DMIN = 1.E-6
      IVAR = 0
      IVARJ = ML(1) - MS
C
C     CALCULATION OF THE COEFFICIENTS IN THE LINEAR SYSTEM OF
C     EQUATIONS
C
  560 DO 570 J = 1, LS1
      DO 570 K = J, LS2
  570 R(J,K) = 0.
      DO 610 N = 1, MPA
      ITEMP = L + N
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      M = IFAS(N)
      N111 = MF(M)
      N112 = ML(M)
      DO 600 I = N111, N112
      IF (Y(I) .EQ. 0.) GO TO 600
      F(I) = G(I) + DLOG(AKT(I))
      R(ITEMP,LS2) = R(ITEMP,LS2) + F(I)*Y(I)
      DO 590 J = 1, L
      IF (A(I,J) .EQ. 0.) GO TO 590
      TEMP = A(I,J)*Y(I)
      R(J,ITEMP) = R(J,ITEMP) + TEMP
      R(J,LS2) = R(J,LS2) + TEMP*F(I)
      DO 580 K = J, L
  580 R(J,K) = R(J,K) + TEMP*A(I,K)
  590 CONTINUE
  600 CONTINUE
      DO 610 J = 1, L
  610 R(J,LS2) = R(J,LS2) - R(J,ITEMP)
      IF (MSA .EQ. 0) GO TO 630
      DO 620 N = 1, MSA
      I = ISOL(N)
      K = L + MPA + N
      R(K,LS2) = GV(I)
      DO 620 J = 1, L
  620 R(J,K) = A(I,J)
  630 DO 640 K = 2, LS1
      N113 = K-1
      DO 640 J = 1, N113
  640 R(K,J) = R(J,K)
      IF (.NOT. NON) GO TO 690
      DO 650 J = 1, L
  650 BO(J) = B(J,NP)
      DO 680 N = 1, MPA
      M = IFAS(N)
      IF (MF(M) .NE. ML(M)) GO TO 680
      MA = MF(M)
      DO 670 J = 1, L
      IF (A(MA,J) .EQ. AO(MA,J)) GO TO 670
      TEMP = (1. - A(MA,J)/AO(MA,J))*Y(MA)
      DO 660 K = 1, L
  660 IF (A(MA,K) .EQ. AO(MA,K)) BO(K) = BO(K) + TEMP*A(MA,K)
      GO TO 680
  670 CONTINUE
  680 CONTINUE
  690 DO 710 K = 1, L
      IF (KH(K) .LT. 4) GO TO 710
      DO 700 J = 1, LS1
  700 R(J,LS2) = R(J,LS2) - PI(K)*R(J,K)
  710 R(K,LS2) = R(K,LS2) + BO(K)
C
C        PREPARATION FOR GAUSSIAN ELIMINATION, PIVOTING
C
      DO 770 K = 1, LS
      IF (KH(K) .GT. 3) GO TO 770
      TEMP = 0.
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      DO 720 J = K, LS1
      IF (DABS(R(J,K)) .LE. TEMP .OR. KH(J) .GT. 3) GO TO 720
      ITEMP = J
      TEMP = DABS(R(J,K))
  720 CONTINUE
      IF (TEMP .GT. 0.) GO TO 730
      IF (K .GT. L) GO TO 770
      IF (BO(K)) 250,770,250
  730 IF (ITEMP .EQ. K) GO TO 750
      DO 740 N = K, LS2
      TEMP = R(ITEMP,N)
      R(ITEMP,N) = R(K,N)
  740 R(K,N) = TEMP
  750 ITEMP = K + 1
      DO 760 J = ITEMP, LS1
      TEMP = -R(J,K)/R(K,K)
      DO 760 N = ITEMP, LS2
  760 R(J,N) = R(J,N) + TEMP*R(K,N)
  770 CONTINUE
C
C     GAUSSIAN ELIMINATION
C
      DO 800 N = 1, LS1
      K = LS2 - N
      IF (KH(K) .GT. 3) GO TO 800
      IF (R(K,K) .NE. 0. .AND. R(K,LS2) .NE. 0.) GO TO 780
      PI(K) = 0.
      K = K - L - MPA
      IF (K) 800,800,190
  780 PI(K) = R(K,LS2)/R(K,K)
      ITEMP = K - 1
      IF (ITEMP .EQ. 0) GO TO 800
      DO 790 J = 1, ITEMP
  790 R(J,LS2) = R(J,LS2) - PI(K)*R(J,K)
  800 CONTINUE
      IF (IVAR .EQ. 0 .OR. IVARJ .GE. 0 .OR. SLAM .LT. 1.) GO TO 1000
      DO 810 J = 1, L
      IF (DABS(PI(J)) .LT. 1.E-4) GO TO 810
      TEMP = OPI(J)/PI(J)
      IF (DABS(TEMP) .LT. 1. .AND. DABS(OPI(J)) .GT. 1.E8) GO TO 180
      IF (DABS(TEMP - 1.) - DMIN) 810,810,1000
  810 CONTINUE
      IF (NEG .GT. 0) GO TO 200
C
C     PREPARE RANKING OF INVARIANTS
C
      IF (MS .LT. M1) GO TO 860
      DO 850 K = M1, MS
      I = INR(K)
      IF (Y(I) .EQ. 0.) GO TO 820
      ALN(K) = 0.
      GO TO 850
  820 IF (NO(I) .EQ. 1) GO TO 830
      ALN(K) = -1.E8
      GO TO 850
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
  830 ALN(K) = -GV(I)
      DO 840 J = 1, L
  840 ALN(K) = ALN(K) + A(I,J)*PI(J)
      ALN(K) = ALN(K)/ASUM(K)
  850 CONTINUE
      IGEN = .TRUE.
C
C        CHECK IF ANY NON-INCLUDED CONDENSED MIXTURES WILL LOWER THE
C        VALUE OF THE TOTAL FREE ENERGY
C
  860 DO 870 N = 1, MPA
      M = IFAS(N)
      CALL XBER(M)
      DO 870 I = MA, MB
      IF (LX(I) .OR. NO(I) .LT. 1 .OR. Y(I) .GT. 0.) GO TO 870
      IF (YTOT(M)*YF(I) - 1.E-8) 870,870,530
  870 CONTINUE
      IF (MPB .GT. MPC) GO TO 940
      DO 880 N = MPB, MPC
      CALL XBER(IFAS(N))
      YFTOT(N) = 0.
      DO 880 I = MA, MB
  880 YFTOT(N) = YFTOT(N) + YF(I)
      IF (IFAS(MPB) .EQ. 1) YFTOT(MPB) = YFTOT(MPB)/PTOT
      NR = 0
      IF (NG .EQ. 1) GO TO 900
      N114 = NG-1
      DO 890 N = 1, N114
  890 IF (NSUM(NG) .EQ. -NSUM(N)) NR = NR + 1
  900 TEMP = 1.
      DO 910 N = MPB, MPC
      IF (YFTOT(N) .LT. TEMP) GO TO 910
      ITEMP = N
      TEMP = YFTOT(N)
  910 CONTINUE
      IF (TEMP .EQ. 1.) GO TO 940
      IF (NR .EQ. 0) GO TO 920
      NR = NR - 1
      YFTOT(ITEMP) = 1.
      GO TO 900
  920 NSUM(NG) = -NSUM(NG)
      M = IFAS(ITEMP)
      YTOT(M) = 1.
      N115 = MF(M)
      N116 = ML(M)
      DO 930 I = N115, N116
  930 Y(I) = YF(I)*BMAX
      GO TO 230
  940 IF (MS .LT. M1) GO TO 960
C
C        THE SAME CHECK FOR INVARIANTS
C
      TEMP = 0.
      DO 950 K = M1, MS
      I = INR(K)
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      IF (NO(I).LT.1.OR.ALN(K).LT.TEMP.OR.Y(I).NE.0.) GO TO 950
      ITEMP = I
      TEMP = ALN(K)
  950 CONTINUE
      IF (TEMP .EQ. 0.) GO TO 960
      Y(ITEMP) = YMAX(ITEMP)
      GO TO 210
  960 IF (NON) GO TO 990
      DO 980 N = 1, MPA
      M = IFAS(N)
      IF (MF(M) .NE. ML(M)) GO TO 980
      MA = MF(M)
      DO 970 J = 1, L
      IF (A(MA,J) .EQ. AO(MA,J)) GO TO 970
      NON = .TRUE.
      GO TO 170
  970 CONTINUE
  980 CONTINUE
  990 IVARJ = 0
 1000 DO 1010 J = 1, L
 1010 OPI(J) = PI(J)
C
C       CHECK FOR NEGATIVE CALCULATED AMOUNTS
C
      SLAM = 1.
      DO 1030 N = 1, MPA
      M = IFAS(N)
      N117 = MF(M)
      N118 = ML(M)
      DO 1030 I = N117, N118
      IF(Y(I) .EQ. 0.) GO TO 1030
      TEMP = F(I) - PI(L+N)
      DO 1020 J = 1, L
 1020 TEMP = TEMP - A(I,J)*PI(J)
      F(I) = TEMP*Y(I)
      IF (TEMP .LT. SLAM) GO TO 1030
      IF (IVAR .LE. 30) SLAM = TEMP
      IF (IVAR .GT. 30) Y(I) = 0.
 1030 CONTINUE
      IF(SLAM .GT. 1.) SLAM = 0.999*(SLAM - 0.5)/(SLAM*SLAM)
      IF (IDEAL .OR. SLAM .LT. FLAM + 0.10) GO TO 1040
      FLAM = AMIN1(FLAM+0.10,0.75)
