CALCULATION OF COMPLEX CHEMICAL EQUILIBRIUM IN SYSTEMS CONTAINING ONE OR MORE CONDENSED PHASES

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CHAPTER 1

INTRODUCTION

1.1 APPLICATIONS OF CHEMICAL EQUILIBRIUM CALCULATIONS (3)

Chemical equilibrium is a condition which theoretically requires infinite reaction time to be achieved. Therefore, it is practically achieved only in case of reactions which approach equilibrium conditions in a period of time comparable with the time requirements for most of the industrial processes. Although that type of reaction is a small percentage of the total, equilibrium calculations are widely used as limiting conditions for design problems or analysis of experimental data, or as approximate solutions for non-equilibrium problems.

Examples of processes which can be solved by equilibrium calculations are gasification, combustion, waste conversion, hydrogen production, and generally, reactions at high temperature.

1.2 OBJECTIVES

The objectives of this work have been:

1) To derive and use the general technique of heterogeneous complex chemical equilibrium calculations based on free energy minimization as the core of a computer program which can be used to solve the majority of the chemical equilibrium problems.
2) To use this program in order to study the Sulphur-Hydrogen-Oxygen and Sulphur-Carbon-Oxygen systems.

The range of the temperature is from 200° to 400°C (the atmospheric boiling point for sulfur is 444.6°C), the range of the pressure from 1 to 10 atm, and elemental ratios vary from 0.01 to 100.00.

1.3 PHASE RULE (2,8)

The phase rule is a means of determining the number of intensive variables which must be specified, in order to fix all other intensive variables in every phase of a system in equilibrium.

The number of these variables (also called degrees of freedom of the system) is given by the phase rule (2):

$$F = C + 2 - P \tag{1.1}$$

where: F = degrees of freedom

C = components of the system in the sense of the phase rule

P = phases of the system

C is given by the formula:

$$C = N - R - S \tag{1.2}$$

where: N = actual number of components in the system

R = number of independent reactions of the system

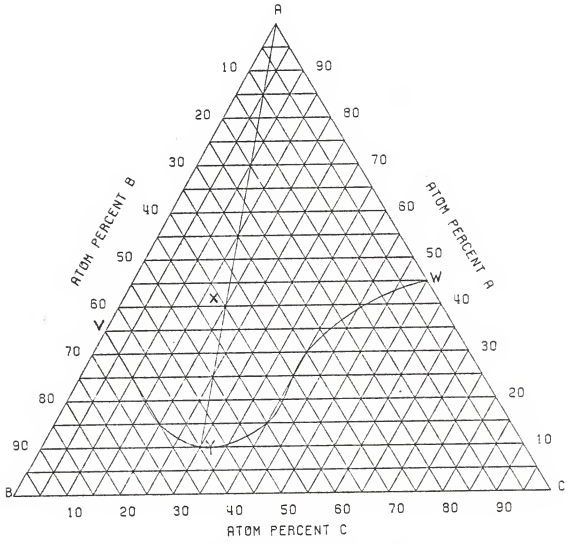
S = additional restrictions

C can also be calculated directly (8) as the rank of the matrix formed by the (N×E) elemental coefficients of the system components, where E is the number of elements in the system.

In the vast majority of cases, C = E.

1.4 TRIANGULAR DIAGRAMS AND DEPOSITION BOUNDARIES (9,3)

For the category of the systems with C = 3, and for a specified temperature and pressure, the stoichiometry of the system can be represented as a point on a set of triangular coordinates (see Graph-1). Since P usually varies from 1 to 3, the value of F varies from 2 to 4, which means that for a specified T and P, 0 to 2 elemental ratios are required to determine the equilibrium composition of the system.



GRAPH-1: TRIANGULAR DIAGRAM FOR A TERNARY SYSTEM

The variables used on this graph are the elemental fractions (%) of the system.

Every point on this graph represents a different composition for the system (in terms of elemental fractions), which composition can be found by drawing (from this particular point) lines parallel to the sides of the triangle differing by 120°, and reading the elemental fractions (%) on the intersection with the sides of the triangle (the sum of the elemental percentages should be 100.0). For example, the coordinates of point X are: (A,B,C) = (40,40,20).

Deposition boundaries are curves on this graph which divide the graph into regions where a condensed phase is or is not present.

For example, curve VYW may represent a deposition boundary of A for the A-B-C system. Above this curve a condensed phase of element A is present and none below it. To find the gas-phase equilibrium composition, a line is drawn connecting the point representing the initial mixture with the point representing the condensed phase under consideration. The intersection of this line with the deposition boundary is the point representing the gas-phase equilibrium composition.

For example, for point X (in relation with a condensed phase of the element A) the gas-phase equilibrium composition is given by point Y, as the intersection of the line AX with the deposition boundary VYW. The amount of the condensed phase A can be calculated using the lever rule, which gives: AX/XY/AY = g-atoms of gas-phase at equilibrium/ g-atoms of condensed phase at equilibrium/ g-atoms of the total equilibrium mixture.

1.5 METHODS OF EQUILIBRIUM CALCULATIONS (4)

There are two general methods of performing chemical equilibrium calculations in complex systems:

1) Solution of equilibrium and material balance equations by either reducing the equations to a single polynomial or by a trial and error method.

2) Minimization of the free energy of the system with material balance constraints.

In this study the latter method is used.

CHAPTER II

FREE ENERGY MINIMIZATION TECHNIQUE

2.1 FORMULATION OF THE PROBLEM

The total free energy of a system containing c chemical components can be written as:

$$G = \sum_{i=1}^{c} n_i \mu_i \tag{2.1}$$

$$\equiv \sum_{i=1}^{c} n_i (\mu_i^0 + RT \ln \hat{f}_i) \tag{2.2}$$

For non-gaseous components,

$$\mu_i = \mu_i^0 + v_{ci} (P-1) \tag{2.3}$$

Even at moderately high pressures, the product $v_{ci}(P-1)$ is small enough compared to μ_i^0 so that (2.3) can be written as:

$$\mu_i = \mu_i^0 \qquad i = 1, \ldots, s \tag{2.4}$$

where s = number of non-gaseous components.

Mohnot (3) calculated the relative error which is the result of the perfect gas-mixture assumption and found that for pressures up to 25 atm it was of the order of 0.1% for the abundant components. Therefore, the fugacity of a component in the system can be replaced by its partial pressure:

$$\hat{f}_i = f_i y_i = P \frac{n_i}{n} \tag{2.5}$$

where

$$n = \sum_{i=s+1}^{c} n_i \tag{2.6}$$

Equation (2.2) can now be written as:

$$g = \frac{G}{RT} = \sum_{i=1}^{s} n_i d_i + \sum_{i=s+1}^{c} n_i [c_i + \ln \frac{n_i}{n}] \tag{2.7}$$

where,

$$c_i = \frac{\mu_i^0}{RT} + \ln P \qquad i = s+1, \ldots, c \tag{2.8}$$

$$d_i = \frac{\mu_i^0}{RT} \qquad i = 1, \ldots, s \tag{2.9}$$

It can be easily shown (3) that the choice of reference state for the free energy data does not influence the equilibrium state of a system, though it changes the magnitude of the free energy of the system. Therefore, it is convenient to choose the elements in their standard states at the temperature of the system as the reference state.

The mass balance constraints can be described as:

$$\sum_{i=1}^{c} a_{ji} n_i = b_j \qquad j = 1, \ldots, m \tag{2.10}$$

where m = number of elements of the system.

In order to find the equilibrium composition of a system, at a certain temperature and pressure, and using the free energy minimization technique, the function $g = g(n_1, \ldots, n_c)$ given by (2.7) has to be minimized under the mass balance constraints given by (2.10).

2.2 DERIVATION OF THE LINEAR SYSTEM OF EQUATIONS USED (1,3)

In order to find the set of mole numbers, n_i, i = 1, ..., c which minimizes the function $g = g(n_1, \ldots, n_c)$ of equation (2.7), the function g is expanded in a Taylor series expansion, Lagrangian multipliers are introduced in order to incorporate the mass balance constraints (equation 2.10) into the objective function, and then the partial derivatives of the objective function with respect to the mole numbers n_i, i = 1, ..., c are equated to zero. This set of c-linear equations plus the set of m-mass balance constraint equations (2.10), which is also linear, represent a set of c+m linear equations, which after being reduced to a set of s+m linear

equations, and also including equation (2.6) for the total mole numbers of the system, can be solved by way of continuous iterations until the desired convergence is obtained.

At first, the function g is linearized by a Taylor series expansion about the v-th iteration, so that all resulting equations are linear.

$$g^{\nu+1} = g^{\nu} + \sum_{i=1}^{c} \Delta_i^{\nu} \left(\frac{\partial g}{\partial n_i}\right)^{\nu} + \frac{1}{2} \sum_{i=1}^{c} \sum_{\ell=1}^{c} \Delta_i^{\nu} \Delta_\ell^{\nu} \left(\frac{\partial^2 g}{\partial n_i \partial n_\ell}\right)^{\nu} \tag{2.11}$$

where

$$\Delta_i^{\nu} = n_i^{\nu+1} - n_i^{\nu} \tag{2.12}$$

The partial derivatives in (2.11) can be derived using (2.7) and remembering that c_i is a function of T and P and d_i is a function of T only. The superscript is removed temporarily for simplicity and generality of the expressions.

$$\frac{\partial g}{\partial n_i} = d_i \qquad i = 1, \ldots, s \tag{2.13}$$

$$\frac{\partial g}{\partial n_i \partial n_\ell} = 0 \qquad \text{when } i \leq s \text{ or } \ell \leq s \tag{2.14}$$

For $i = s + 1, \ldots, c$

$$\frac{\partial g}{\partial n_i} = \frac{\partial}{\partial n_i}\left[\sum_{k=s+1}^{c} n_k\left(c_k + \ln \frac{n_k}{n}\right)\right]$$

$$= \frac{\partial}{\partial n_i}\left[c_i n_i + n_i \ln n_i - n_i \ln n + \sum_{\substack{k=s+1 \\ k\neq i}}^{c} (c_k n_k + n_k \ln n_k - n_k \ln n)\right]$$

$$= c_i + \frac{n_i}{n_i} + \ln n_i - \ln n - \frac{n_i}{n} + \sum_{\substack{k=s+1 \\ k\neq i}}^{c} n_k\left(-\frac{1}{n}\right)$$

$$= c_i + \ln \frac{n_i}{n} + 1 - (n_i + \sum_{\substack{k=s+1 \\ k\neq i}}^{c} n_k)/n$$

$$= c_i + \ln \frac{n_i}{n} + 1 - 1 = c_i + \ln \frac{n_i}{n} = A_i \qquad (2.15)$$

$$\frac{\partial^2 g}{\partial n_i 2} = \frac{\partial A_i}{\partial n_i} = \frac{\partial}{\partial n_i} (c_i + \ln n_i - \ln n) = \frac{1}{n_i} - \frac{1}{n} \quad i = s+1, \ldots, c \qquad (2.16)$$

For $\ell = s+1, \ldots, c \qquad i = s+1, \ldots, c \qquad \ell \neq i$

$$\frac{\partial^2 g}{\partial n_i \partial n_\ell} = \frac{\partial}{\partial n_\ell} (c_i + \ln n_i - \ln n) = -\frac{1}{n} \qquad (2.17)$$

Using these expressions of second partial derivatives, the second order term in (2.11) becomes:

$$\sum_{i=1}^{c} \sum_{\ell=1}^{c} \Delta_i \Delta_\ell \frac{\partial^2 g}{\partial n_i \partial n_\ell} = \sum_{i=s+1}^{c} \sum_{\ell=s+1}^{c} \Delta_i \Delta_\ell \frac{\partial^2 g}{\partial n_i \partial n_\ell}$$

$$= \sum_{i=s+1}^{c} \Delta_i \left(\sum_{\ell=s+1}^{c} \Delta_\ell \frac{\Delta^2 g}{\partial n_i \partial n_\ell} \right)$$

$$= \sum_{i=s+1}^{c} \Delta_i \left[\Delta_i \left(\frac{1}{n_i} - \frac{1}{n}\right) + \sum_{\substack{\ell=s+1 \\ \ell\neq i}}^{c} \Delta_\ell \left(-\frac{1}{n}\right) \right]$$

$$= \sum_{i=s+1}^{c} \left[\frac{\Delta_i^2}{n_i} - \frac{\Delta_i}{n} \sum_{\ell=s+1}^{c} \Delta_\ell \right] = \sum_{i=s+1}^{c} \frac{\Delta_i^2}{n_i} - \frac{\Delta}{n} \sum_{i=s+1}^{c} \Delta_i$$

$$= \sum_{i=s+1}^{c} \frac{\Delta_i^2}{n_i} - \frac{\Delta^2}{n} \qquad (2.18)$$

Using equations (2.7), (2.13), (2.15) and (2.18), equation (2.11) can be written as:

$$g^{\nu+1} = \sum_{i=1}^{s} n_i^{\nu} d_i + \sum_{i=s+1}^{c} A_i^{\nu} n_i^{\nu} + \sum_{i=1}^{s} d_i \Delta_i^{\nu} + \sum_{i=s+1}^{c} A_i^{\nu} \Delta_i^{\nu} +$$

$$+\frac{1}{2}\left[\sum_{i=s+1}^{c}\frac{(\Delta_i^{\nu})^2}{n_i^{\nu}}-\frac{(\Delta^{\nu})^2}{n^{\nu}}\right] \tag{2.19}$$

Introducing Lagrangian multipliers to incorporate the mass balance constraints into the objective function, (2.19) can be written as:

$$F^{\nu+1}=g^{\nu+1}+\sum_{j=1}^{m}\pi_j\left(b_j-\sum_{i=1}^{c}a_{ji}n_i^{\nu+1}\right) \tag{2.20}$$

To minimize $F^{\nu+1}$, the conditions are:

$$\frac{\partial F^{\nu+1}}{\partial n_i^{\nu+1}}=0 \qquad i=1,\ \ldots,\ c \tag{2.21}$$

Therefore, performing this operation on equation (2.20) yields:

$$d_i-\sum_{j=1}^{m}\pi_j a_{ji}=0 \qquad i=1,\ \ldots,\ s \tag{2.22}$$

$$A_i^{\nu}+\frac{1}{2}\left(\frac{n_i^{\nu+1}}{n_i^{\nu}}-\frac{n^{\nu+1}}{n^{\nu}}\right)+\sum_{j=1}^{m}\pi_j a_{ji}=0 \qquad i=s+1,\ \ldots,\ c \tag{2.23}$$

And

$$\sum_{i=1}^{c}a_{ji}n_i^{\nu+1}=b_j \qquad j=1,\ \ldots,\ m \tag{2.24}$$

$$n^{\nu+1}=\sum_{i=s+1}^{c}n_i^{\nu+1} \tag{2.25}$$

Equations (2.22) to (2.25) form a system of c+1+m linear equations with c+1+m unknowns, which are:

$$n_i^{\nu+1} \qquad i=1,\ \ldots,\ c$$

$$n^{\nu+1}$$

$$\pi_j \qquad j=1,\ \ldots,\ m$$

This system can be reduced to a system of s+1+m linear equations with s+1+m unknowns, which are:

$n_i^{\nu+1}$ $\quad i = 1, \ldots, s$

$n^{\nu+1}$

$\pi_j \quad j = 1, \ldots, m$

Using equation (2.23) to solve for $n_i^{\nu+1}$ results in:

$$n_i^{\nu+1} = n_i^{\nu} \left(\frac{n^{\nu+1}}{n^{\nu}} + \sum_{j=1}^{m} \pi_j a_{ji} - A_i^{\nu}\right) \qquad i = s+1, \ldots, c \quad (2.26)$$

Summing these over all i = s+1, ..., c gives:

$$\sum_{i=s+1}^{c} n_i^{\nu} \left(\sum_{j=1}^{m} \pi_j a_{ji}\right) - \sum_{i=s+1}^{c} B_i^{\nu} = 0 \quad (2.27)$$

where:

$$B_i = n_i A_i = n_i(c_i + \ln \frac{n_i}{n}) \qquad i = s+1, \ldots, c \quad (2.28)$$

Multiplying equation (2.22) by n_i^{ν} and summing over i = 1, ..., s, gives:

$$\sum_{i=1}^{s} n_i^{\nu} d_i = \sum_{i=1}^{s} n_i^{\nu} \left(\sum_{j=1}^{m} \pi_j a_{ji}\right) = \sum_{j=1}^{m} \pi_j \sum_{i=1}^{s} a_{ji} n_i^{\nu} \quad (2.29)$$

Similarly, interchanging the order of summation of the first term in equation (2.27) gives,

$$\sum_{j=1}^{m} \pi_j \sum_{i=s+1}^{c} a_{ji} n_i^{\nu} - \sum_{i=s+1}^{c} B_i^{\nu} = 0 \quad (2.30)$$

By adding equations (2.29) and (2.30) and using equation (2.24) results in:

$$\sum_{i=1}^{s} n_i^{\nu} d_i = \sum_{j=1}^{m} \pi_j b_j - \sum_{i=s+1}^{c} B_i^{\nu} = 0 \quad (2.31)$$

Combining equation (2.26) with equation (2.24), produces:

$$\sum_{i=1}^{s} a_{ji} n_i^{\nu+1} + \sum_{i=s+1}^{c} a_{ji} \left(n_i^{\nu} \frac{n^{\nu+1}}{n^{\nu}} + n_i^{\nu} \sum_{\ell=1}^{m} \pi_\ell a_{\ell j} - n_i^{\nu} A_i^{\nu}\right)$$

$$= b_j \qquad j = 1, \ldots, m \quad (2.32)$$

Using equation (2.28) and defining

$$r_{j\ell} = \sum_{i=s+1}^{c} a_{ji} a_{\ell i} n_i^{\nu} , \tag{2.33}$$

equation (2.32) can be written as:

$$\sum_{i=1}^{s} a_{ji} n_i^{\nu+1} + \frac{n^{\nu+1}}{n^{\nu}} \sum_{i=s+1}^{c} a_{ji} n_i^{\nu} + \sum_{\ell=1}^{m} \pi_{\ell} r_{j\ell} =$$

$$= b_j + \sum_{i=s+1}^{c} a_{ji} B_i^{\nu} \qquad j = 1, \ldots, m \tag{2.34}$$

Equations (2.22) and (2.31) can be rearranged to contain the unknown terms on the left hand side:

$$\sum_{j=1}^{m} \pi_j a_{ji} = d_i \qquad i = 1, \ldots, s \tag{2.22a}$$

$$\sum_{j=1}^{m} \pi_j b_j = \sum_{i=1}^{s} n_i^{\nu} d_i + \sum_{i=s+1}^{c} B_i^{\nu} \tag{2.31a}$$

Equations (2.34), (2.22a) and (2.31a) form the desired linear system of s+1+m equations.

If an initial composition guess (satisfying the mass balance constraints) is available, the values of π_j, j = 1, ..., m; $n^{\nu+1}$; and $n_i^{\nu+1}$, i = 1, ..., s can be found from the s+1+m linear equations mentioned above. The equation (2.26) will provide the values of $n_i^{\nu+1}$, i = s+1, ..., c.

The new mole numbers n_i^{k+1} i = 1, ..., c can be used as the starting system for the next iteration, only if they are positive and convergence of the iterative scheme is guaranteed.

Let the computed changes in mole numbers, $\Delta_i = n_i^{\nu+1} - n_i^{\nu}$, be direction numbers which indicate the "best" direction of travel, but

not necessarily the "best" length of travel. The distance traveled should be restricted to the maximum possible fraction of the calculated travel, such that:

(1) All $n_i^{\nu+1}$ are positive, and

(2) $\frac{\partial g}{\partial \lambda}$ does not become positive, that is, the minimum is not passed.

In order to derive the expression for $\frac{\partial g}{\partial \lambda}$, equation (2.7) for the $\nu+1$ iteration, can be rewritten in terms of the ν-th iteration and λ, as:

$$g^{\nu+1} = \sum_{i=1}^{s} d_i(n_i^{\nu} + \lambda\Delta_i) + \sum_{i=s+1}^{c} [c_i(n_i^{\nu} + \lambda\Delta_i) + (n_i^{\nu} + \lambda\Delta_i) \ln \frac{n_i^{\nu} + \lambda\Delta_i}{n^{\nu} + \lambda\Delta}]$$

Differentiating with respect to λ gives,

$$\frac{\partial g^{\nu+1}}{\partial \lambda} = \sum_{i=1}^{s} d_i\Delta_i + \sum_{i=s+1}^{c} [c_i\Delta_i + \Delta_i \ln \frac{n_i^{\nu} + \lambda\Delta_i}{n^{\nu} + \lambda\Delta} + (n_i^{\nu} + \lambda\Delta_i)(\frac{\Delta_i}{n_i^{\nu} + \lambda\Delta_i} - \frac{\Delta}{n^{\nu} + \lambda\Delta})] \qquad (2.35)$$

But the last term in equation (2.35) can be written as:

$$\sum_{i=s+1}^{c} (n_i^{\nu} + \lambda\Delta_i)(\frac{\Delta_i}{n_i^{\nu} + \lambda\Delta_i} - \frac{\Delta}{n^{\nu} + \lambda\Delta}) = \sum_{i=s+1}^{c} \Delta_i - \frac{\Delta}{n^{\nu} + \lambda\Delta} \sum_{i=s+1}^{c} (n_i^{\nu} + \lambda\Delta_i)$$

$$= \Delta - \frac{\Delta}{n^{\nu} + \lambda\Delta} (n^{\nu} + \lambda\Delta) = \Delta - \Delta = 0$$

Therefore:

$$\frac{\partial g}{\partial \lambda} = \sum_{i=1}^{s} d_i \Delta_i + \sum_{i=s+1}^{c} \Delta_i \left(c_i + \ln \frac{n_i^{\nu} + \lambda \Delta_i}{n^{\nu} + \lambda \Delta}\right) \tag{2.36}$$

where

$$n_i^{\nu+1} = n_i^{\nu} + \lambda \Delta_i \qquad i = 1, \ldots, c \tag{2.37}$$

It should be noted that the mass balance constraints are satisfied independently of the values of λ, since if n_i^{ν} and $n_i^{\nu+1}$ satisfy the constraints separately, a linear combination of them

$$= n_i^{\nu} + \lambda(n_i^{\nu+1} - n_i^{\nu}) = (1-\lambda) n_i^{\nu} + \lambda n_i^{\nu+1}$$

will also satisfy those constraints.

More details about the requirements that all n_i's are positive and the derivative $\frac{\partial g}{\partial \lambda}$ negative, are given in Chapter 3.

Although equations (2.21) cannot be used directly to compute the equilibrium mole numbers, they can, however, be used to obtain a good estimate of the mole number of any trace gaseous species.

Since equation (2.20) can be written as:

$$F = g + \sum_{j=1}^{m} \pi_j \left(b_j - \sum_{i=1}^{c+Fl} a_{ji} n_i\right) \tag{2.38}$$

where

$$g = \sum_{i=1}^{s} n_i d_i + \sum_{i=s+1}^{c+Fl} n_i \left(c_i + \ln \frac{n_i}{n}\right) \tag{2.39}$$

and Fl = number of trace gaseous species, the condition $\frac{\partial F}{\partial n_i} = 0$, i = c+1, . . ., c+Fl provides:

$$c_i + \ln \frac{n_i}{n} + n_i \frac{\partial}{\partial n_i} \ln n_i + \sum_{i=s+1}^{c+Fl} n_i \frac{\partial}{\partial n_i} (-\ln n) - \sum_{j=1}^{M} \pi_j a_{ji} = 0$$

or $$c_i + \ln \frac{n_i}{n} + 1 - 1 - \sum_{j=1}^{M} \pi_j a_{ji} = 0$$

or $$n_i = n \exp\left(\sum_{j=1}^{M} \pi_j a_{ji} - c_i\right) \tag{2.40}$$

CHAPTER III

COMPUTER PROGRAM

3.1 GENERAL INFORMATION

The final form of the program used is given on pages 21 through 29. It consists of three routines:

1. The main routine or MAIN (pages 21 to 26).
2. The subroutine JF (page 27).
3. The subroutine JF1 (pages 28 to 29).

In subroutine JF1, several Calcomp subroutines are used after slight modification, so that they can be used in the KSU Computing Center Calcomp (model 663) incremental drum plotter. These subroutines are called by means of a CALL statement as for regular FORTRAN subroutines.

This program can calculate the equilibrium composition of any system which has:

(1) Degrees of freedom ≥ 2

(2) No condensed components which contain an element nonexistent in the gaseous components when $C > S + M - 1$. If condition (1) is not satisfied the problem cannot be solved. If condition (1) is satisfied but condition (2) is not, then in order to solve the problem, a ficticious gaseous component has to be introduced, containing the element of condition (2) and having a highly positive free energy value.

Some statements of the program are not the same for all systems which can be solved using this program. Those are statements #35, 38, 55, 57, 220, 223, 227, 229 in the main program, and statements #25 through #33 in the subroutine JF1. Those statements are related to the representation of the results, and in order to make the program as compact as possible, they

are unique for every system under consideration. For example statements #35 and #38 print the titles for the tables of the results presented in Chapter IV and they are different for every system under consideration.

A compact flow chart is given on page 22.

3.2 MAIN ROUTINE

There are 9 READ statements in the main routine:

1. Statement #11 reads C,M,S,F1,ITMAX,W,Y,Z, where:
   C = number of components in the system
   M = number of elements in the system
   S = number of non-gaseous components in the system
   F1 = number of trace components in the system to be calculated
   ITMAX = max number of iterations permitted
   W = number of temperatures to be used
   Y = number of elemental ratios to be used
   Z = number of pressures to be used
2. Statement #20 reads the atomic species coefficient matrix ((A(J,I), J = 1,M), I = 1,C) where rows are the elements and columns the components of the system. The first S columns must contain all the non-gaseous components, and the last M columns must contain a set of components such that they contain all elements of the system.
3. Statement #25 reads the atomic species coefficient matrix ((A(I,J), I = 1,M), J = c+1, C+F1) of the trace components to be considered, where rows are the elements and columns are the components. This statement is executed only if F1 $\neq$ 0.
4. Statement #30 reads the pressure P of the system.
5. Statement #40 reads the temperature T of the system.

6. Statement #42 reads the free energy values (G(I), I = 1,C) of the components of the system at the temperature of statement #40, and in the same order of components as in statement #20.
7. Statement #45 reads the free energy values (G1(I), I = 1,F1) of the trace components to be considered at the temperature of statement #40, and in the same order of components as in statement #25.
8. Statement #52 reads the input mole numbers (NN(I), I = 1,C) of the system in the same order of components as in statements #20 and 42.
9. Statement #59 reads the initial guesses for the mole numbers of the first C-M components of the system in the same order of components as in statements #20, 42 and 52 (for the first C-M components), which guesses will be used to calculate initial guesses for the remaining M mole numbers using the atomic mass balance equations. These C-M-M=C guesses will be used to start the iterative scheme. Special attention should be given to the mole numbers read by this statement, because they must be such that the remaining M mole numbers to be calculated are all positive. Setting all C-M mole numbers equal to a number 100 to 1000 times less than the magnitude of the smallest number in statement #52 usually satisfies the above requirement, but in some cases an analysis is required in order to find the appropriate values.

The rest of the main routine includes:

1. Calculation of the last M initial guesses, statements #61-78.
2. Loading the matrix of the linear system of equations (2.34), (2.22a), (2.31a), and calculating the new mole numbers, statements #80-126.

3. Satisfying conditions requiring all mole numbers to be positive and $\frac{\partial g}{\partial \lambda}$ negative, statements #127-140 and #141-171.
4. Check for convergence and maximum number of iterations permitted, statements #184-194.
5. Calculation of mole numbers of the trace components to be considered, statements #201-213.
6. Calculation of the points to be used for plotting, statements #229-241.

The number of cards and the execution time depend heavily on the values of z,w,v in the three main DO-loops (statements #28, 32, 51).

3.3 SUBROUTINES JF AND JF1

3.3.1 Subroutine JF

Subroutine JF is a standard subroutine to solve a system of linear equations using the Gauss elimination method (10).

It uses an input of the system's matrix, the constants' column and the number of equations to be solved and returns to the main routine the solution column. It is used twice in the main routine, in statement #73 to calculate the last M mole number initial guesses and in statement #115 to calculate the new mole number for the non-gaseous components and the Lagrangian multipliers.

3.3.2 Subroutine JF1

This subroutine uses the points (X1,YY) calculated in statements #240 and 241 of the main routine to plot one or more curves on a triangular diagram. Statements #5-23 plot the triangle, statements #24-43 plot all titles and scales on the diagram and statements #44-57 plot the curves.

The Calcomp subroutines used are:

a) PLOT (A,B,C), which moves the pen to the point (A,B) from its previous position, with pen down or up for C=+2,+3 respectively, or relocates the origin at the same time for C=+22,+23.

b) SYMBOL (A,B,C,D,E,F), which draws text such as titles, captions and legends.

(A,B) are the coordinates of the lower left hand side of the first character to be produced.

C is the height, in inches, of the character string to be plotted.

D is the text to be plotted.

E is the angle, in degrees from the X-axis, at which the annotation is to be plotted.

F is the number of characters to be plotted.

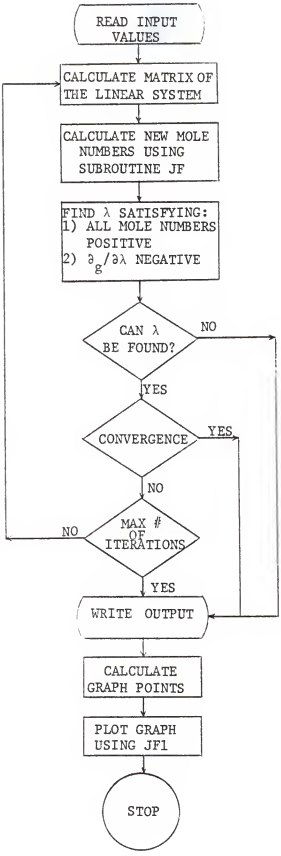
c) NUMBER (A,B,C,D,E,F)

A,B,C,E are the same as in b).

D is the floating-point number to be converted and plotted.

F controls the precision of the conversion of the number D. If F > 0 it specifies the number of digits to the right of the decimal point that are to be converted and plotted. If F=0 only the integer part and the decimal point of the number are plotted, if F=-1 only the integer part is plotted and if F < -1, F-1 digits are truncated from the integer portion after rounding.

d) SMOOTH (A,B,C), which draws a smooth curve through a set of data points (A,B). A certain number of calls on this subroutine are needed before a curve can be computed. The curve starts from the point with C = 0,1 for an open or closed curve respectively, continues through the points with C = 2,3 with pen down or up respectively and closes the curve at the point with C = 24.



FLOW CHART OF THE COMPUTER PROGRAM USED FOR THE EQUILIBRIUM CALCULATIONS

```
                C       THIS IS A PROGRAM TO CALCULATE THE EQUILIBRIUM COMPOSITION OF ANY INITIAL
                C       MIXTURE CONTAINING UP TO 25 COMPOUNDS AND 15 ELEMENTS
                C       THE ONLY PROBLEM THIS PROGRAM CANNOT SOLVE, IS THE CASE WHEN:
                C       1) A NON GASEOUS COMPOUNT CONTAINS AN ELEMENT NON-EXISTENT IN THE OTHER
                C       COMPOUNTS   21  C=S+M-1
                C       TO SOLVE THAT KIND OF PROBLEMS, ADD A FICTICIOUS GASEOUS COMPOUNT
                C       CONTAINING THIS ELEMENT, AND HAVING A HIGHLY POSITIVE G-VALUE
0001                    INTEGER C,M,S,I,SI,CM,Q,A(15,25),FI,C1,CFI,W,V,WW,Z
0002                    REAL N,NN,IAM,MI,NT,LL
0003                    LOGICAL CHECK
0004                    DIMENSION NM(25),G(25),DEL(25),DFOE(25),XX(25),GRT(25),POEL(20),
                       1P1(25),B(25),AA(20,20),CC(20),N(25),GRTT(25),FN(2C),PM(2C),FFL(5)
                       1,G1(15),GP12(15),TX(15),XF(25),XI(30),YY(15C),BUFF(4CQ0)
0005                    COMMON /AREA1/XI,YY,W,V,DWF,JJJ
0006                    COMMCN /AREA2/Q,AA,CC
0007                    CALL PLOTS (BUFF,4000)
0008                    CALL PLOT (0.,-11.,-3)
0009                    CALL PLOT (3.,3.,-3)
0010                    DATA R/1.9872/,KK/0/,PLAM/2./,DELTAI/0.01/,DELTA/0.005/,NT/0./
                C       INPUT DATA
0011                 10 READ (5,20) C,M,S,FI,ITMAX,W,V,Z
0012                 20 FORMAT (8I4)
0013                    WW=W+V
0014                    SI=S+1
0015                    MI=M+1
0016                    MS=M+S
0017                    MSI=MS+1
0018                    MS2=M+S+2
0019                    CM=C-M
                C       COEFFICIENT MATRIX
                C       ROWS ARE THE ELEMENTS AND COLUMNS THE COMPONENTS
                C       THE FIRST S COLUMNS MUST CONTAIN ALL THE NON-GASEOUS COMPONENTS
                C       AND THE LAST M COLUMNS MUST CONTAIN THE COMPONENTS WHOSE INITIAL GUESS-
                C       MOLE NUMBERS ARE TO BE CALCULATED, AND WHICH MUST CONTAIN ALL ELEMENTS OF
                C       THE SYSTEM
                C       THE SAME ORDER OF COLUMNS MUST BE USED FOR THE REST OF THE INPUT DATA
0020                 29 READ (5,30) ((A(J,I),J=1,MI),I=1,C1
0021                 30 FORMAT (8E10.1)
0022                    IF (FI.EQ.0.) GO TO 32
0023                    CFI=C+FI
0024                    C1=C+1
0025                    READ (5,702) ((A(I,J),I=1,MI),J=C1,CFI)
0026                 702 FORMAT (8E10.1)
0027                 32 CONTINUE
0028                    DO 1999 IJ=1,Z
0029                    L5=0
0030                    READ (5,231 P
0031                 23 FORMAT (F6.1)
0032                    DO 1999 JJ=1,W
0033                    IF (JJJ.EQ.1) GO TO 1010
0034                    WRITE (6,999)
0035                 999 FORMAT ('1',1X,2X,'S/O',6X,'S2',7X,'S3',7X,'S4',7X,'S5',7X,'S6',7X
                       1,'S7',7X,'S8',7X,'CO',7X,'COS',6X,'CO2',6X,'SO2',6X,'CS2'I
0036                    GO TO 1011
0037                1010 WRITE (6,777)
0038                 777 FORMAT ('1',1X,'EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O
                       1 SYSTEM'
                       1       /1X,'TABLE-17' P=5 ATM,T=673 K'//1X,2X,'C/O',6X,'S2',6X,
```

```
                1*S3',7X,*S4',7X,*S5',7X,*S6',7X,*S7',7X,*S8',7X,*CO' ,7X,*COS',6X,
               1*CO2',6X,*SC2',6X,*CS2')
0039          1011 CONTINUE
0040               READ (5,22) T
0041            22 FORMAT (1A)
                C     G VALUES
0042               READ (5,60) (G(I),I=1,C)
0043            60 FORMAT (8E10.3)
0044               IF (II.EQ.0.) GO TO 63
0045               READ (5,703) (G1(I),I=1,F1)
0046           703 FORMAT (8E10.3)
0047            63 CONTINUE
0048               DO 61 I=1,C
0049               GAT(I)=G(I)/(R*T)
0050            61 GAT1(I)=G1(I)/(R*T)
0051               DO 1999 I=1,V
                C     INLET AMOUNTS
0052               READ (5,40) (ANI(I),I=1,C)
0053            40 FORMAT  (8E10.4)
0054               IF (JJ.EQ.2) GO TO 44
0055               CK=ANI(1)/(2*ANI(5))
0056               GO TO 45
0057            44 SO=ANI(2)/ANI(6)
0058            45 CONTINUE
                C     INITIAL COMPOSITION GUESSES
                C     INITIAL GUESSES OF  NI(I) MUST SATISFY MATERIAL BALANCES
                C     THEREFORE, C-M  NI(I)'S MAY BE CHOSEN AND THE REST M  NI(I)'S MUST BE
                C      CALCULATED SO THAT THE MATERIAL BALANCES ARE SATISFIED
                C     TAKE CARE OF: 1) THE CALCULATED  NI(I)'S CONTAIN ALL ATOM SPECIES
                C     2) THE CHOSEN  NI(I)'S DO NOT EXCEED INLET AMOUNTS
0059               READ (5,41) (NI(I),I=1,CM)
0060            41 FORMAT (10E7.3)
0061               DO 100 J=1,M
0062               B(J)=0.0
0063               DO 100 I=1,C
0064           100 B(J)=B(J)+A(J,I)*ANI(I)
0065               DO 49 I=1,M
0066               DO 49 J=1,M
0067            49 AA(I,J)=A(I,C-M+J)
0068               DO 51 I=1,M
0069               CC(I)=B(I)
0070               DO 51 J=1,CM
0071            51 CC(I)=CC(I)-A(I,J)*NI(J)
0072               C=M
                C     CALCULATION OF LAST M-INITIAL MOLE GUESSES
0073               CALL JF(XX)
0074               DO 52 I=1,M
0075            52  NI(C+I)=XX(I)
0076               NT=0.
0077               DO 50 I=1,C
0078            50 NT=NT+NI(I)
                C     BEGIN EVALUATION OF NEW COMPOSITION
0079           220 JJ=1
                C     LOAD THE COEFFICIENT MATRIX (M*S+1,M*S+1) AND THE CONSTANTS,COLUMN
                C    1(M*S+1),11
0080           235 DO 230 J=1,M
0081               DO 230 L=1,M
0082               AA(J,L)=0.0
```

```
0083              DO 230 J=S1,C
                C     ROWS 1 TO M,COLUMNS 1TO M
0084               230  AA(J,L)=AA(J,L)+A(J,I)*A(L,I)*N(I)
0085              DO 270 J=1,M
0086              CC(J)=B(J)
0087              IF (S.EQ.0.) GO TO 261
0088              DO 260 I=1,S
                C     ROWS 1TO M, COLUMNS 1 TO S
0089               260  AA(J,I+M)=A(J,I)
0090               261  AA(J,M+S+1)=0.0
0091              DO 270 I=S1,C
                C     CONSTANTS, COLUMN ,ROWS 1 TO M
0092                    CC(J)=CC(J)+A(J,I)*N(I)*(GRT1(I)*ALOG(P(I))/RT))
                C     ROWS 1 TO M, COLUMN M+S+1
0093               270  AA(J,M+S+1)=AA(J,M+S+1)+A(J,I)*N(I)/RT
0094              IF (S.EQ.0.) GO TO 281
0095              DO 280 L=M1,MS
0096              DO 275 K=1,M
                C     ROWS M+1 TO M+S, COLUMNS 1 TO M
0097               275  AA(L,K)=A(K,L-M)
0098              DO 278 K=M1,MS)
                C     ROWS M+1 TO M+S, COLUMNS M+1 TO M+S+1
0099               278  AA(L,K)=0.0
                C     CONSTANTS, COLUMN, ROWS M+1 TO M+S
0100               280  CC(L)=GRT1(L-M)
0101               281  DO 290 K=1,M
                C     ROW M+S+1, COLUMNS 1 TO M
0102               290  AA(M+S+1,K)=B(K)
0103              IF (S.EQ.0.) GO TO 301
0104              DO 300 K=M1,MS
                C     ROW M+S+1, COLUMNS M+1 TO M+S
0105               300  AA(M+S+1,K)=0.0
                C     ROW M+S+1 , COLUMN M+S+1
0106               301  AA(M+S+1,M+S+1)=0
0107              L=M+S+1
0108              CC(L)=0.0
0109              IF (S.EQ.0.) GO TO 311
0110              DO 310 K=1,S
0111               310  CC(L)=CC(L)+N(K)*GRT(K)
0112               311  DO 320 K=S1,C
                C     CONSTANTS, COLUMN, ROW M+S+1
0113               320  CC(L)=CC(L)+N(K)*(GRT1(K)*ALOG(N(K)/NT))
                C     INVERT THE MATRIX AND SOLVE FOR P1,S, NT, AND SOLID NEIL,S
0114              S=MS)
0115              CALL JF(XX)
0116              DO 340 K=1,M
0117               340  P(K)=XX(K)
0118              IF (S.EQ.0.) GO TO 361
0119              DO 360 K=M1,MS
0120               360  NN(K-M)=XX(K)
0121               361  NNT=XX(M+S+1)
                C     DETERMINE NEW GASEOUS MOLE NUMBERS
0122              DO 380 I=S1,C
0123              SUM=0.0
0124              DO 370 J=1,M
0125               370  SUM=SUM+P(I)*A(J,I)
0126               380  NN(I)=N(I)*(NNT/NT+SUM-GRT1(I)-ALOG(N(I)/NT))
                C     FIND MAX LAMBDA FOR CONDITION 1-ALL MOLE NUMBERS POSITIVE
```

```
0127            DO 400 I=1,6
0128          400 DELI(I)=NN(I)-NI(I)
0129            DELT=NNT-NT
0130            LAM=1.0
0131            LL=1.0
0132            DO 420 I=1,6
0133            IF (NN(I).GE.0.0) GO TO 420
0134            LL=(NI(I)*0.99999/(NI(I)-NN(I)))
0135            IF (LL.LT.LAM) LAM=LL
0136          420 CONTINUE
0137            IF(NNT.GE.0.0) GO TO 92
0138            LL=(NT*0.99999/(NT-NNT))
0139            IF (LL.LT.LAM) LAM=LL
0140           92 IF (LAM.LT.0.0001) GO TO 102
0141        C     FIND MAX LAMBDA FOR CONDITION 2-DERIVATIVE NEGATIVE
0142            DFDLI101=0.
0143            IF (S.EQ.0) GO TO 401
0144            DO 402 I=1,6
0145          402 DFDLI101=DFDLI(I0)+DELI(I)*GRI(I)
0146          401 CO  403 I=S1,6
0147          403 DFDLI101=DFDLI(I0)+DELI(I)*(GRI(I)+ALOG((NI(I)+LAM*DELI(I))/(NT+DELT*LAM)))
                  (LAM))
0148            IF (DFDLI101.LT.0.) GO TO 555
0149            DO 520 L=1,9
0150            LL=LAM-11.-0.10*L)
0151            DFDL(L)=0.0
0152            IF (S.EQ.0.) GO TO 511
0153            DO 510 I=1,S
0154          510 DFDL(L)=DFDL(L)+DEL(I)*GRI(I)
0155          511 DO 520 I=S1,6
0156          520  DFDLI(L)=DFDL(L)+DELI(I)*(GRI(I)+ALOG1(NI(I)+LL*DELI(I))/(NT+DELT*LL)))
                  ))
0157            DO 530 L=1,9
0158            LI=L
0159            IF (DFDL(L).LE.0.01 GO TO 552
0160          530 CONTINUE
0161            GO TO 560
0162          552 LAM=LAM*11.-0.10*L))
0163            IF (LAM.LT.0.0001) GO TO 102
0164            GO TO 555
0165        C     IF NO LAMBDA CAN BE FOUND ,DECREASE LAMBDA OF PREVIOUS ITERATION
0166        C     BY 10% AND REPEAT CALCULATION
0167          560 KK=KK+1
0168            IF (PLAM.EQ.2.0) GO TO 591
0169            IF (KK.EQ.10) GO TO 102
0170            PPLAM=11.-0.10*KK)*PLAM
0171            DO 572 I=1,6
0172          572 NI(I)=(NI(I))+PPLAM*DELI(I)
0173            NT=(NT+PPLAM*DELT
0174            GO TO 235
0175        C     STORE N(I),NT,DELI(I),LAM,DELT OF PREVIOUS ITERATION FOR POSSIBLE  USE
0176          555 DO 571 I=1,6
0177          571 PNI(I)=NI(I)
0178            PNT=NT
0179            DO 601 I=1,6
0180          601 PDELI(I)=DELI(I)
0181            PLAM=LAM
0182            PDELT=DELT
```

```
                C     DOWN TO THIS POINT NI(I),NI ARE THE OLD MOLE NUMBERS AND NN(I),NNT THE NEW
0179                  DO 570 I=1,C
0180              570 NE(I)=NE(I)+LZM*DEL(I)
0181                  NT=NT+LAM*DELT
0182                  IT=IT+1
0183                  KK=0
                C     CHECK FOR CONVERGENCE
0184                  CHECK=.TRUE.
0185                  DO 620 I=1,C
0186                  IF (NE(I).LT.0.01) GO TO 618
0187                  IF (ABS(DEL(I)/NE(I)).GT.DELTA) GO TO 619
0188                  GO TO 620
0189              618 IF (ABS(DEL(I))/NE(I).LT.DELTA) GO TO 620
0190              619 CHECK=.FALSE.
0191              620 CONTINUE
0192                  IF (ABS(DELT/NT).GT.DELTA) CHECK=.FALSE.
0193                  IF (CHECK) GO TO 102
0194                  IF (IT.LT.ITMAX) GO TO 235
0195              102 CONTINUE
0196                  IF (KK.NE.10) GO TO 11
0197                  DO 4 I=1,C
0198              4   NE(I)=EN(I)+LAM*DEL(I)
0199                  NT=EN(I)+LAM*DELT
0200              11  CONTINUE
0201                  TN=0.
0202                  DO 101 I=S1,C
0203              101 TN=TN+NE(I)
0204                  DO 104 I=S1,C
0205              104 PM(I)=NE(I)/TN
                C     CALCULATION OF TRACE COMPONENTS DENOTED AS FI
0206                  IF (FI.EQ.0.) GO TO 435
0207                  DO 701 I=1,FI
0208              701 FF(I)=0
0209                  DO 705 I=1,FI
0210              705 GR12(I)=G1II(I)/(R*T))*ALOG(P)
0211                  DO 706 I=1,FI
0212                  DO 707 J=1,M
0213              707 FF(I)=FF(I)+A(J,I)*C)*P(J)
0214              706 TX(I)=EXP(FF(I)-GR12(I))
0215                  DO 709 I=1,FI
0216              709 TXTF(I)=TX(I)*NT
0217                  DO 708 I=1,FI
0218              708 TN=TN+TX(F(I)
0219                  IF (J.EQ.2) GO TO 1001
0220                  WRITE (6,432) CO,  (TX(I),I=1,FI),(PM(I),I=S1,C)
0221              432 FORMAT (1X,F6.2,3X,      1512X,F7.5))
0222                  GO TO 1002
0223             1001 WRITE (6,432) SO,  (TX(I),I=1,FI),(PM(I),I=S1,C)
0224             1002 CONTINUE
0225                  GO TO 434
0226              435 IF(J.EQ.2) GO TO 1003
0227                  WRITE (6,432) CO,(PM(I),I=S1,C)
0228                  GO TO 434
0229             1003 WRITE (6,432) SO,(PM(I),I=S1,C)
0230              434   TNF=TN/NT
0231                  IF (ABS(TNF-1.).LT.0.10) GO TO 2
0232                  GO TO 504
0233                2 CONTINUE
```

```
                C       CALCULATE THE ELEMENTAL FRACTIONS
0234                    DO 710 I=1,M
0235              710   XF(I)=0.
0236                    DO 711 I=1,M
0237                    DO 711 J=S1,C
0238              711   XF(I)=XF(I)+A(I,J)*PP(J)
0239                    XFT=0.
0240                    DO 712 I=1,M
0241              712   XFT=XFT+XF(I)
0242                    DO 713 I=1,M
0243              713   XF(I)=XF(I)/XFT
                C       ACCUMULATE DATA POINTS--PRIMARY SYSTEM CASE
0244                    LS=LS+1
0245                    X(LS)=6.5*(XF(3)+XF(1)*COS(1.047211
0246                    YY(LS)=XF(1)*SIN(1.04721*6.5
0247                    IF (LS.LT.WW) GO TO 1999
0248                    WRITE (6,433)
0249              433   FORMAT ('1')
0250                    WRITE (6,888) (X(I),I=1,WW),(YY(I),I=1,WW)
0251              888   FORMAT (1X,11(1X,E10.4))
0252                    CALL JET
0253             1999   CONTINUE
0254                    GO TO 593
0255              591   WRITE (6,5921
0256              592   FORMAT (1X,'***WARNING***  NO LAMBDA CAN BE FOUND'1
0257                    GO TO 593
0258              594   WRITE (6,595) INF
0259              595   FORMAT (1X,'***WARNING***  INF=',F4.2)
0260              593   CALL PLOT (0.,0.,999)
0261                    STOP
0262                    END
```

```
0001            SUBROUTINE JF(XX)
                C       THIS IS A SUBROUTINE TO SOLVE A LINEAR SYSTEM OF EQUATIONS
                C       IT IS GENERAL AND CAN BE USED  AT ANY POINT OF THE PROGRAM
                C       ITS INPUT IS THE MATRIX AA, Q=THE NUMBER OF ECUATIONS AND CC=THE CONSTANTS
                C       COLUMN,  XX=THE SOLUTION
0002            DIMENSION Y(251,XX125),FF125,201,AA12C,2C),CC(201
0003            INTEGER Q,E,D
0004            COMMON /AREA2/C,AA,CC
0005            D=C()
0006            E=Q-1
0007            DO 17 I=1,Q
0008          17 AA(I,D1=CC(I)
0009            MM=D
0010            NN1=E
0011            DO 1000 I=1,Q
0012            DO 1000 J=1,D
0013       1000 FF(I,J)=AA(I,J)
                C       DETERMINE THE ROW POSITION OF THE DESIRED PIVOT
0014            DO 800 II=1,NN1
0015            II1=II+1
0016            DO 16 I=II,Q
0017          16 Y(II)=ABS(FF(I,II))
0018            KK=0
0019            IR=Y(II)
0020            DO 13 I=III,Q
0021            IF (Y(II)-IR) 11,11,12
0022          12 IR=Y(II)
0023            KK=I
0024          11 CONTINUE
                C       INTERCHANGE ROWS TO PROPERLY PLACE PIVOT
0025            IF (KK) 13,14,13
0026          13 DO 15 I=II,MM
0027            STORE=FF(KK,I)
0028            FF(KK,I)=FF(II,I)
0029          15 FF(II,I)=STORE
                C       PERFORM THE ELIMINATION PROCESS
0030          14 K=II+1
0031            DO 800 K=K,C
0032            DO 800 J=K,MM
0033       800 FF(I,J)=FF(I,J)-FF(I,K-1)*FF(K-1,J)/FF(K-1,K-1)
                C       BACK-SUBSTITUTE TO DETERMINE THE SOLUTION SET
0034            XX(Q)=FF(Q,MM)/FF(Q,Q)
0035            DO 86 K=2,Q
0036            J=MM-K
0037            L=J+1
0038            XX(J)=0
0039            DO 87 I=L,Q
0040          87 XX(J)=XX(J)+FF(J,I)*XX(I)
0041          86 XX(J)=(FF(J,MM)-XX(J))/FF(J,J)
0042            RETURN
0043            END
```

```
0001            SUBROUTINE JF1
                C     THIS IS A SUBROUTINE TO PREPARE THE TRIANGULAR GRAPH AND PLOT A SMOOTH
                C     CURVE THROUGH THE DATA POINTS--ALL THIS IN THE CASE OF A TRINARY SYSTEM
0002                  DIMENSION BUFF(40000),X(40),Y(20),X1(150),YY(150)
0003                  INTEGER W,V,V1,W1,L(9)
0004                  COMMON /AREA1/X1,YY,W,V,BUFF,JJJ
0005                  DO 1 I=1,20
0006                1 Y(I)=16.545*(ALOG(.04721/20)*I
0007                  DO 2 I=1,40
0008                2 X(I)=(6.5/40)*I
                C     PLOT TRIANGLE
0009                  DO 9 I=1,40,2
0010                  CALL PLOT (X(I),Y(I),2)
0011                  CALL PLOT (X(I+1),0.,2)
0012                9 CONTINUE
0013                  CALL PLOT (0.,0.,2)
0014                  CALL PLOT (X(1),Y(1),3)
0015                  DO 3 K=2,20
0016                  KK=40-K
0017                  DO 4 I=K,KK,2
0018                  CALL PLOT (X(I),Y(K),2)
0019                  CALL PLOT (X(I+1),Y(K-1),2)
0020                4 CONTINUE
0021                  CALL PLOT (X(K-1),Y(K-1),2)
0022                  CALL PLOT (X(K),Y(K),3)
0023                3 CONTINUE
                C     PLOT TITLES
0024                  H=0.105
0025                  CALL SYMBOL (X(20),+5.75,H,'S',0.,1)
0026                  CALL SYMBOL (X(30),Y(15),H,'ATOM PERCENT S',-60.,14)
0027                  CALL SYMBOL (+6.6,0.,H,'O',0.,1)
0028                  CALL SYMBOL (X(16),-0.5,H,'ATOM PERCENT O',0.,14)
0029                  CALL SYMBOL (-0.1,0.,H,'C',0.,1)
0030                  CALL SYMBOL (X(5),Y(9),H,'ATOM PERCENT C',60.,14)
0031                  CALL SYMBOL (0.,Y(20),H,'FIGURE-17',0.,9)
0032                  CALL SYMBOL (0.,Y(19),H,'P=5 AT',0.,6)
0033                  CALL SYMBOL (0.,Y(18),H,'T=613 K',0.,7)
0034                  L(1)=10
0035                  DO 5 I=2,9
0036                5 L(I)=L(I-1)*10
0037                  DO 6 I=1,H
0038                6 CALL NUMBER (X(18-2*I),Y(20-2*I),H,FLOAT(L(I)),0.,-1)
0039                  CALL NUMBER (0.,Y(2),H,FLOAT(L(9)),0.,-1
0040                  DO 7 I=1,9
0041                7 CALL NUMBER (X(49*I),-0.25,H,FLOAT(L(I)),0.,-1)
0042                  DO 8 I=1,9
0043                8 CALL NUMBER (X(41-2*I),Y(2*I),H,FLOAT(L(I)),0.,-1)
                C     PLOT CURVE
0044               23 CONTINUE
0045                  V1=V-1
0046                  W1=W-1
0047                  CALL SMOOTH (X(1),YY(1),.01
0048                  DO 10 I=2,V1
0049               10 CALL SMOOTH (X(I),YY(I),2)
0050                  CALL SMOOTH (X(V),YY(V1,24)
0051                  IF (W.EQ.1) GO TO 17
0052                  DO 11 J=1,W1
0053                  CALL SMOOTH (X(1,J+V+1),YY(1,J+V+1),.01
```

```
0054              DO 11 I=2,VI
0055           11 CALL SMOOTH (X1((J*V+I),YY(J*V+I),2)
0056              CALL SMOOTH (X1((J+1)*V),YY((J+1)*V),24)
0057           17 CONTINUE
0058              RETURN
0059              END
```