      IF (IVARJ .LE. 0 .AND. FLAM .GT. 0.25) FLAM = 0.25
      GO TO 1050
 1040 FLAM = SLAM
C
C       CALCULATION OF NEW POSITIVELY-VALUED STARTING ESTIMATES AND
C       WITHDRAWAL OF SPECIES FORMED WITH AMOUNTS LESS THAN 1.E-10 MOL
C
 1050 NEG = 0
      IF (MSA .EQ. 0) GO TO 1070
      DO 1060 K = 1, MSA
      I = ISOL(K)
      J = L + MPA + K
      IF (PI(J) .LT. 0.) NEG = I
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      IF (DABS(PI(J)).GT.DABS(Y(I)).AND.Y(I)/YMAX(I).LT.-1.E8) GO TO 190
 1060 Y(I) = PI(J)
 1070 DO 1090 N = 1, MPA
      M = IFAS(N)
      MA = MF(M)
      MB = ML(M)
      DO 1080 I = MA, MB
      IF (Y(I) .EQ. 0.) GO TO 1080
      Y(I) = Y(I) - FLAM*F(I)
      IF (Y(I) .LT. 1.E-10) Y(I) = 0.
 1080 CONTINUE
      CALL ABER(M)
      IF (M .EQ. 1 .OR. YTOT(M) .GE. 1.E-8) GO TO 1090
      NSUM(NG) = -NSUM(NG)
      YTOT(M) = 0.
      GO TO 230
 1090 CONTINUE
      IVAR = IVAR + 1
      IF (IVAR .EQ. 30) DMIN = 100.*DMIN
      IF (IVAR .EQ. 60) GO TO 180
      IF (IVARJ .GT. 0 .AND. SLAM .LT. 1.) IVARJ = 0
      IF (IVARJ .LT. 0 .OR. SLAM .LT. 1.) GO TO 560
      IF (NEG .GT. 0) GO TO 200
      IVARJ = IVARJ + 1
      IF (IVARJ .LT. 15) GO TO 1100
      IF (LIVARJ) GO TO 1120
      LIVARJ = .TRUE.
      GO TO 550
 1100 DO 1110 N = 1, MPA
      M = IFAS(N)
      N119 = MF(M)
      N120 = ML(M)
      DO 1110 I = N119, N120
      IF (Y(I) .EQ. 0.) GO TO 1110
      IF (DABS(F(I))/Y(I) - 1.E-6) 1110,1110,560
 1110 CONTINUE
C
C     CALCULATION OF EQUILIBRIUM AMOUNTS FOR PREVIOUSLY WITHDRAWN
C     SPECIES
C
 1120 DO 1150 N = 1, MPA
      M = IFAS(N)
      CALL XBER(M)
      IF (MA .NE. MB) GO TO 1140
      DO 1130 J = 1, L
 1130 IF (A(MA,J) .NE. AO(MA,J)) Y(MA) = A(MA,J)/AO(MA,J)*Y(MA)
 1140 DO 1150 I = MA, MB
      IF (NO(I) .LT. 1 .OR. Y(I) .GT. 0.) GO TO 1150
      Y(I) = YTOT(M)*YF(I)
      IF (.NOT. LX(I) .AND. Y(I) .GT. 1.E-10) GO TO 540
      IF (LX(I) .AND. Y(I) .GT. 1.E-8) GO TO 180
 1150 CONTINUE
C
C     CALCULATION OF HYPOTHETICAL MOLE FRACTIONS IN NON-INCLUDED
C     CONDENSED MIXTURES AND HYPOTHETICAL ACTIVITIES FOR NON-INCLUDED
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
C       INVARIANTS
C
      IF (MPA .EQ. MP) GO TO 1190
      DO 1160 N = MPB, MP
      CALL XBER(IFAS(N))
      YFTOT(N) = 0.
      DO 1160 I = MA, MB
      AKT(I) = 0.
 1160 YFTOT(N) = YFTOT(N) + YF(I)
      IF (LYFTOT .OR. MPB .GT. MPC) GO TO 1190
      IF (IFAS(MPB) .EQ. 1) YFTOT(MPB) = YFTOT(MPB)/PTOT
      DO 1180 N = MPB, MPC
      IF (YFTOT(N) .LT. 1.) GO TO 1180
      M = IFAS(N)
      YTOT(M) = 1.
      N121 = MF(M)
      N122 = ML(M)
      DO 1170 I = N121, N122
 1170 Y(I) = YF(I)*BMAX
      IF (MPA .GT. 1) YTOT(IFAS(MPA)) = 0.
      LYFTOT = .TRUE.
      GO TO 170
 1180 CONTINUE
 1190 IF (MS .LT. M1) RETURN
      DO 1220 I = M1, MS
      IF (MOD(NO(I),2) .EQ. 0) GO TO 1220
      IF (Y(I) .EQ. 0.) GO TO 1200
      AKT(I) = 1.
      GO TO 1220
 1200 TEMP = -GV(I)
      DO 1210 J = 1, L
 1210 TEMP = TEMP + A(I,J)*PI(J)
      IF (DABS(TEMP) .GT. POTM) TEMP = SIGN(POTM,TEMP)
      AKT(I) = DEXP(TEMP)
 1220 CONTINUE
      RETURN
      END
      SUBROUTINE ABER(M)
      DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
      COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
     *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
      DOUBLE PRECISION POTM,RINV,V,YTOT
      COMMON /SGAX/ MA, MB, NO(80), POTM, RINV, V, YTOT(9)
C
C       CALCULATION OF ACTIVITIES FROM MOLE FRACTIONS
C
      YTOT(M) = 0.
      DO 10 I = MA, MB
   10 YTOT(M) = YTOT(M) + Y(I)
      IF (YTOT(M) .LT. 1.E-8) RETURN
      IF (M .GT. 1) GO TO 20
      IF (V .GT. 0.) PTOT = T*YTOT(1)/(101.325*RINV*V)
      YTOT(1) = YTOT(1)/PTOT
   20 DO 30 I = MA, MB
   30 YF(I) = Y(I)/YTOT(M)
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      CALL FACTOR(M)
      DO 40 I = MA, MB
   40 AKT(I) = AKTF(I)*YF(I)
      RETURN
      END
      SUBROUTINE XBER(M)
      DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
      COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
     *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
      DOUBLE PRECISION POTM,RINV,V,YTOT
      COMMON /SGAX/ MA, MB, NO(80), POTM, RINV, V, YTOT(9)
      DOUBLE PRECISION OYF
      DIMENSION OYF(80)
C
C        CALCULATION OF MOLE FRACTIONS FROM ACTIVITIES
C
      MA = MF(M)
      MB = ML(M)
      DO 30 I = MA, MB
      IF (YTOT(M) .EQ. -1. .AND. NO(I) .EQ. -1) GO TO 10
      IF (NO(I) .LT. 1 .OR. Y(I) .GT. 0.) GO TO 30
   10 TEMP = -G(I)
      DO 20 J = 1, L
   20 TEMP = TEMP + A(I,J)*PI(J)
      IF (ABS(TEMP) .GT. POTM) TEMP = SIGN(POTM,TEMP)
      AKT(I) = EXP(TEMP)
      YF(I) = AKT(I)
   30 CONTINUE
      IVAR = 0
   40 IVAR = IVAR + 1
      IF (IVAR .EQ. 60) RETURN
      CALL FACTOR(M)
      DO 50 I = MA, MB
      IF (AKT(I).EQ.0..OR.AKTF(I).EQ.1..OR.YF(I).EQ.0.) GO TO 50
      OYF(I) = YF(I)
      TEMP = AKTF(I)*YF(I)
      YF(I) = YF(I) - TEMP*DLOG(TEMP/AKT(I))/(DAKTF(I)*YF(I) + AKTF(I))
      IF (YF(I) .GT. 2.*OYF(I)) YF(I) = 2.*OYF(I)
      IF (YF(I) .LT. 0.5*OYF(I)) YF(I) = 0.5*OYF(I)
   50 CONTINUE
      DO 60 I = MA, MB
      IF (AKT(I).EQ.0..OR.AKTF(I).EQ.1..OR.YF(I).EQ.0.) GO TO 60
      IF (DABS(OYF(I)/YF(I) - 1.) - 1.E-6) 60,60,40
   60 CONTINUE
      RETURN
      END
      SUBROUTINE HETTA
      DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
      COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
     *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
      DOUBLE PRECISION C,HOM,TOM
      COMMON /CP/ C(80,6,6), HOM(80,6), NOM(80), TOM(80,6)
      DOUBLE PRECISION HF,S,XI
      COMMON /SGHE/ HF(80),IIN(25),IN,IOUT,KVAL1,KVAL2,MIN,S(80),XI(80)
      COMMON /TEXT/ IDENT(80,2)
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      DOUBLE PRECISION HCT,HFT
      DIMENSION HCT(80), HFT(80)
      CHARACTER*5 IDENT
      GO TO (90,90,90,90,90,50,50,50,10), KVAL1
   10 WRITE (6,500)
      DO 20 I = 1, MS
      READ (5,510) HF(I), S(I), NOM(I)
      N123 = NOM(I)
      DO 20 J = 1, N123
      READ (5,520) (C(I,J,K), K = 1, 6), TOM(I,J), HOM(I,J)
   20 WRITE (6,530) (IDENT(I,K), K = 1, 2), (C(I,J,K), K = 1, 6)
      WRITE (6,540)
      DO 40 I = 1, MS
      IF (NOM(I) .GT. 1) GO TO 30
      WRITE (6,550) (IDENT(I,J), J = 1, 2), HF(I), S(I)
      GO TO 40
   30 WRITE (6,550) (IDENT(I,J),J=1,2),HF(I),S(I),TOM(I,1),HOM(I,1)
      N124 = NOM(I)-1
      IF (NOM(I) .GT. 2) WRITE (6,560) ((IDENT(I,K), K = 1, 2),
     *TOM(I,J), HOM(I,J), J = 2, N124)
   40 CONTINUE
      IF (KVAL2 .EQ. 2) RETURN
      READ (5,570) MIN, (IIN(N), N = 1, MIN)
      READ (5,520) TO
      WRITE (6,580) TO
   50 IF (KVAL2 .EQ. 2) RETURN
      DO 60 I = 1, MS
      ITEMP = I
      HCT(I) = 1.E-3*HEAT(ITEMP,T)
   60 HFT(I) = HCT(I) + 1.E-3*HF(I)
      DO 70 J = 1, L
      K = IEL(J)
      DO 70 I = 1, MS
   70 HFT(I) = HFT(I) - A(I,J)/A(K,J)*HCT(K)
      DO 80 N = 1, MIN
      I = IIN(N)
   80 HCT(I) = HCT(I) - 1.E-3*HEAT(I,TO)
      RETURN
   90 HP = 0.
      HR = 0.
      DO 100 N = 1, MIN
      I = IIN(N)
      HP = HP + HCT(I)*XI(I)
  100 HR = HR - HFT(I)*XI(I)
      DO 110 I = 1, MS
  110 HR = HR + HFT(I)*Y(I)
      WRITE (6,590) HP, HR, HP+HR
      RETURN
  500 FORMAT(/19X,'A',10X,'B',11X,'C',11X,'D',11X,'E',11X,'F')
  510 FORMAT(2E10.0,I2)
  520 FORMAT(8E10.0)
  530 FORMAT(1X, 2A5, F12.3, 5(1X, E11.4))
  540 FORMAT(/16X, 'HF298', 9X, 'S298', 8X, 'T TR', 8X, 'H TR')
  550 FORMAT(1X, 2A5, F12.3, 2F12.1)
  560 FORMAT(1X, 2A5, 24X, 2F12.1)
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
  570 FORMAT(40I2)
  580 FORMAT(/' TO =', F8.2, ' K')
  590 FORMAT(/' ENTHALPY OF HEATING =', F9.2, ' KJ'// ' ENTHALPY OF REAC
     *TION =', F9.2, ' KJ'// ' TOTAL ENTHALPY =', F9.2, ' KJ')
      END
      FUNCTION HEAT(I,T)
C
C        CALCULATION OF THE ENTHALPY DIFFERENCE BETWEEN 298 AND T K FOR
C        SPECIES I
C
      DOUBLE PRECISION C,HOM,TOM
      COMMON /CP/ C(80,6,6), HOM(80,6), NOM(80), TOM(80,6)
      IF (NOM(I) .EQ. 1 .OR. TOM(I,1) .GT. T) GO TO 20
      HEAT = CPINT(298.15,TOM(I,1),C(I,1,1),C(I,1,2),C(I,1,3),C(I,1,4),C
     *(I,1,5),C(I,1,6),0.,0.,0.)
      N = NOM(I) - 1
      DO 10 J = 1, N
      K = J + 1
      TEMP = TOM(I,K)
      IF (J .EQ. N .OR. TEMP .GT. T) TEMP = T
      HEAT = HEAT + HOM(I,J) + CPINT(TOM(I,J),TEMP,C(I,K,1),C(I,K,2),C(I
     *,K,3),C(I,K,4),C(I,K,5),C(I,K,6),0.,0.,0.)
      IF (TEMP .EQ. T) RETURN
   10 CONTINUE
   20 HEAT = CPINT(298.15,T,C(I,1,1),C(I,1,2),C(I,1,3),C(I,1,4),C(I,1,5)
     *,C(I,1,6),0.,0.,0.)
      RETURN
      END
      FUNCTION SO(I,T)
C
C        CALCULATION OF THE ENTROPY DIFFERENCE BETWEEN 298 AND T K FOR
C        SPECIES I
C
      DOUBLE PRECISION C,HOM,TOM
      COMMON /CP/ C(80,6,6), HOM(80,6), NOM(80), TOM(80,6)
      IF (NOM(I) .EQ. 1 .OR. TOM(I,1) .GT. T) GO TO 20
      SO = CPINT(298.15,TOM(I,1),C(I,1,2),C(I,1,4),0.,0.,C(I,1,3),0.,C(I
     *,1,1),C(I,1,5),C(I,1,6))
      N = NOM(I) - 1
      DO 10 J = 1, N
      K = J + 1
      TEMP = TOM(I,K)
      IF (J .EQ. N .OR. TEMP .GT. T) TEMP = T
      SO = SO + HOM(I,J)/TOM(I,J) + CPINT(TOM(I,J),TEMP,C(I,K,2),C(I,K,4
     *),0.,0.,C(I,K,3),0.,C(I,K,1),C(I,K,5),C(I,K,6))
      IF (TEMP .EQ. T) RETURN
   10 CONTINUE
   20 SO = CPINT(298.15,T,C(I,1,2),C(I,1,4),0.,0.,C(I,1,3),0.,C(I,1,1),C
     *(I,1,5),C(I,1,6))
      RETURN
      END
      FUNCTION CPINT(TO,T1,CA,CB,CC,CD,CE,CF,CG,CH,CI)
C
C        CALCULATION OF THE CP AND CP/T INTEGRAL
C
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
      DATA OTO/O./, OT1/O./
      IF (TO .EQ. OTO .AND. T1 .EQ. OT1) GO TO 10
      OTO = TO
      OT1 = T1
      T2 = TO + T1
      T3 = TO*T1
      T4 = T3*T3
      TA = T1 - TO
      TB = TA*T2/2.
      TC = TA/T3
      TD = TA*(T2*T2 - T3)/3.
      TE = TB/T4
      TF = 2.*(SQRT(T1) - SQRT(TO))
      TG = ALOG(T1/TO)
      TH = TD/(T3*T4)
      TI = TF/SQRT(T3)
   10 CPINT=CA*TA+CB*TB+CC*TC+CD*TD+CE*TE+CF*TF+CG*TG+CH*TH+CI*TI
      RETURN
      END
      SUBROUTINE FACTOR(M)
      DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
      COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
     *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
C
C        FACTOR IS A SUBROUTINE FOR THE CALCULATION OF EXPRESSIONS,
C        SUPPLIED BY THE USER, GIVING ACTIVITY COEFFICIENTS FOR SPECIES
C        IN NON-IDEAL MIXTURES OR STOICHIOMETRIC COEFFICIENTS FOR NON-
C        STOICHIOMETRIC SOLIDS.
C
C        THE ACTIVITY COEFFICIENT EXPRESSIONS AND THEIR DERIVATIVES
C        WITH RESPECT TO THE MOLE FRACTIONS ARE INSERTED AFTER THE
C        STATEMENT NUMBER WHICH CORRESPONDS TO THE MIXTURE NUMBER. MAXI-
C        MUM ONE STOICHIOMETRIC COEFFICIENT IS ALLOWED TO DEVIATE FOR
C        SOLIDS WITH VARIABLE STOICHIOMETRY WHICH ARE REGARDED AS SEPA-
C        RATE MIXTURES (CF. CHEM. SCR. 1975, 8, 100-3).
C
C        A SPECIES FOR WHICH THE AMOUNT BECOMES LESS THAN 1.E-10 MOL
C        DURING THE ITERATIVE PROCEDURE IS TEMPORARILY REMOVED FROM THE
C        CALCULATION. THE ACTIVITY FOR SUCH A REMOVED SPECIES IS CALCU-
C        LATED BY USING THE LAGRANGIAN MULTIPLIERS ACCORDING TO EQN. (2)
C        IN CHEM. SCR. 1975, 8, 100-3.
C
C        DEFINE UPPER AND LOWER BOUNDS ON THE MOLE FRACTIONS IF MOLE
C        FRACTIONS FAR FROM THE EQUILIBRIUM VALUES CAN CAUSE EXPONENTS
C        OUT OF THE RANGE ALLOWED. RECOMMENDED EXPRESSION:
C        IF (YF(I) .GT. 2.) YF(I) = 2.
C
C        AKT(I) = ACTIVITY FOR SPECIES I
C        AKTF(I) = ACTIVITY COEFFICIENT FOR SPECIES I
C        AO(I,J) = A DEVIATING STOICHIOMETRIC COEFFICIENT FOR SPECIES I
C        DAKTF(I) = DERIVATIVE OF AKTF WITH RESPECT TO YF FOR SPECIES I
C        G(I) = (MUO/RT) FOR SPECIES I
C        MF(M) = LOWEST SPECIES NUMBER IN MIXTURE M
C        ML(M) = HIGHEST SPECIES NUMBER IN MIXTURE M
C        MS = TOTAL NUMBER OF SPECIES CONSIDERED
```

SOLGASMIX PROGRAM (BATCH VERSION)

(continued)