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 SULPHUR-OXYGEN-HYDROGEN SYSTEM

The results of the chemical equilibrium calculations for the sulphur-oxygen-hydrogen system are given on Tables #6 to #8, and they are also plotted on the triangular diagrams of the Figures #1 to #8, respectively.

The degrees of freedom for this system are equal to four or three, since there can be one or two phases at equilibrium: the gas phase, and the phase of liquid sulphur.

The temperature (473, 573, 673°K), the pressure (1, 2, 5, 10 atm) and the oxygen to hydrogen atomic ratio (100.0 to 0.01) were chosen as the independent variables to be used. The O/H ratio was chosen because all lines of constant O/H ratio pass through the point S of the condensed phase of liquid sulphur.

The major species of the system were found to be: $S(\ell)$, S_2, S_3, S_4, S_5, S_6, S_7, S_8, H_2O, SO_2 and H_2S. Species like O_2, H_2, SO, H_2SO_4, H_2O_2, SO_3 and others, were found to have equilibrium mole fractions of 10^{-4} or less, using the trace-component calculations.

The equilibrium gas mixture is essentially a mixture of H_2O, SO_2 and H_2S with the sulphur species representing at most, (low pressures, high temperatures), 5% of the mixture's moles.

For constant pressure, higher temperatures result in transformation of liquid sulphur into gaseous components containing sulphur, and thus displacing the liquid sulphur deposition boundaries towards the point S on the triangular graph (Figures 1 to 4). In contrary, higher pressures (for constant temperature) result in transformation of sulphur-containing

gaseous components into liquid sulphur, and thus displacing the liquid sulphur deposition boundaries away from the point S (Figures 6 to 8).

An interesting result is that the mole fractions for the sulphur species S_x, x = 2, ..., 8 in the gas phase are independent of the O/H ratio. The reason for this can be easily seen, if one writes as independent reactions for the equilibrium calculations, the reactions $xS(\ell) \rightleftarrows S_x(g)$, with $K_x(T) = y_{S_x} P$, or $y_{S_x} = \frac{K_x(T)}{P}$, which is a function of temperature and pressure only.

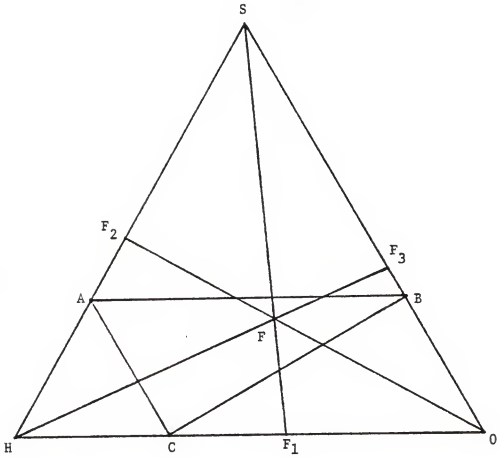
The S_x-mole fractions for very big or very small O/H ratios are not accurate, because in these cases the number of iterations is at most three (because of the computational scheme itself), and mole fractions less than 10^{-3} cannot be calculated accurately.

The deposition boundary separates the graph into two areas:

a) The area above the boundary, or the area containing the point S of the condensed phase of liquid sulphur, where both liquid sulphur and the gas-phase are present and the equilibrium gas-composition can be found on the boundary as described in 1.4. Mixtures in this area have three degrees of freedom (T,P and one elemental ratio).

b) The area below the boundary, or the area not containing the point S, where only the gas-phase is present. Mixtures in this area have four degrees of freedom (T,P and two elemental ratios). Equilibrium compositions were not calculated for this region.

The above mentioned fact that the equilibrium gas phase of the system consists basically from H_2O, H_2S and SO_2 implies that all sulphur deposition boundaries lie within the triangle ABC (Graph #2) where the points A, B and C represent pure H_2S, SO_2 and H_2O respectively. An



GRAPH-2: COMPUTATIONAL SCHEME FOR THE COMPOSITION OF ANY POINT F CONSISTING OF H_2S, H_2O, SO_2 ONLY

easy way to find the composition of any equilibrium point F (consisting of H_2O, H_2S and SO_2 only), is to determine its O/H, S/H and S/O elemental ratios as the intersections of the lines SF with HO (point F_1), OF with SH (point F_2) and HF with SO (point F_3), respectively.