```
C          PI(J) = LAGRANGIAN MULTIPLIER FOR ELEMENT J
C          Y(I) = AMOUNT OF SUBSTANCE FOR SPECIES I
C          YF(I) = MOLE FRACTION OR PARTIAL PRESSURE FOR SPECIES I
C          CONSULT THE INPUT GUIDE FOR AN EXPLANATION OF THE FOLLOWING
C          VARIABLES: A(I,J), B(J,NP), IEL(J), L, MP, PTOT, T
C
      GO TO (1,2,3,4,5,6,7,8,9), M
    1 CONTINUE
      RETURN
    2 CONTINUE
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      RETURN
    6 CONTINUE
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
      END
      SUBROUTINE SPEQUA
      DOUBLE PRECISION A,AKT,AKTF,AO,B,DAKTF,G,PI,PTOT,T,Y,YF
      COMMON A(80,12),AKT(80),AKTF(80),AO(80,12),B(12,25),DAKTF(80),
     *G(80),IEL(12),L,MF(10),ML(10),MP,MS,NP,PI(24),PTOT,T,Y(80),YF(80)
C
C          SPEQUA IS A SUBROUTINE FOR THE CALCULATION OF QUANTITIES WHICH
C          ARE DERIVABLE FROM THE EQUILIBRIUM COMPOSITION.
C
      RETURN
      END
$ENTRY
/*
//FT06F001 DD DSN=JONES.WAT.LIST,DISP=(NEW,DELETE),VOL=SER=VOL011,
//   UNIT=SYSDA,SPACE=(133,(500,100),RLSE)
```

APPENDIX C

Sample Output from SOLGASMIX

DATA FILE 2

A copy of the computer print out of the Data File 2. This data file constitutes an equilibrium system obtainable from a reaction between 1 mole of C_2H_6 and 4 moles of H_2O at $1000^\circ K$. Initial guess composition would be generated by the program.

```
DATA2 FILE
 3 1 1 9
CH4          1.0  0.0  4.0
C2H4         2.0  0.0  4.0
C2H2         2.0  0.0  2.0
CO2          1.0  2.0  0.0
CO           1.0  1.0  0.0
O2           0.0  2.0  0.0
H2           0.0  0.0  2.0
H2O          0.0  1.0  2.0
C2H6         2.0  0.0  6.0
C            1.0  0.0  0.0
10 6 7
 1
 1 2
 .1923E+05
 .1181E+06
 .1697E+06
-.3955E+06
-.2004E+06
0.
0.
-.1924E+06
 .1092E+06
0.
   1000.00
 2
 1
 2 2 2
2.0
4.0
14.0
10
```

OUTPUT FOR DATA FILE 2

```
DATA2 FILE

FORMULA UNITS
CH4           1.0  0.0  4.0
C2H4          2.0  0.0  4.0
C2H2          2.0  0.0  2.0
CO2           1.0  2.0  0.0
CO            1.0  1.0  0.0
O2            0.0  2.0  0.0
H2            0.0  0.0  2.0
H2O           0.0  1.0  2.0
C2H6          2.0  0.0  6.0
C             1.0  0.0  0.0

               COEFF 2      COEFF
CH4           0.1923E 05
C2H4          0.1181E 06
C2H2          0.1697E 06
CO2          -0.3955E 06
CO           -0.2004E 06
O2            0.0000E 00
H2            0.0000E 00
H2O          -0.1924E 06
C2H6          0.1092E 06
C             0.0000E 00
```

```
T = 1000.00 K
P = 1.000D 00 ATM

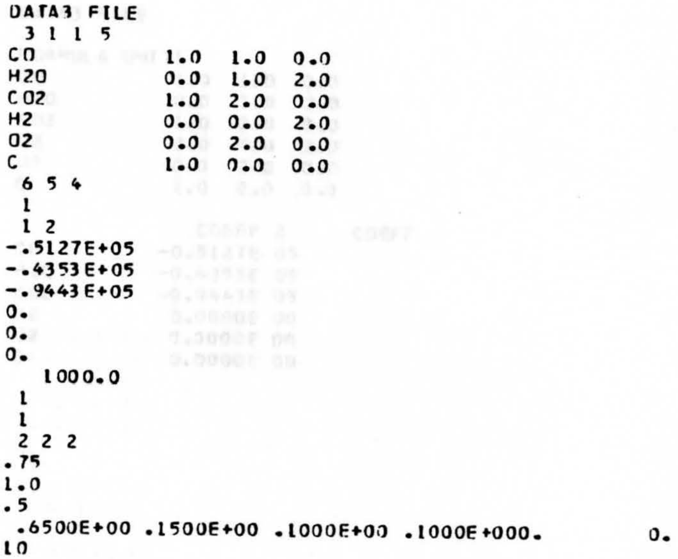
                  X*/MOL          Y/MOL           P/ATM          ACTIVITY
CH4           0.00000D 00     0.66991D-01     0.75559D-02     0.75559D-02
C2H4          0.00000D 00     0.96361D-07     0.10869D-07     0.10869D-07
C2H2          0.00000D 00     0.32239D-09     0.36362D-10     0.36362D-10
CO2           0.00000D 00     0.54606D 00     0.61591D-01     0.61591D-01
CO            0.00000D 00     0.13869D 01     0.15643D 00     0.15643D 00
O2            0.20000D 01     0.57047D-20     0.64343D-21     0.64343D-21
H2            0.70000D 01     0.53451D 01     0.60287D 00     0.60287D 00
H2O           0.00000D 00     0.15209D 01     0.17155D 00     0.17155D 00
C2H6          0.00000D 00     0.16944D-06     0.19111D-07     0.19111D-07

C             0.20000D 01     0.00000D 00                     0.21004D 00

STATEMENTS EXECUTED=    12134
```

DATA FILE 3

A copy of the computer print out of the Data File 3. This data file constitutes a system containing CO, CO_2, H_2, O_2 and invarient C at 1000°K. The initial guess estimate was supplied as input data.