These elemental ratios are related to the mole fractions of H_2S, H_2O and SO_2 in the system through the equations:

$$O/H = a = \frac{y_{H_2O} + 2y_{SO_2}}{2y_{H_2S} + 2y_{H_2O}} \tag{4.2.1}$$

$$S/H = \beta = \frac{y_{H_2S} + y_{SO_2}}{2y_{H_2S} + 2y_{H_2O}} \tag{4.2.2}$$

$$S/O = \gamma = \frac{y_{H_2S} + y_{SO_2}}{y_{H_2O} + 2y_{SO_2}} \tag{4.2.3}$$

Using any two of the above equations plus the inherent equation $y_{H_2O} + y_{SO_2} + y_{H_2S} = 1$, the mole fractions y_{H_2O}, y_{H_2S} and y_{SO_2} can be calculated.

4.2 SULPHUR-CARBON-OXYGEN SYSTEM

The results of the chemical equilibrium calculations for the sulphur-carbon-oxygen system are given on the two-page Tables #9 to #20, and they are also plotted on the triangular diagrams of the Figures #9 to #20, respectively. The degrees of freedom for this system are equal to four or three or two, since there can be one or two or three phases at equilibrium: the gas phase, the phase of liquid sulphur and the phase of solid carbon.

The temperature (473, 573, 673°K), the pressure (1, 2, 5, 10 atm) the carbon to oxygen ratio (100.0 to 0.01) and the sulphur to oxygen ratio (100.0 to 0.01) were chosen as the independent variables.

The C/O ratio was chosen because all lines of constant C/O ratio pass through the point S of the condensed phase of liquid sulphur and the S/O ratio was chosen because all lines of constant S/O ratio pass through the point C of the condensed phase of solid carbon.

The major species of the system were found to be S(ℓ), C(S), S_2, S_3, S_4, S_5, S_6, S_7, S_8, CO, COS, CO_2, SO_2, CS_2. Species like O_2, SO, SO_3 and others, were found to have equilibrium mole fractions of 10^{-4} or less, using the trace-component calculations.

For constant pressure, higher temperatures result (as for the S-H-O system) in transformation of liquid sulphur into gaseous components containing sulphur and thus displacing the liquid sulphur deposition boundaries towards the point S. Since, according to the phase rule, the two deposition boundaries cannot have more than one point of intersection (two degrees of freedom only), the carbon deposition boundary covers a wider range of S/O ratios (starting from 0.01) as the temperature increases.

Conversely, for constant temperature, higher pressures result in transformation of sulphur containing gaseous components into liquid sulphur, and thus displacing the liquid sulphur deposition away from the point S, and if the temperature is not high enough, the left end of the sulphur deposition boundary can be practically on the line CO. This means that there is no carbon deposition boundary, or in other words there can be no system consisting only of solid carbon and the gas-phase under a particular temperature and pressure (example: Figure #9).

The equilibrium gas mixture is essentially a mixture of COS, CO_2, SO_2 and CS_2 with the sulphur species and CO representing at most (low pressures, high temperatures), 5% of the mixture.

In general, the graphical representation of the system on a triangular graph has the form of Figure #11. The carbon deposition boundary is the curve IA and the sulphur deposition boundary is the curve IB. The triangle SCO is thus separated in four areas:

(a) Area SCI, where both solid carbon and liquid sulphur are present along with the gas phase and the equilibrium composition of the gas-phase is that of the point I.

(b) Area SIB, where only liquid sulphur is present with the gas-phase and the equilibrium composition of the gas phase can be found on the boundary IB as described in 1.4.

(c) Area CIA, similar to SIB, where only solid carbon is present with the gas-phase, whose composition is found on the boundary IA.

(d) Area IAOB, where only the gas-phase is present. Mixtures in area SCI have only two degrees of freedom (T and P), in areas SIB and CIA three degrees of freedom (T, P and one elemental ratio), and in area IAOB four degrees of freedom (T, P and two elemental ratios). The point I (Figures #9 to 20), which represents the equilibrium gas-phase for the three-phase sulphur-carbon-oxygen system, has the following composition (Table A):

Table A. Equilibrium gas-phase composition for point I

P(atm)	T(°K)	S(%)	C(%)	O(%)
1	453	0.4	33.4	66.2
1	573	1.8	41.4	56.8
1	673	26.3	29.9	43.8
2	473	0.3	33.3	66.4
2	573	3.8	33.9	63.2
2	673	17.2	31.6	51.2
5	573	2.0	33.2	64.8
5	673	9.8	32.6	57.6
10	573	1.2	33.3	65.5
10	673	6.4	33.0	60.6

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-H-O SYSTEM
TABLE-6: T=473 K

O/H	P(ATM)	S2	S3	S4	S5	S6	S7	S8	H2O	SO2	H2S
100.00	1.0	0.0	0.0	0.0	0.00001	0.00015	0.00004	0.00029	0.00994	0.98956	0.0
9.00	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00074	0.10511	0.89369	0.00003
4.00	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00077	0.22105	0.77684	0.00009
2.33	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00077	0.35235	0.64629	0.00015
1.50	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00077	0.49908	0.49956	0.00024
1.00	1.0	0.0	0.0	0.0	0.00001	0.00030	0.00014	0.00078	0.66530	0.33307	0.00040
0.67	1.0	0.0	0.0	0.0	0.00001	0.00030	0.00015	0.00078	0.83449	0.16363	0.00079
0.50	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00078	0.91353	0.08308	0.00117
0.43	1.0	0.0	0.0	0.0	0.00001	0.00030	0.00015	0.00078	0.93610	0.0	0.14267
0.33	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00078	0.66508	0.0	0.33289
0.25	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00078	0.49743	0.0	0.49749
0.11	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00077	0.22156	0.0	0.77693
0.01	1.0	0.0	0.0	0.0	0.00001	0.00029	0.00015	0.00072	0.01998	0.0	0.97837
100.00	2.0	0.0	0.0	0.0	0.0	0.00008	0.00005	0.00017	0.00955	0.98975	0.0
9.00	2.0	0.0	0.0	0.0	0.0	0.00015	0.00004	0.00039	0.10316	0.89419	0.00003
4.00	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00038	0.22206	0.77731	0.00009
2.33	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00039	0.35262	0.64666	0.00011
1.50	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00037	0.49950	0.49972	0.00017
1.00	2.0	0.0	0.0	0.0	0.0	0.00015	0.00001	0.00039	0.66552	0.33325	0.00029
0.67	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00039	0.83581	0.16302	0.00055
0.50	2.0	0.0	0.0	0.0	0.0	0.00015	0.00002	0.00039	0.99208	0.00246	0.00491
0.43	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00039	0.85624	0.0	0.14274
0.33	2.0	0.0	0.0	0.0	0.0	0.00015	0.00003	0.00039	0.66629	0.0	0.33310
0.25	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00039	0.49570	0.0	0.49924
0.11	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00039	0.22209	0.0	0.77733
0.01	2.0	0.0	0.0	0.0	0.0	0.00015	0.00008	0.00039	0.01999	0.0	0.97840
100.00	5.0	0.0	0.0	0.0	0.0	0.00005	0.00003	0.00013	0.00955	0.98984	0.0
9.00	5.0	0.0	0.0	0.0	0.0	0.00006	0.00002	0.00016	0.10322	0.89453	0.00002
4.00	5.0	0.0	0.0	0.0	0.0	0.00006	0.0	0.00016	0.22214	0.77761	0.00004
2.33	5.0	0.0	0.0	0.0	0.0	0.00006	0.00003	0.00015	0.35230	0.64669	0.00007
1.50	5.0	0.0	0.0	0.0	0.0	0.00006	0.00002	0.00015	0.49915	0.49990	0.00011
1.00	5.0	0.0	0.0	0.0	0.0	0.00006	0.00001	0.00015	0.66627	0.33331	0.00018
0.67	5.0	0.0	0.0	0.0	0.0	0.00006	0.0	0.00016	0.83571	0.16322	0.00086
0.50	5.0	0.0	0.0	0.0	0.0	0.00006	0.00001	0.00015	0.99424	0.00165	0.00309
0.43	5.0	0.0	0.0	0.0	0.0	0.00006	0.0	0.00016	0.85700	0.0	0.14273
0.33	5.0	0.0	0.0	0.0	0.0	0.00006	0.00001	0.00016	0.66656	0.0	0.33322
0.25	5.0	0.0	0.0	0.0	0.0	0.00006	0.00002	0.00016	0.49989	0.0	0.49947
0.11	5.0	0.0	0.0	0.0	0.0	0.00006	0.00003	0.00016	0.22217	0.0	0.77758
0.01	5.0	0.0	0.0	0.0	0.0	0.00005	0.00002	0.00016	0.02000	0.0	0.97917
100.00	10.0	0.0	0.0	0.0	0.0	0.00003	0.00002	0.00007	0.00995	0.98993	0.0
9.00	10.0	0.0	0.0	0.0	0.0	0.00003	0.0	0.00008	0.10324	0.89464	0.00001
4.00	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.22217	0.77769	0.00003
2.33	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.35286	0.64697	0.00005
1.50	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.49984	0.49996	0.00008
1.00	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00007	0.66645	0.33335	0.00012
0.67	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.83668	0.16256	0.00025
0.50	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.00006	0.99342	0.00151	0.00200
0.43	10.0	0.0	0.0	0.0	0.0	0.00003	0.0	0.00008	0.85710	0.0	0.14277
0.33	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.66661	0.0	0.33327
0.25	10.0	0.0	0.0	0.0	0.0	0.00003	0.0	0.00008	0.49994	0.0	0.49995
0.11	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.22221	0.0	0.77768
0.01	10.0	0.0	0.0	0.0	0.0	0.00003	0.00001	0.00008	0.02000	0.0	0.97908

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-H-O SYSTEM
TABLE-21 T=573 K

O/H	PIATI	S2	S3	S4	S5	S6	S7	S8	H2O	SO2	H2S
100.00	1.0	0.00020	0.00002	0.00001	0.00033	0.00072	0.00053	0.00086	0.00993	0.98797	0.0
9.00	1.0	0.00020	0.00002	0.00001	0.00033	0.00438	0.00245	0.00506	0.10344	0.88458	0.00059
4.00	1.0	0.00020	0.00002	0.00001	0.00033	0.00434	0.00243	0.00584	0.21790	0.76796	0.00133
2.33	1.0	0.00020	0.00002	0.00001	0.00033	0.00435	0.00243	0.00584	0.34572	0.63916	0.00231
1.50	1.0	0.00020	0.00002	0.00001	0.00033	0.00435	0.00243	0.00583	0.48697	0.49450	0.00371
1.00	1.0	0.00020	0.00002	0.00001	0.00033	0.00438	0.00245	0.00588	0.64559	0.33106	0.00606
0.67	1.0	0.00020	0.00002	0.00001	0.00033	0.00439	0.00246	0.00599	0.82455	0.16402	0.01167
0.50	1.0	0.00020	0.00002	0.00001	0.00033	0.00437	0.00244	0.00587	0.93150	0.05841	0.01381
0.43	1.0	0.00020	0.00002	0.00001	0.00033	0.00439	0.00246	0.00593	0.94321	0.00131	0.04283
0.33	1.0	0.00020	0.00002	0.00001	0.00033	0.00436	0.00243	0.00582	0.65782	0.00011	0.32927
0.25	1.0	0.00020	0.00002	0.00001	0.00033	0.00437	0.00244	0.00587	0.49349	0.00001	0.49160
0.11	1.0	0.00020	0.00002	0.00001	0.00033	0.00428	0.00241	0.00571	0.21943	0.0	0.76757
0.01	1.0	0.00020	0.00002	0.00001	0.00033	0.00145	0.00112	0.00167	0.01952	0.0	0.97585
100.00	2.0	0.00010	0.00001	0.00001	0.00017	0.00072	0.00051	0.00080	0.00993	0.98797	0.0
9.00	2.0	0.00010	0.00001	0.00001	0.00017	0.00215	0.00131	0.00292	0.10345	0.88693	0.00042
4.00	2.0	0.00010	0.00001	0.00001	0.00017	0.00217	0.00131	0.00292	0.21975	0.77299	0.00094
2.33	2.0	0.00010	0.00001	0.00001	0.00017	0.00217	0.00131	0.00292	0.34477	0.64319	0.00164
1.50	2.0	0.00010	0.00001	0.00001	0.00017	0.00205	0.00127	0.00270	0.49424	0.49736	0.00251
1.00	2.0	0.00010	0.00001	0.00001	0.00017	0.00219	0.00132	0.00294	0.65668	0.33261	0.00426
0.67	2.0	0.00010	0.00001	0.00001	0.00017	0.00220	0.00133	0.00299	0.83961	0.16552	0.00837
0.50	2.0	0.00010	0.00001	0.00001	0.00017	0.00217	0.00132	0.00291	0.93656	0.05501	0.01003
0.43	2.0	0.00010	0.00001	0.00001	0.00017	0.00220	0.00133	0.00295	0.95020	0.00051	0.04281
0.33	2.0	0.00010	0.00001	0.00001	0.00017	0.00219	0.00133	0.00294	0.66220	0.00006	0.33129
0.25	2.0	0.00010	0.00001	0.00001	0.00017	0.00218	0.00132	0.00293	0.49676	0.00001	0.49800
0.11	2.0	0.00010	0.00001	0.00001	0.00017	0.00214	0.00131	0.00283	0.22081	0.0	0.77203
0.01	2.0	0.00010	0.00001	0.00001	0.00017	0.00144	0.00099	0.00170	0.01962	0.0	0.97586
100.00	5.0	0.00004	0.0	0.0	0.00007	0.00041	0.00027	0.00052	0.00992	0.98886	0.00062
9.00	5.0	0.00004	0.0	0.0	0.00007	0.00086	0.00053	0.00115	0.10373	0.89248	0.00020
4.00	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00117	0.22093	0.77805	0.00040
2.33	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00116	0.35087	0.64556	0.00101
1.50	5.0	0.00004	0.0	0.0	0.00007	0.00086	0.00052	0.00114	0.49586	0.49910	0.00151
1.00	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00117	0.66129	0.33339	0.00274
0.67	5.0	0.00004	0.0	0.0	0.00007	0.00088	0.00053	0.00118	0.84725	0.14491	0.00535
0.50	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00117	0.96438	0.01102	0.02243
0.43	5.0	0.00004	0.0	0.0	0.00007	0.00085	0.00051	0.00114	0.85425	0.00027	0.14246
0.33	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00117	0.66439	0.00002	0.33252
0.25	5.0	0.00004	0.0	0.0	0.00007	0.00086	0.00053	0.00115	0.49819	0.0	0.49873
0.11	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00117	0.22169	0.0	0.77531
0.01	5.0	0.00004	0.0	0.0	0.00007	0.00087	0.00053	0.00117	0.01995	0.0	0.97748
100.00	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00058	0.00992	0.98879	0.00032
9.00	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00057	0.10492	0.89301	0.00020
4.00	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00057	0.22142	0.77665	0.00047
2.33	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00058	0.35161	0.64435	0.00077
1.50	10.0	0.00002	0.0	0.0	0.00003	0.00044	0.00026	0.00058	0.49789	0.49964	0.00119
1.00	10.0	0.00002	0.0	0.0	0.00003	0.00044	0.00026	0.00059	0.66251	0.33364	0.00217
0.67	10.0	0.00002	0.0	0.0	0.00003	0.00044	0.00027	0.00059	0.85059	0.14431	0.00510
0.50	10.0	0.00002	0.0	0.0	0.00003	0.00044	0.00026	0.00059	0.97147	0.00852	0.01783
0.43	10.0	0.00002	0.0	0.0	0.00003	0.00044	0.00026	0.00059	0.85975	0.00010	0.14266
0.33	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00058	0.66578	0.00001	0.33293
0.25	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00059	0.49937	0.0	0.49935
0.11	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00058	0.22198	0.0	0.77632
0.01	10.0	0.00002	0.0	0.0	0.00003	0.00043	0.00026	0.00058	0.01998	0.0	0.97875