```
DATA3 FILE
 3 1 1 5
CO             1.0  1.0  0.0
H2O            0.0  1.0  2.0
C O2           1.0  2.0  0.0
H2             0.0  0.0  2.0
O2             0.0  2.0  0.0
C              1.0  0.0  0.0
 6 5 4
 1
 1 2
-.5127E+05
-.4353 E+05
-.9443 E+05
0.
0.
0.
   1000.0
 1
 1
 2 2 2
.75
1.0
.5
 .6500E+00 .1500E+00 .1000E+00 .1000E +000.          0.
10
```

OUTPUT FOR DATA FILE 3

```
DATA3 FILE

FORMULA UNITS
CO          1.0  1.0  0.0
H2O         0.0  1.0  2.0
CO2         1.0  2.0  0.0
H2          0.0  0.0  2.0
O2          0.0  2.0  0.0
C           1.0  0.0  0.0
              COEFF 2     COEFF
CO         -0.5127E 05
H2O        -0.4353E 05
CO2        -0.9443E 05
H2          0.0000E 00
O2          0.0000E 00
C           0.0000E 00





T = 1000.00 K
P = 1.0000D 00 ATM

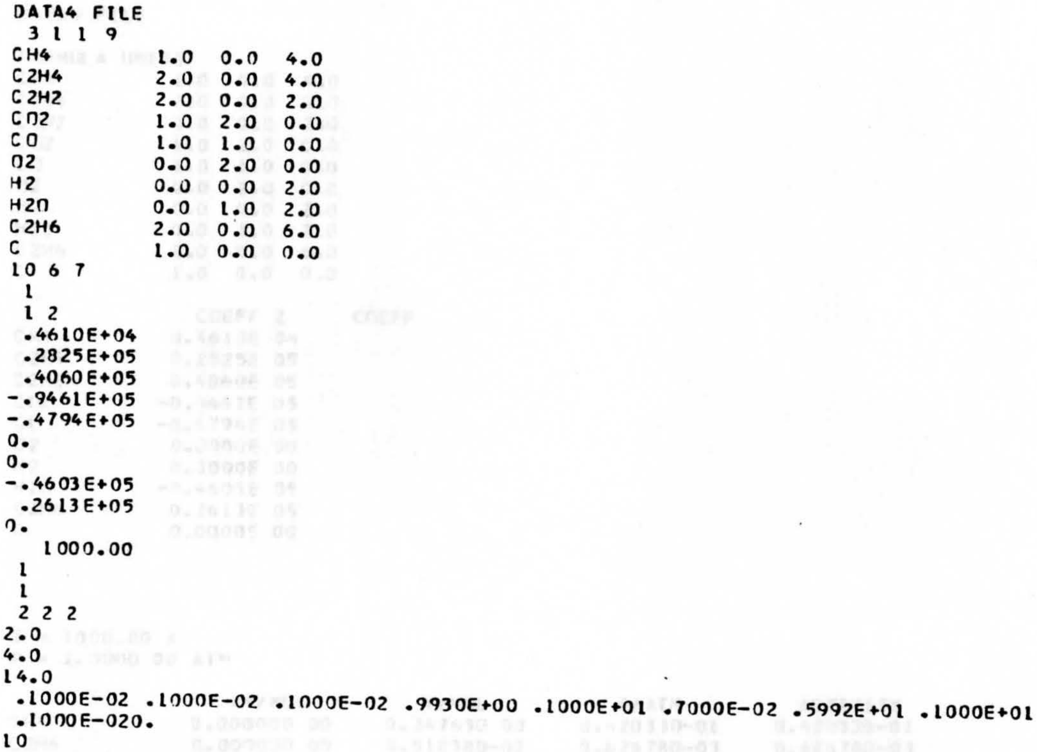
                 X*/MOL          Y/MOL          P/ATM          ACTIVITY
CO            0.00000D 00    0.56408D 00    0.56408D 00    0.56408D 00
H2O           0.00000D 00    0.64071D-01    0.64071D-01    0.64071D-01
CO2           0.00000D 00    0.18592D 00    0.18592D 00    0.18592D 00
H2            0.25000D 00    0.18593D 00    0.18593D 00    0.18593D 00
O2            0.50000D 00    0.33659D-05    0.33659D-05    0.33659D-05

C             0.75000D 00    0.00000D 00                   0.64525D 00

STATEMENTS EXECUTED=    4030
```

DATA FILE 4

A copy of the computer print out of the Data File 4. This data file constitutes an equilibrium system obtainable from a reaction between 1 mole of C_2H_6 and 4 moles of H_2O at 1000^oK. Initial guess composition is supplied as input data.



```
DATA4 FILE
 3 1 1 9
CH4            1.0  0.0  4.0
C2H4           2.0  0.0  4.0
C2H2           2.0  0.0  2.0
C02            1.0  2.0  0.0
CO             1.0  1.0  0.0
02             0.0  2.0  0.0
H2             0.0  0.0  2.0
H20            0.0  1.0  2.0
C2H6           2.0  0.0  6.0
C              1.0  0.0  0.0
10 6 7
 1
 1 2
 .4610E+04
 .2825E+05
 .4060E+05
-.9461E+05
-.4794E+05
0.
0.
-.4603E+05
 .2613E+05
0.
   1000.00
 1
 1
 2 2 2
2.0
4.0
14.0
 .1000E-02 .1000E-02 .1000E-02 .9930E+00 .1000E+01 .7000E-02 .5992E+01 .1000E+01
 .1000E-020.
10
```

OUTPUT FOR DATA FILE 4

```
DATA4 FILE

FORMULA UNITS
CH4          1.0  0.0  4.0
C2H4         2.0  0.0  4.0
C2H2         2.0  0.0  2.0
CO2          1.0  2.0  0.0
CO           1.0  1.0  0.0
O2           0.0  2.0  0.0
H2           0.0  0.0  2.0
H2O          0.0  1.0  2.0
C2H6         2.0  0.0  6.0
C            1.0  0.0  0.0

              COEFF 2      COEFF
CH4          0.4610E 04
C2H4         0.2825E 05
C2H2         0.4060E 05
CO2         -0.9461E 05
CO          -0.4794E 05
O2           0.0000E 00
H2           0.0000E 00
H2O         -0.4603E 05
C2H6         0.2613E 05
C            0.0000E 00


T = 1000.00 K
P = 1.000D 00 ATM

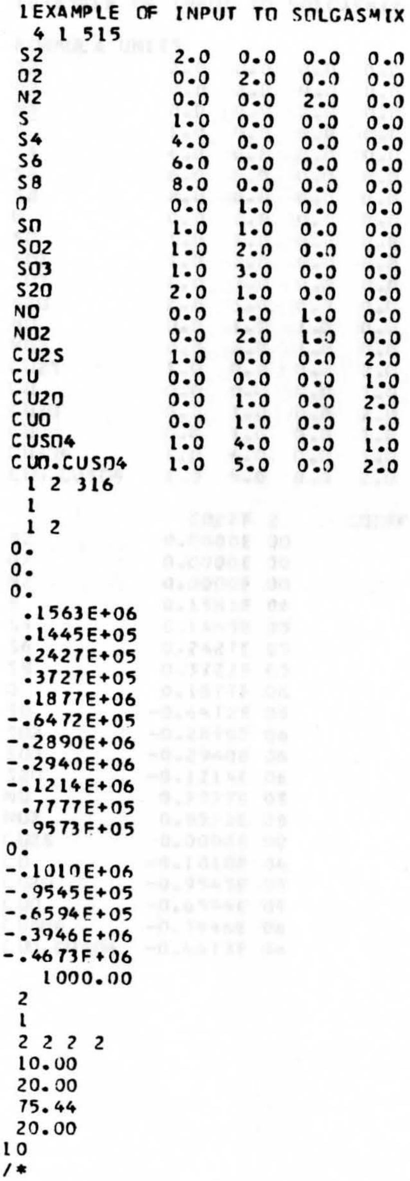
                X*/MOL          Y/MOL           P/ATM          ACTIVITY
CH4          0.000000D 00    0.347630D 00    0.42033D-01    0.42033D-01
C2H4         0.000000D 00    0.51838D-02     0.62678D-03    0.62678D-03
C2H2         0.000000D 00    0.21955D-02     0.26546D-03    0.26546D-03
CO2          0.000000D 00    0.50939D 00     0.61591D-01    0.61591D-01
CO           0.000000D 00    0.11211D 01     0.13555D 00    0.13555D 00
O2           0.20000D 01     0.22741D-04     0.27496D-05    0.27496D-05
H2           0.70000D 01     0.44213D 01     0.53459D 00    0.53459D 00
H2O          0.000000D 00    0.18601D 01     0.22491D 00    0.22491D 00
C2H6         0.000000D 00    0.35760D-02     0.43239D-03    0.43239D-03

C            0.20000D 01     0.00000D 00                    0.25606D 00

STATEMENTS EXECUTED=    6717
```

DATA FILE 7

A copy of the computer print out of the Data File 7. The system contains one gas phase containing 15 species and 5 invarients. Initial guess composition is generated by the program.



```
1EXAMPLE OF INPUT TO SOLGASMIX
  4 1 515
 S2              2.0   0.0   0.0   0.0
 O2              0.0   2.0   0.0   0.0
 N2              0.0   0.0   2.0   0.0
 S               1.0   0.0   0.0   0.0
 S4              4.0   0.0   0.0   0.0
 S6              6.0   0.0   0.0   0.0
 S8              8.0   0.0   0.0   0.0
 O               0.0   1.0   0.0   0.0
 SO              1.0   1.0   0.0   0.0
 SO2             1.0   2.0   0.0   0.0
 SO3             1.0   3.0   0.0   0.0
 S2O             2.0   1.0   0.0   0.0
 NO              0.0   1.0   1.0   0.0
 NO2             0.0   2.0   1.0   0.0
 CU2S            1.0   0.0   0.0   2.0
 CU              0.0   0.0   0.0   1.0
 CU2O            0.0   1.0   0.0   2.0
 CUO             0.0   1.0   0.0   1.0
 CUSO4           1.0   4.0   0.0   1.0
 CUO.CUSO4       1.0   5.0   0.0   2.0
  1 2 316
  1
  1 2
 0.
 0.
 0.
  .1563E+06
  .1445E+05
  .2427E+05
  .3727E+05
  .1877E+06
 -.6472E+05
 -.2890E+06
 -.2940E+06
 -.1214E+06
  .7777E+05
  .9573E+05
 0.
 -.1010E+06
 -.9545E+05
 -.6594E+05
 -.3946E+06
 -.4673E+06
     1000.00
  2
  1
  2 2 2  2
  10.00
  20.00
  75.44
  20.00
 10
 /*
```

OUTPUT FOR DATA FILE 7

```
1EXAMPLE OF INPUT TO SOLGASMIX

FORMULA UNITS
S2             2.0  0.0  0.0  0.0
O2             0.0  2.0  0.0  0.0
N2             0.0  0.0  2.0  0.0
S              1.0  0.0  0.0  0.0
S4             4.0  0.0  0.0  0.0
S6             6.0  0.0  0.0  0.0
S8             8.0  0.0  0.0  0.0
O              0.0  1.0  0.0  0.0
SO             1.0  1.0  0.0  0.0
SO2            1.0  2.0  0.0  0.0
SO3            1.0  3.0  0.0  0.0
S2O            2.0  1.0  0.0  0.0
NO             0.0  1.0  1.0  0.0
NO2            0.0  2.0  1.0  0.0
CU2S           1.0  0.0  0.0  2.0
CU             0.0  0.0  0.0  1.0
CU2O           0.0  1.0  0.0  2.0
CUO            0.0  1.0  0.0  1.0
CUSO4          1.0  4.0  0.0  1.0
CUO.CUSO4      1.0  5.0  0.0  2.0

                 COEFF 2     COEFF
S2             0.0000E 00
O2             0.0000E 00
N2             0.0000E 00
S              0.1563E 06
S4             0.1445E 05
S6             0.2427E 05
S8             0.3727E 05
O              0.1877E 06
SO            -0.6472E 05
SO2           -0.2890E 06
SO3           -0.2940E 06
S2O           -0.1214E 06
NO             0.7777E 05
NO2            0.9573E 05
CU2S           0.0000E 00
CU            -0.1010E 06
CU2O          -0.9545E 05
CUO           -0.6594E 05
CUSO4         -0.3946E 06
CUO.CUSO4     -0.4673E 06
```

OUTPUT FOR DATA FILE 7 (continuation)

```
T = 1000.00 K
P = 1.000D 00 ATM

                 X*/MOL         Y/MOL          P/ATM         ACTIVITY
S2           0.50000D 01    0.57607D-06    0.12072D-07    0.12072D-07
02           0.10000D 02    0.73007D-10    0.15299D-11    0.15299D-11
N2           0.37720D 02    0.37720D 02    0.79044D 00    0.79044D 00
S            0.00000D 00    0.35921D-10    0.75275D-12    0.75275D-12
S4           0.00000D 00    0.12231D-14    0.25631D-16    0.25631D-16
S6           0.00000D 00    0.45321D-23    0.94972D-25    0.94972D-25
S8           0.00000D 00    0.11456D-31    0.24006D-33    0.24006D-33
O            0.00000D 00    0.92604D-14    0.19406D-15    0.19406D-15
SO           0.00000D 00    0.15579D-04    0.32646D-06    0.32646D-06
S02          0.00000D 00    0.10000D 02    0.20955D 00    0.20955D 00
SO3          0.00000D 00    0.22569D-04    0.47294D-06    0.47294D-06
S20          0.00000D 00    0.15634D-05    0.32762D-07    0.32762D-07
NO           0.00000D 00    0.45467D-08    0.95278D-10    0.95278D-10
N02          0.00000D 00    0.64849D-15    0.13589D-16    0.13589D-16
CU2S         0.00000D 00    0.14731D-12    0.30870D-14    0.30870D-14

CU           0.20000D 02    0.20000D 02                   0.10000D 01
CU2O         0.00000D 00    0.00000D 00                   0.33632D-11
CUO          0.00000D 00    0.00000D 00                   0.18239D-07
CUS04        0.00000D 00    0.00000D 00                   0.55749D-12
CUO.CUS04    0.00000D 00    0.00000D 00                   0.22926D-19

STATEMENTS EXECUTED=   69854
```

DATA FILE 8

A copy of the computer print out of the Data File 8. This data file constitutes equilibrium systems obtainable from reaction at 1000°K between one mole of C_2H_6 and 4, 3, 2, 5 and 6 moles of H_2O respectively. Initial guess composition would be generated by the program.