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-H-O SYSTEM
TABLE-8: T=673 K

O/H	PIATI	S2	S3	S4	S5	S6	S7	S8	H2O	SO2	H2S
100.00	1.0	0.00623	0.00062	0.00033	0.00292	0.00065	0.00051	0.00055	0.00792	0.98837	0.00201
9.00	1.0	0.00623	0.00062	0.00033	0.00292	0.00853	0.00617	0.00688	0.09565	0.87559	0.00317
4.00	1.0	0.00623	0.00062	0.00033	0.00292	0.01085	0.01181	0.01379	0.20606	0.76404	0.00746
2.33	1.0	0.00623	0.00062	0.00033	0.00292	0.02013	0.01232	0.01449	0.32098	0.61900	0.01308
1.53	1.0	0.00623	0.00062	0.00033	0.00292	0.02020	0.01236	0.01453	0.45040	0.48167	0.02084
1.00	1.0	0.00623	0.00062	0.00033	0.00292	0.01997	0.01226	0.01441	0.59149	0.32881	0.03306
0.67	1.0	0.00623	0.00062	0.00033	0.00292	0.01955	0.01210	0.01418	0.73265	0.18179	0.05942
0.50	1.0	0.00623	0.00062	0.00033	0.00292	0.02015	0.01233	0.01450	0.86950	0.05435	0.10869
0.43	1.0	0.00623	0.00062	0.00033	0.00292	0.02012	0.01231	0.01448	0.76021	0.01984	0.17302
0.33	1.0	0.00623	0.00062	0.00033	0.00292	0.01996	0.01225	0.01439	0.62541	0.00382	0.32617
0.25	1.0	0.00623	0.00062	0.00033	0.00292	0.02013	0.01232	0.01449	0.47199	0.00101	0.47885
0.11	1.0	0.00623	0.00062	0.00033	0.00292	0.01976	0.01215	0.01428	0.21156	0.0	0.74184
0.01	1.0	0.00623	0.00062	0.00033	0.00292	0.00156	0.00132	0.00143	0.01991	0.0	0.97501
100.00	2.0	0.00312	0.00031	0.00016	0.00146	0.00079	0.00060	0.00066	0.00950	0.98862	0.00243
9.00	2.0	0.00312	0.00031	0.00016	0.00146	0.00523	0.00383	0.00423	0.06040	0.87531	0.00243
4.00	2.0	0.00312	0.00031	0.00016	0.00146	0.01006	0.00612	0.00720	0.21096	0.76026	0.00547
2.33	2.0	0.00312	0.00031	0.00016	0.00146	0.01000	0.00613	0.00721	0.33353	0.63144	0.00549
1.53	2.0	0.00312	0.00031	0.00016	0.00146	0.01001	0.00614	0.00721	0.46936	0.49212	0.01516
1.00	2.0	0.00312	0.00031	0.00016	0.00146	0.01002	0.00614	0.00722	0.61855	0.33308	0.02660
0.67	2.0	0.00312	0.00031	0.00016	0.00146	0.00993	0.00613	0.00719	0.77388	0.18855	0.04432
0.50	2.0	0.00312	0.00031	0.00016	0.00146	0.01007	0.00616	0.00724	0.89451	0.05457	0.08995
0.43	2.0	0.00312	0.00031	0.00016	0.00146	0.00952	0.00594	0.00697	0.80810	0.01823	0.16422
0.33	2.0	0.00312	0.00031	0.00016	0.00146	0.00993	0.00611	0.00719	0.66446	0.00261	0.32527
0.25	2.0	0.00312	0.00031	0.00016	0.00146	0.01006	0.00616	0.00724	0.48700	0.00051	0.48976
0.11	2.0	0.00312	0.00031	0.00016	0.00146	0.01005	0.00615	0.00723	0.21693	0.00004	0.75560
0.01	2.0	0.00312	0.00031	0.00016	0.00146	0.00161	0.00129	0.00119	0.01951	0.0	0.97379
100.00	5.0	0.00125	0.00012	0.00007	0.00058	0.00064	0.00051	0.00068	0.00982	0.98734	0.00111
9.00	5.0	0.00125	0.00012	0.00007	0.00058	0.00356	0.00226	0.00263	0.10272	0.88720	0.00157
4.00	5.0	0.00125	0.00012	0.00007	0.00058	0.00600	0.00245	0.00288	0.21624	0.77091	0.00352
2.33	5.0	0.00125	0.00012	0.00007	0.00058	0.00582	0.00238	0.00279	0.34256	0.64231	0.00613
1.50	5.0	0.00125	0.00012	0.00007	0.00058	0.00601	0.00246	0.00289	0.47776	0.50888	0.01382
1.00	5.0	0.00125	0.00012	0.00007	0.00058	0.00602	0.00246	0.00290	0.63931	0.33549	0.01582
0.67	5.0	0.00125	0.00012	0.00007	0.00058	0.00604	0.00247	0.00291	0.80688	0.15418	0.02952
0.50	5.0	0.00125	0.00012	0.00007	0.00058	0.00603	0.00246	0.00290	0.83757	0.03434	0.06849
0.43	5.0	0.00125	0.00012	0.00007	0.00059	0.00601	0.00246	0.00290	0.62168	0.00669	0.15284
0.33	5.0	0.00125	0.00012	0.00007	0.00058	0.00603	0.00246	0.00290	0.65325	0.00081	0.32155
0.25	5.0	0.00125	0.00012	0.00007	0.00058	0.00602	0.00246	0.00290	0.49460	0.00020	0.49562
0.11	5.0	0.00125	0.00012	0.00007	0.00059	0.00602	0.00246	0.00283	0.22311	0.00002	0.77051
0.01	5.0	0.00125	0.00012	0.00007	0.00058	0.00161	0.00124	0.00114	0.01991	0.0	0.97577
100.00	10.0	0.00062	0.00006	0.00003	0.00029	0.00087	0.00060	0.00068	0.00968	0.98793	0.00006
9.00	10.0	0.00062	0.00006	0.00003	0.00029	0.00209	0.00123	0.00144	0.10160	0.89061	0.00111
4.00	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00144	0.21839	0.77442	0.00251
2.33	10.0	0.00062	0.00006	0.00003	0.00029	0.00196	0.00121	0.00142	0.34607	0.64487	0.00447
1.53	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00144	0.48592	0.49960	0.00700
1.00	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.64853	0.33553	0.01125
0.67	10.0	0.00062	0.00006	0.00003	0.00029	0.00202	0.00124	0.00145	0.82241	0.15141	0.02147
0.50	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.91187	0.02782	0.05561
0.43	10.0	0.00062	0.00006	0.00003	0.00029	0.00202	0.00123	0.00145	0.84376	0.00328	0.14929
0.33	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.66245	0.00041	0.33244
0.25	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.49741	0.00010	0.49780
0.11	10.0	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.22117	0.00001	0.77414
0.01	10.0	0.00062	0.00006	0.00003	0.00029	0.00162	0.00115	0.00135	0.01991	0.0	0.97575

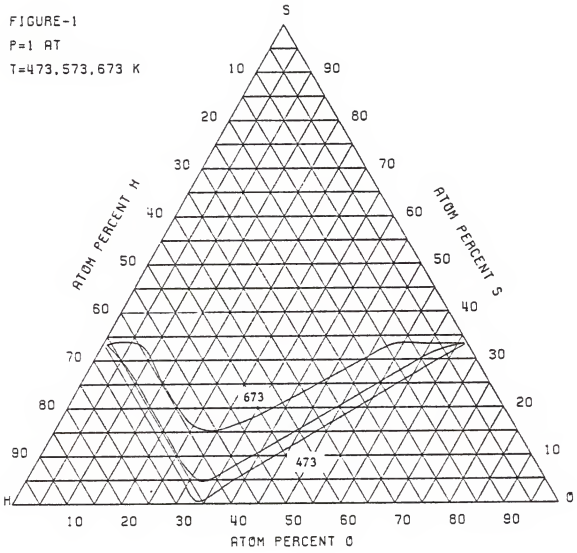


FIGURE-1
P=1 AT
T=473,573,673 K
S
H
O
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
673
473

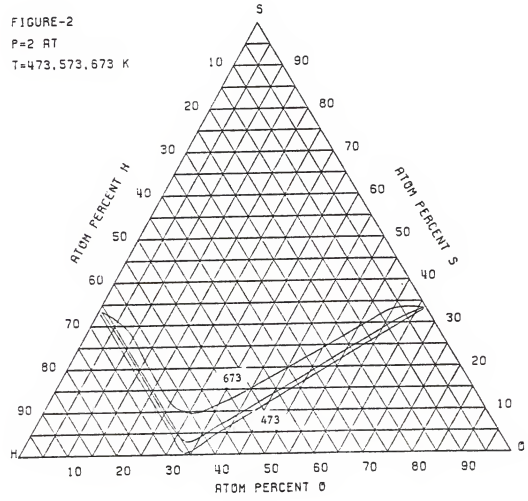


FIGURE-2
P=2 AT
T=473,573,673 K
S
H
O
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
673
473

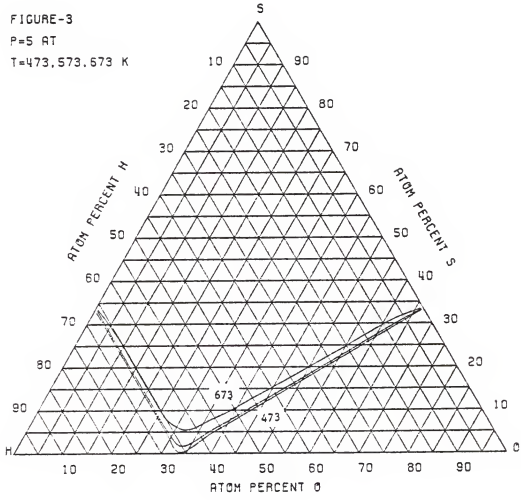


FIGURE-3
P=5 AT
T=473,573,673 K
S
H
O
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
673
473

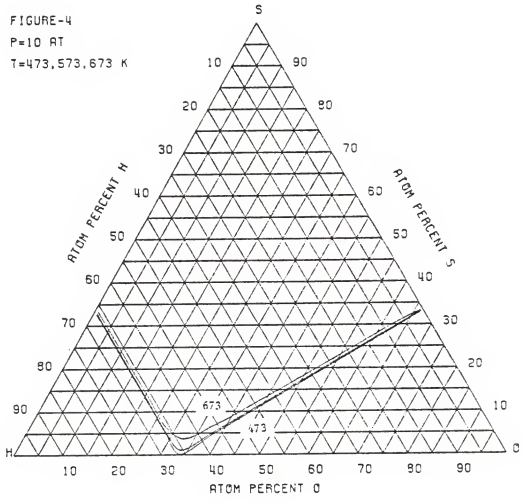


FIGURE-4
P=10 AT
T=473,573,673 K
S
H
O
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
673
573
473

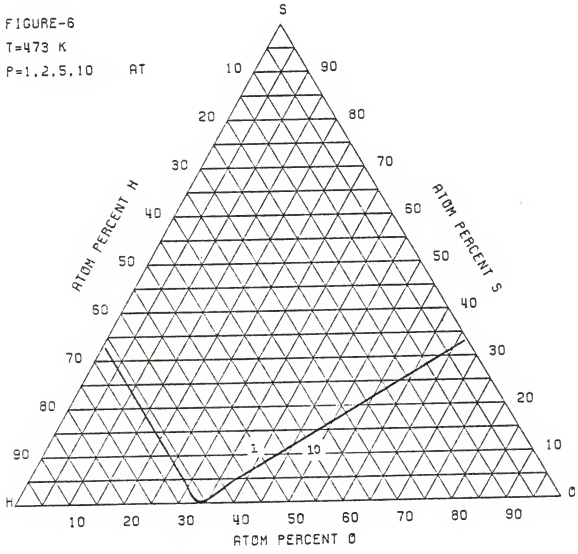


FIGURE-6
T=473 K
P=1,2,5,10 AT
S
H
O
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
1
10

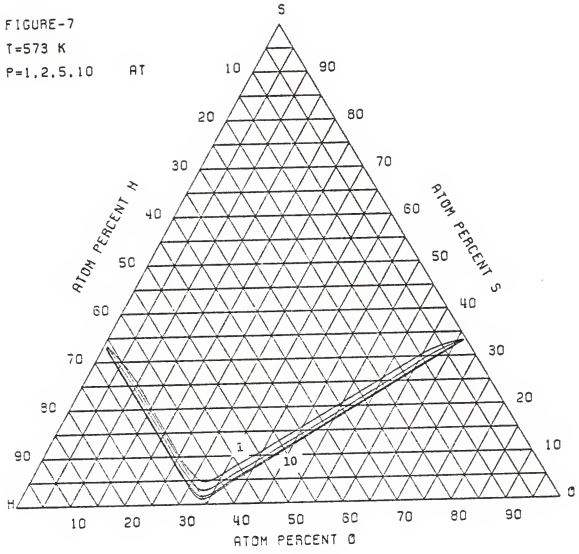


FIGURE-7
T=573 K
P=1,2,5,10 AT
S
H
O
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
1
10

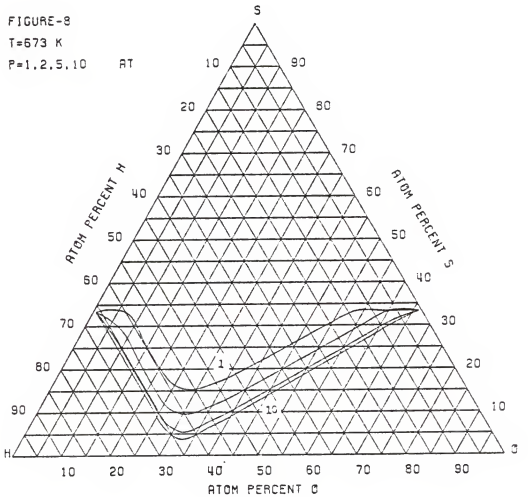


FIGURE-8
T=673 K
P=1,2,5,10 AT
S
H
C
ATOM PERCENT H
ATOM PERCENT S
ATOM PERCENT C
10
20
30
40
50
60
70
80
90
1
10

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-9: P=1 ATM,T=473 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00072	0.00000	0.01262	0.98621	0.00000	0.00001
9.09	0.00000	0.00000	0.00000	0.00001	0.00030	0.00015	0.00079	0.00001	0.01257	0.98616	0.00000	0.00003
4.00	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00076	0.00000	0.01259	0.98616	0.00000	0.00004
2.33	0.00000	0.00000	0.00000	0.00001	0.00033	0.00016	0.00077	0.00001	0.01262	0.98608	0.00000	0.00004
1.50	0.00000	0.00000	0.00000	0.00001	0.00028	0.00015	0.00072	0.00001	0.01307	0.98573	0.00000	0.00003
1.00	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00075	0.00001	0.01240	0.98637	0.00000	0.00003
0.82	0.00000	0.00000	0.00000	0.00001	0.00028	0.00015	0.00073	0.00001	0.01268	0.98616	0.00000	0.00002
0.67	0.00000	0.00000	0.00000	0.00001	0.00028	0.00015	0.00069	0.00001	0.01321	0.98564	0.00000	0.00002
0.50	0.00000	0.00000	0.00000	0.00001	0.00033	0.00016	0.00067	0.00038	0.03439	0.93256	0.02211	0.00030
0.43	0.00000	0.00000	0.00000	0.00001	0.00018	0.00012	0.00030	0.00457	0.01980	0.82184	0.15320	0.00000
0.33	0.00000	0.00000	0.00000	0.00001	0.00017	0.00012	0.00026	0.00365	0.01567	0.64057	0.33957	0.00000
0.25	0.00000	0.00000	0.00000	0.00001	0.00022	0.00014	0.00037	0.00417	0.01516	0.47550	0.50444	0.00000
0.11	0.00000	0.00000	0.00000	0.00001	0.00018	0.00013	0.00028	0.00265	0.00830	0.20991	0.77854	0.00000
0.01	0.00000	0.00000	0.00000	0.00001	0.00013	0.00011	0.00017	0.00060	0.00122	0.01743	0.97963	0.00071

S/D	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00078	0.00000	0.01251	0.98622	0.00000	0.00004
9.00	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00068	0.00000	0.00993	0.98890	0.00000	0.00004
4.00	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00078	0.00000	0.01247	0.98627	0.00000	0.00004
2.33	0.00000	0.00000	0.00000	0.00001	0.00030	0.00016	0.00080	0.00001	0.01265	0.98604	0.00000	0.00004
1.50	0.00000	0.00000	0.00000	0.00001	0.00030	0.00016	0.00080	0.00001	0.01268	0.98601	0.00000	0.00004
1.00	0.00000	0.00000	0.00000	0.00001	0.00030	0.00015	0.00078	0.00000	0.01163	0.98711	0.00000	0.00004
0.67	0.00000	0.00000	0.00000	0.00001	0.00030	0.00015	0.00078	0.00000	0.01251	0.98621	0.00000	0.00004
0.54	0.00000	0.00000	0.00000	0.00001	0.00030	0.00015	0.00077	0.00000	0.01068	0.98806	0.00000	0.00004
0.43	0.00000	0.00000	0.00000	0.00001	0.00030	0.00016	0.00080	0.00001	0.01266	0.98603	0.00000	0.00004
0.33	0.00000	0.00000	0.00000	0.00001	0.00030	0.00015	0.00079	0.00000	0.01200	0.98673	0.00000	0.00004
0.25	0.00000	0.00000	0.00000	0.00001	0.00030	0.00015	0.00079	0.00001	0.01258	0.98614	0.00000	0.00003
0.18	0.00000	0.00000	0.00000	0.00001	0.00028	0.00015	0.00075	0.00001	0.01229	0.98647	0.00000	0.00004
0.11	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00075	0.00000	0.00806	0.99071	0.00000	0.00004
0.01	0.00000	0.00000	0.00000	0.00001	0.00029	0.00015	0.00077	0.00001	0.01089	0.98788	0.00000	0.00000

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-C SYSTEM
TABLE-10: P=1 ATM.T=573 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00020	0.00002	0.00001	0.00033	0.00265	0.00178	0.00332	0.00055	0.09477	0.89659	0.00000	0.00035
9.00	0.00020	0.00002	0.00001	0.00033	0.00444	0.00269	0.00597	0.00054	0.10998	0.87271	0.00000	0.00367
4.00	0.00020	0.00002	0.00001	0.00033	0.00450	0.00272	0.00605	0.00054	0.11068	0.87178	0.00000	0.00372
2.33	0.00020	0.00002	0.00001	0.00033	0.00440	0.00266	0.00591	0.00054	0.10957	0.87356	0.00000	0.00335
1.50	0.00020	0.00002	0.00001	0.00033	0.00445	0.00269	0.00598	0.00054	0.11008	0.87258	0.00000	0.00368
1.00	0.00020	0.00002	0.00001	0.00033	0.00430	0.00260	0.00578	0.00053	0.10840	0.87482	0.00000	0.00356
0.82	0.00020	0.00002	0.00001	0.00033	0.00427	0.00258	0.00573	0.00053	0.10808	0.87654	0.00000	0.00227
0.67	0.00020	0.00002	0.00001	0.00033	0.00429	0.00260	0.00577	0.00053	0.10826	0.87504	0.00000	0.00351
0.50	0.00020	0.00002	0.00001	0.00033	0.00153	0.00121	0.00174	0.01628	0.04473	0.90397	0.03053	0.00000
0.43	0.00020	0.00002	0.00001	0.00033	0.00107	0.00084	0.00122	0.01134	0.03507	0.78561	0.16348	0.00138
0.33	0.00020	0.00002	0.00001	0.00033	0.00103	0.00082	0.00118	0.01171	0.03037	0.60857	0.34631	0.00001
0.25	0.00020	0.00002	0.00001	0.00033	0.00084	0.00067	0.00095	0.00891	0.02313	0.45872	0.50678	0.00000
0.11	0.00020	0.00002	0.00001	0.00033	0.00061	0.00051	0.00068	0.00469	0.01129	0.20407	0.77816	0.00000
0.01	0.00020	0.00002	0.00001	0.00033	0.00035	0.00032	0.00037	0.00107	0.00168	0.01720	0.97901	0.00000

S/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00020	0.00002	0.00001	0.00033	0.00413	0.00255	0.00546	0.00054	0.10443	0.88002	0.00000	0.00287
9.00	0.00020	0.00002	0.00001	0.00033	0.00436	0.00264	0.00586	0.00054	0.10907	0.87393	0.00000	0.00360
4.00	0.00020	0.00002	0.00001	0.00033	0.00437	0.00264	0.00587	0.00054	0.10914	0.87384	0.00000	0.00361
2.33	0.00020	0.00002	0.00001	0.00033	0.00438	0.00265	0.00588	0.00054	0.10925	0.87370	0.00000	0.00362
1.50	0.00020	0.00002	0.00001	0.00033	0.00451	0.00273	0.00606	0.00054	0.11063	0.87179	0.00000	0.00372
1.00	0.00020	0.00002	0.00001	0.00033	0.00441	0.00267	0.00592	0.00054	0.10957	0.87326	0.00000	0.00364
0.67	0.00020	0.00002	0.00001	0.00033	0.00440	0.00267	0.00591	0.00054	0.10947	0.87586	0.00000	0.00364
0.54	0.00020	0.00002	0.00001	0.00033	0.00443	0.00268	0.00594	0.00054	0.10982	0.87293	0.00000	0.00366
0.43	0.00020	0.00002	0.00001	0.00033	0.00448	0.00271	0.00601	0.00054	0.11034	0.87222	0.00000	0.00370
0.33	0.00020	0.00002	0.00001	0.00033	0.00440	0.00266	0.00591	0.00054	0.10948	0.87338	0.00000	0.00363
0.25	0.00020	0.00002	0.00001	0.00033	0.00442	0.00267	0.00594	0.00054	0.10973	0.87305	0.00000	0.00365
0.18	0.00020	0.00002	0.00001	0.00033	0.00428	0.00259	0.00575	0.00053	0.10714	0.87616	0.00000	0.00354
0.11	0.00020	0.00002	0.00001	0.00033	0.00427	0.00258	0.00573	0.00053	0.10796	0.87541	0.00000	0.00353
0.01	0.00020	0.00002	0.00001	0.00033	0.00055	0.00044	0.00062	0.00021	0.00183	0.99301	0.00000	0.00334

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-11: P=1 ATM,T=673 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00623	0.00062	0.00033	0.00292	0.02016	0.01234	0.01451	0.00616	0.36933	0.50934	0.00000	0.06815
9.00	0.00623	0.00062	0.00033	0.00292	0.02022	C.C1238	0.01456	0.00616	0.36957	0.50884	0.00000	C.C6827
4.00	0.00623	0.00062	0.00033	0.00292	0.02029	C.C1242	C.C1460	C.CC617	0.36984	0.50823	0.00000	C.C6845
2.33	0.00623	0.00062	0.00033	0.00292	0.02019	0.01236	0.01453	0.00616	0.36932	0.50928	0.00000	0.06816
1.50	0.00623	0.00062	0.00033	C.00292	0.01954	C.C1227	C.C1441	C.00568	0.36807	0.51136	0.00000	0.06826
1.00	0.00623	0.00062	0.00033	0.00292	0.01996	0.01222	0.01437	0.00607	0.36820	0.51178	0.00000	0.06740
0.82	0.00623	C.00062	0.00033	0.00292	0.01951	0.01215	0.01433	0.00611	0.36783	0.51242	0.00000	0.06721
0.67	0.00623	0.00062	C.00033	0.00292	0.01951	C.C1215	C.C1253	C.CC403	0.34069	0.54647	0.00000	C.06729
0.50	0.00623	0.00062	0.00033	0.00292	0.01749	C.C1112	0.00431	0.00112	0.00239	0.71594	0.11204	0.06525
0.43	0.00623	0.00062	0.00033	0.00292	0.00494	0.00401	0.00237	0.00193	0.00207	0.01980	0.04281	0.03783	0.22619	0.06701
0.33	0.00623	C.00062	0.00033	0.00292	0.00237	0.00193	0.00207	0.00188	0.01607	0.03373	0.48415	0.39289	0.06737
0.25	0.00623	0.00062	0.00033	0.00292	0.00214	0.00177	0.00188	0.01607	0.03373	0.48415	0.39289	0.06737
0.11	0.00623	0.00062	0.00033	0.00292	0.00200	0.00167	0.00177	0.01313	0.02614	0.35215	0.53909	0.06405
0.01	0.00623	C.00062	C.00033	0.00292	0.00164	0.00140	0.00167	0.00829	0.01397	0.15276	0.78470	C.03578
	0.00623	0.00062	0.00033	0.00292	0.00010	C.0001C	C.00010	0.00010	0.00010	0.00055	C.98010	0.01885

S/0	S2	S3	S4	S5	S6	S7	S8	CG	COS	CC2	SO2	CS2
100.00	0.00623	0.00062	0.00033	0.00292	0.02020	0.01236	0.01454	0.00616	0.36935	0.50927	0.00000	0.06813
9.00	0.00623	0.00062	0.00033	0.00292	0.02018	0.01235	0.01453	0.00617	0.36832	0.51029	0.00000	0.06817
4.00	0.00623	0.00062	0.00033	0.00292	0.02026	0.01240	0.01458	0.00616	0.36966	0.50861	0.00000	0.06833
2.33	0.00623	0.00062	0.00033	0.00292	0.02018	0.01234	0.01452	0.00616	0.36921	0.50953	0.00000	0.06805
1.50	0.00623	0.00062	0.00033	0.00292	0.02025	0.01239	0.01457	0.00616	0.36960	0.50873	0.00000	0.06829
1.00	0.00623	0.00062	0.00033	0.00292	0.02041	0.01251	0.01483	0.00619	0.37143	0.50480	0.00000	0.06952
0.67	0.00623	0.00062	0.00033	0.00292	0.02016	0.01237	0.01454	0.00631	0.35030	0.52786	0.00000	0.06845
0.54	0.00623	0.00062	0.00033	0.00292	0.01981	0.01224	0.01436	0.00647	0.32056	0.55804	0.00000	0.06851
0.43	0.00623	0.00062	0.00033	0.00292	0.01811	0.01152	0.01339	0.00682	0.22814	0.65379	0.00000	0.06823
0.33	0.00623	0.00062	0.00033	0.00292	0.01550	0.01026	0.01178	0.00671	0.14975	0.73827	0.00000	0.06773
0.25	0.00623	0.00062	0.00033	0.00292	0.01204	0.00836	0.00945	0.00595	0.08802	0.80930	0.00000	0.06688
0.18	0.00623	0.00062	0.00033	0.00292	0.00868	0.00603	0.00666	0.00470	0.03770	0.87033	0.00000	0.06645
0.11	0.00623	0.00062	0.00033	0.00292	0.00363	0.00251	0.00313	0.00248	0.01272	0.91283	0.00000	0.06230
0.01	0.00623	0.00062	0.00033	0.00292	0.00005	0.00005	0.00005	0.00005	0.00007	0.99038	0.00000	0.00935

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-C SYSTEM
TABLE-12: P=2 ATM,T=473 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00000	0.00000	0.00000	0.00000	0.00016	0.00008	0.00042	0.00001	0.00922	0.99038	0.00000	0.00002
9.00	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00888	0.99048	0.00000	0.00002
4.00	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00038	0.00000	0.00919	0.99020	0.00000	0.00000
2.33	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00000	0.00894	0.99041	0.00000	0.00002
1.50	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00036	0.00000	0.00926	0.99013	0.00000	0.00002
1.00	0.00000	0.00000	0.00000	0.00000	0.00014	0.00008	0.00038	0.00000	0.00881	0.99138	0.00000	0.00001
0.82	0.00000	0.00000	0.00000	0.00000	0.00014	0.00008	0.00037	0.00000	0.00900	0.99039	0.00000	0.00001
0.67	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00038	0.00000	0.00884	0.99054	0.00000	0.00002
0.50	0.00000	0.00000	0.00000	0.00000	0.00013	0.00008	0.00041	0.00750	0.03132	0.94116	0.01946	0.00000
0.43	0.00000	0.00000	0.00000	0.00000	0.00012	0.00008	0.00022	0.00445	0.01915	0.82312	0.15287	0.00000
0.33	0.00000	0.00000	0.00000	0.00000	0.00012	0.00008	0.00023	0.00352	0.01511	0.64159	0.33939	0.00000
0.25	0.00000	0.00000	0.00000	0.00000	0.00014	0.00006	0.00025	0.00373	0.01405	0.47756	0.50419	0.00000
0.11	0.00000	0.00000	0.00000	0.00000	0.00013	0.00008	0.00021	0.00257	0.00808	0.21030	0.77864	0.00000
0.01	0.00000	0.00000	0.00000	0.00000	0.00011	0.00005	0.00014	0.00059	0.00121	0.01787	0.97969	0.00030