```
ETHANE-STEAM SYSTEM, 1MOLE ETHANE,STEAM VARIES BETWEEN 2 AND 6 MOLES.
 3 1 1 9
CH4          1.0  0.0  4.0
C2H4         2.0  0.0  4.0
C2H2         2.0  0.0  2.0
CO2          1.0  2.0  0.0
CO           1.0  1.0  0.0
O2           0.0  2.0  0.0
H2           0.0  0.0  2.0
H2O          0.0  1.0  2.0
C2H6         2.0  0.0  6.0
C            1.0  0.0  0.0
10 6 7
 1
 1 2
 .1923E+05
 .1181E+06
 .1697E+06
-.3955E+06
-.2004E+06
0.
0.
-.1924E+06
 .1092E+06
0.
  1000.00
 2
 5
 2 1 1
2.0
4.0         3.0         2.0         5.0         6.0
14.0        12.0        10.0        16.0        18.0
10
```

OUTPUT FOR DATA FILE 8

```
ETHANE-STFAM SYSTEM, 1MOLE ETHANE,STEAM VARIES BETWEEN 2 AND 6 MOLES.
FORMULA UNITS
CH4           1.0  0.0  4.0
C2H4          2.0  0.0  4.0
C2H2          2.0  0.0  2.0
CO2           1.0  2.0  0.0
CO            1.0  1.0  0.0
O2            0.0  2.0  0.0
H2            0.0  0.0  2.0
H2O           0.0  1.0  2.0
C2H6          2.0  0.0  6.0
C             1.0  0.0  0.0

               COEFF 2   COEFF
CH4           0.1923E 05
C2H4          0.1181E 06
C2H2          0.1697E 06
CO2          -0.3955E 06
CO           -0.2004E 06
O2            0.0000E 00
H2            0.0000E 00
H2O          -0.1924E 06
C2H6          0.1092E 06
C             0.0000E 00
T = 1000.00 K
P = 1.000D 00 ATM
                 X*/MOL         Y/MOL          P/ATM          ACTIVITY
CH4            0.00000D 00    0.66991D-01    0.75559D-02    0.75559D-02
C2H4           0.00000D 00    0.96361D-07    0.10869D-07    0.10869D-07
C2H2           0.00000D 00    0.32239D-09    0.36362D-10    0.36362D-10
CO2            0.00000D 00    0.54606D 00    0.61591D-01    0.61591D-01
CO             0.00000D 00    0.13869D 01    0.15643D 00    0.15643D 00
O2             0.20000D 01    0.57047D-20    0.64343D-21    0.64343D-21
H2             0.70000D 01    0.53451D 01    0.60287D 00    0.60287D 00
H2O            0.00000D 00    0.15209D 01    0.17155D 00    0.17155D 00
C2H6           0.00000D 00    0.16944D-06    0.19111D-07    0.19111D-07

C              0.20000D 01    0.00000D 00                   0.21004D 00
T = 1000.00 K
P = 1.000D 00 ATM
                 X*/MOL         Y/MOL          P/ATM          ACTIVITY
CH4            0.00000D 00    0.14265D 00    0.18491D-01    0.18491D-01
C2H4           0.00000D 00    0.44989D-06    0.58316D-07    0.58316D-07
C2H2           0.00000D 00    0.14246D-08    0.18467D-09    0.18467D-09
CO2            0.00000D 00    0.34178D 00    0.44303D-01    0.44303D-01
CO             0.00000D 00    0.15156D 01    0.19645D 00    0.19645D 00
O2             0.15000D 01    0.16286D-20    0.21110D-21    0.21110D-21
H2             0.60000D 01    0.49138D 01    0.63694D 00    0.63694D 00
H2O            0.00000D 00    0.80087D 00    0.10381D 00    0.10381D 00
C2H6           0.00000D 00    0.83578D-06    0.10834D-06    0.10834D-06

C              0.20000D 01    0.00000D 00                   0.46051D 00
```

OUTPUT FOR DATA FILE 8 (continuation)

```
T = 1000.00 K
P = 1.0000D 00 ATM

                  X*/MOL        Y/MOL         P/ATM         ACTIVITY
CH4             0.00000D 00   0.26948D 00   0.43219D-01   0.43219D-01
C2H4            0.00000D 00   0.18454D-05   0.29598D-06   0.29598D-06
C2H2            0.00000D 00   0.56329D-08   0.90342D-09   0.90342D-09
CO2             0.00000D 00   0.15454D 00   0.24785D-01   0.24785D-01
CO              0.00000D 00   0.13501D 01   0.21653D 00   0.21653D 00
O2              0.10000D 01   0.33910D-21   0.54385D-22   0.54385D-22
H2              0.50000D 01   0.41202D 01   0.66080D 00   0.66080D 00
H2O             0.00000D 00   0.34085D 00   0.54665D-01   0.54665D-01
C2H6            0.00000D 00   0.35568D-05   0.57044D-06   0.57044D-06

C               0.20000D 01   0.22590D 00                 0.10000D 01


T = 1000.00 K
P = 1.0000D 00 ATM

                  X*/MOL        Y/MOL         P/ATM         ACTIVITY
CH4             0.00000D 00   0.36362D-01   0.36628D-02   0.36628D-02
C2H4            0.00000D 00   0.28897D-07   0.29108D-08   0.29108D-08
C2H2            0.00000D 00   0.10321D-09   0.10396D-10   0.10396D-10
CO2             0.00000D 00   0.71521D 00   0.72045D-01   0.72045D-01
CO              0.00000D 00   0.12484D 01   0.12576D 00   0.12576D 00
O2              0.25000D 01   0.13524D-19   0.13623D-20   0.13623D-20
H2              0.80000D 01   0.56061D 01   0.56472D 00   0.56472D 00
H2O             0.00000D 00   0.23211D 01   0.23382D 00   0.23382D 00
C2H6            0.00000D 00   0.47596D-07   0.47944D-08   0.47944D-08

C               0.20000D 01   0.00000D 00                 0.11604D 00


T = 1000.00 K
P = 1.0000D 00 ATM

                  X*/MOL        Y/MOL         P/ATM         ACTIVITY
CH4             0.00000D 00   0.21691D-01   0.19797D-02   0.19797D-02
C2H4            0.00000D 00   0.10648D-07   0.97183D-09   0.97183D-09
C2H2            0.00000D 00   0.40658D-10   0.37108D-11   0.37108D-11
CO2             0.00000D 00   0.85274D 00   0.77829D-01   0.77829D-01
CO              0.00000D 00   0.11256D 01   0.10273D 00   0.10273D 00
O2              0.30000D 01   0.26103D-19   0.23824D-20   0.23824D-20
H2              0.90000D 01   0.57877D 01   0.52823D 00   0.52823D 00
H2O             0.00000D 00   0.31690D 01   0.28923D 00   0.28923D 00
C2H6            0.00000D 00   0.16405D-07   0.14973D-08   0.14973D-08

C               0.20000D 01   0.00000D 00                 0.71682D-01

STATEMENTS EXECUTED=    45339
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