S/0	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00000	0.00000	0.00000	0.00000	0.00012	0.00017	0.00026	0.00000	0.00747	0.99207	0.00000	0.00002
9.00	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00037	0.00001	0.00768	0.99169	0.00000	0.00002
4.00	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00000	0.00787	0.99049	0.00000	0.00002
2.33	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00705	0.99231	0.00000	0.00002
1.50	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00868	0.99068	0.00000	0.00002
1.00	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00000	0.00871	0.99065	0.00000	0.00002
0.67	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00000	0.00890	0.99045	0.00000	0.00002
0.54	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00000	0.00888	0.99048	0.00000	0.00002
0.43	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00799	0.99137	0.00000	0.00002
0.33	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00040	0.00000	0.00892	0.99043	0.00000	0.00002
0.25	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00890	0.99046	0.00000	0.00001
0.18	0.00000	0.00000	0.00000	0.00000	0.00015	0.00007	0.00038	0.00001	0.00629	0.99307	0.00000	0.00002
0.11	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00746	0.99190	0.00000	0.00002
0.01	0.00000	0.00000	0.00000	0.00000	0.00015	0.00008	0.00039	0.00001	0.00825	0.99112	0.00000	0.00000

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-13: P=2 ATM,T=573 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00010	0.00001	0.00001	0.00017	0.00135	0.00091	0.00169	0.00033	0.07387	0.92003	0.00000	0.00182
9.00	0.00010	0.00001	0.00001	0.00017	0.00219	0.00133	0.00294	0.00039	0.07914	0.91242	0.00000	0.00155
4.00	0.00010	0.00001	0.00001	0.00017	0.00220	0.00134	0.00256	0.00039	0.07930	0.91233	0.00000	0.00149
2.33	0.00010	0.00001	0.00001	0.00017	0.00222	0.00134	0.00298	0.00039	0.07943	0.91216	0.00000	0.00149
1.50	0.00010	0.00001	0.00001	0.00017	0.00207	0.00128	0.00275	0.00038	0.07739	0.91572	0.00000	0.00141
1.00	0.00010	0.00001	0.00001	0.00017	0.00215	0.00130	0.00289	0.00038	0.07833	0.91348	0.00000	0.00146
0.82	0.00010	0.00001	0.00001	0.00017	0.00214	0.00130	0.00286	0.00039	0.07820	0.91449	0.00000	0.00063
0.67	0.00010	0.00001	0.00001	0.00017	0.00215	0.00130	0.00289	0.00038	0.07836	0.91357	0.00000	0.00133
0.50	0.00010	0.00001	0.00001	0.00017	0.00112	0.00087	0.00129	0.01555	0.04264	0.90939	0.02914	0.00000
0.43	0.00010	0.00001	0.00001	0.00017	0.00059	0.00046	0.00068	0.00867	0.02895	0.80194	0.15871	0.00000
0.33	0.00010	0.00001	0.00001	0.00017	0.00063	0.00045	0.00072	0.00833	0.02527	0.62066	0.34390	0.00000
0.25	0.00010	0.00001	0.00001	0.00017	0.00066	0.00052	0.00075	0.00865	0.02236	0.46028	0.50678	0.00000
0.11	0.00010	0.00001	0.00001	0.00017	0.00043	0.00035	0.00048	0.00423	0.01052	0.20554	0.77844	0.00000
0.01	0.00010	0.00001	0.00001	0.00017	0.00025	0.00022	0.00026	0.00086	0.00141	0.01575	0.97935	0.00190

S/0	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00010	0.00001	0.00001	0.00017	0.00220	0.00133	0.00255	0.00039	0.07912	0.91219	0.00000	0.00182
9.00	0.00010	0.00001	0.00001	0.00017	0.00218	0.00132	0.00292	0.00008	0.07866	0.91307	0.00000	0.00177
4.00	0.00010	0.00001	0.00001	0.00017	0.00219	0.00133	0.00295	0.00039	0.07877	0.91257	0.00000	0.00181
2.33	0.00010	0.00001	0.00001	0.00017	0.00219	0.00132	0.00294	0.00039	0.07767	0.91369	0.00000	0.00181
1.50	0.00010	0.00001	0.00001	0.00017	0.00221	0.00134	0.00297	0.00039	0.07935	0.91191	0.00000	0.00183
1.00	0.00010	0.00001	0.00001	0.00017	0.00222	0.00134	0.00297	0.00039	0.07657	0.91467	0.00000	0.00184
0.67	0.00010	0.00001	0.00001	0.00017	0.00221	0.00134	0.00296	0.00039	0.07687	0.91441	0.00000	0.00183
0.54	0.00010	0.00001	0.00001	0.00017	0.00220	0.00133	0.00296	0.00039	0.07901	0.91229	0.00000	0.00182
0.43	0.00010	0.00001	0.00001	0.00017	0.00221	0.00134	0.00297	0.00039	0.07938	0.91187	0.00000	0.00183
0.33	0.00010	0.00001	0.00001	0.00017	0.00220	0.00133	0.00296	0.00039	0.07944	0.91287	0.00000	0.00182
0.25	0.00010	0.00001	0.00001	0.00017	0.00221	0.00134	0.00297	0.00039	0.07907	0.91220	0.00000	0.00183
0.18	0.00010	0.00001	0.00001	0.00017	0.00212	0.00128	0.00284	0.00038	0.07768	0.91356	0.00000	0.00175
0.11	0.00010	0.00001	0.00001	0.00017	0.00216	0.00131	0.00290	0.00039	0.07419	0.91725	0.00000	0.00179
0.01	0.00010	0.00001	0.00001	0.00017	0.00068	0.00051	0.00079	0.00025	0.00335	0.99314	0.00000	0.00129

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-14: P=2 ATM.T=673 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00312	0.00031	0.00016	0.00146	0.01014	0.00621	0.00730	0.00490	0.29412	0.64312	0.00000	0.03421
9.00	0.00312	0.00031	0.00016	0.00146	0.01013	0.00620	0.00729	0.00490	0.29408	0.64361	0.00000	0.03379
4.00	0.00312	0.00031	0.00016	0.00146	0.00988	0.00605	0.00715	0.00427	0.28966	0.64890	0.00000	0.03405
2.33	0.00312	0.00031	0.00016	0.00146	0.01029	0.00625	0.00740	0.00493	0.29565	0.64074	0.00000	0.03470
1.50	0.00312	0.00031	0.00016	0.00146	0.01013	0.00620	0.00729	0.00487	0.29393	0.64344	0.00000	0.03415
1.00	0.00312	0.00031	0.00016	0.00146	0.01003	0.00614	0.00722	0.00487	0.29272	0.64516	0.00000	0.03387
0.82	0.00312	0.00031	0.00016	0.00146	0.00994	0.00610	0.00717	0.00481	0.29091	0.64727	0.00000	0.03380
0.67	0.00312	0.00031	0.00016	0.00146	0.00991	0.00606	0.00713	0.00487	0.29228	0.64991	0.00000	0.02983
0.50	0.00312	0.00031	0.00016	0.00146	0.00366	0.00284	0.00308	0.02928	0.06458	0.84968	0.04654	0.00000
0.43	0.00312	0.00031	0.00016	0.00146	0.00187	0.00145	0.00161	0.02081	0.04565	0.73590	0.18079	0.01189
0.33	0.00312	0.00031	0.00016	0.00146	0.00164	0.00133	0.00143	0.01641	0.03528	0.55278	0.36550	0.02522
0.25	0.00312	0.00031	0.00016	0.00146	0.00148	0.00121	0.00130	0.01291	0.02678	0.40089	0.52376	0.03167
0.11	0.00312	0.00031	0.00016	0.00146	0.00138	0.00116	0.00123	0.00825	0.01397	0.15868	0.76423	0.01110
0.01	0.00312	0.00031	0.00016	0.00146	0.00010	0.00010	0.00010	0.00010	0.00310	0.00057	0.98009	0.01884

S/D	S2	S3	S4	S5	S6	S7	S8	CC	CCS	CC2	SC2	CS2
100.00	0.00312	0.00031	0.00016	0.00146	0.01010	0.00619	0.00728	0.00491	0.25308	0.64424	0.00000	0.03421
9.00	0.00312	0.00031	0.00016	0.00146	0.01006	0.00616	0.00724	0.00489	0.25299	0.64474	0.00000	0.03393
4.00	0.00312	0.00031	0.00016	0.00146	0.01011	0.00618	0.00727	0.00490	0.25375	0.64369	0.00000	0.03409
2.33	0.00312	0.00031	0.00016	0.00146	0.01008	0.00617	0.00725	0.00489	0.25342	0.64421	0.00000	0.03399
1.50	0.00312	0.00031	0.00016	0.00146	0.01019	0.00624	0.00734	0.00491	0.29467	0.64227	0.00000	0.03438
1.00	0.00312	0.00031	0.00016	0.00146	0.01037	0.00635	0.00746	0.00495	0.29656	0.63933	0.00000	0.03499
0.67	0.00312	0.00031	0.00016	0.00146	0.01016	0.00622	0.00732	0.00494	0.28666	0.65038	0.00000	0.03432
0.54	0.00312	0.00031	0.00016	0.00146	0.01021	0.00625	0.00735	0.00492	0.29349	0.64334	0.00000	0.03444
0.43	0.00312	0.00031	0.00016	0.00146	0.01023	0.00626	0.00736	0.00492	0.29401	0.64273	0.00000	0.03450
0.33	0.00312	0.00031	0.00016	0.00146	0.01026	0.00628	0.00738	0.00493	0.29417	0.64238	0.00000	0.03461
0.25	0.00312	0.00031	0.00016	0.00146	0.00973	0.00666	0.00769	0.00523	0.15967	0.74216	0.00000	0.03406
0.18	0.00312	0.00031	0.00016	0.00146	0.00849	0.00554	0.00639	0.00515	0.10632	0.83458	0.00000	0.03354
0.11	0.00312	0.00031	0.00016	0.00146	0.00543	0.00402	0.00451	0.00395	0.04093	0.90715	0.00000	0.03381
0.01	0.00312	0.00031	0.00016	0.00146	0.00006	0.00006	0.00006	0.00006	0.00009	0.99042	0.00000	0.00926

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-16: P=5 ATM.T=573 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00118	0.00025	0.05108	0.94536	0.00000	0.00073
9.00	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00118	0.00024	0.05084	0.94574	0.00000	0.00060
4.00	0.00004	0.00000	0.00000	0.00007	0.00088	0.00054	0.00119	0.00025	0.05109	0.94540	0.00000	0.00066
2.33	0.00004	0.00000	0.00000	0.00007	0.00089	0.00054	0.00120	0.00025	0.05124	0.94517	0.00000	0.00071
1.50	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00117	0.00025	0.05086	0.94583	0.00000	0.00048
1.00	0.00004	0.00000	0.00000	0.00007	0.00086	0.00052	0.00115	0.00025	0.05026	0.94630	0.00000	0.00067
0.82	0.00004	0.00000	0.00000	0.00007	0.00086	0.00052	0.00115	0.00025	0.05043	0.94650	0.00000	0.00030
0.67	0.00004	0.00000	0.00000	0.00007	0.00086	0.00052	0.00115	0.00025	0.05051	0.94610	0.00000	0.00060
0.50	0.00004	0.00000	0.00000	0.00007	0.00071	0.00052	0.00083	0.01478	0.04043	0.91515	0.02762	0.00000
0.43	0.00004	0.00000	0.00000	0.00007	0.00033	0.00025	0.00038	0.00739	0.02522	0.80975	0.15669	0.00000
0.33	0.00004	0.00000	0.00000	0.00007	0.00032	0.00025	0.00037	0.00627	0.02066	0.63016	0.34159	0.00000
0.25	0.00004	0.00000	0.00000	0.00007	0.00029	0.00023	0.00033	0.00391	0.00989	0.20670	0.77965	0.00000
0.11	0.00004	0.00000	0.00000	0.00007	0.00029	0.00023	0.00033	0.00391	0.00989	0.20670	0.77965	0.00000
0.01	0.00004	0.00000	0.00000	0.00007	0.00018	0.00016	0.00020	0.00078	0.00133	0.01610	0.97952	0.00172

S/N	S2	S3	S4	S5	S6	S7	S8	CC	COS	CO2	SO2	CS2
100.00	0.00004	0.00000	0.00000	0.00007	0.00087	0.00053	0.00117	0.00025	0.05070	0.94576	0.00000	0.00072
9.00	0.00004	0.00000	0.00000	0.00007	0.00087	0.00053	0.00117	0.00025	0.05065	0.94583	0.00000	0.00072
4.00	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00118	0.00025	0.05006	0.94639	0.00000	0.00072
2.33	0.00004	0.00000	0.00000	0.00007	0.00087	0.00053	0.00117	0.00025	0.05076	0.94569	0.00000	0.00072
1.50	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00119	0.00025	0.05096	0.94545	0.00000	0.00073
1.00	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00118	0.00025	0.05070	0.94573	0.00000	0.00073
0.67	0.00004	0.00000	0.00000	0.00007	0.00088	0.00054	0.00119	0.00025	0.04968	0.94673	0.00000	0.00073
0.54	0.00004	0.00000	0.00000	0.00007	0.00088	0.00054	0.00119	0.00025	0.05077	0.94564	0.00000	0.00073
0.43	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00119	0.00025	0.05090	0.94552	0.00000	0.00073
0.33	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00119	0.00025	0.05103	0.94539	0.00000	0.00073
0.25	0.00004	0.00000	0.00000	0.00007	0.00088	0.00053	0.00119	0.00025	0.05035	0.94607	0.00000	0.00073
0.18	0.00004	0.00000	0.00000	0.00007	0.00086	0.00052	0.00116	0.00025	0.05048	0.94601	0.00000	0.00071
0.11	0.00004	0.00000	0.00000	0.00007	0.00086	0.00052	0.00116	0.00025	0.05044	0.94605	0.00000	0.00071
0.01	0.00004	0.00000	0.00000	0.00007	0.00056	0.00038	0.00070	0.00021	0.00686	0.99058	0.00000	0.00070

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-C SYSTEM
TABLE-17: P=5 ATM,T=673 K

C/C	S2	S3	S4	S5	S6	S7	S8	CC	COS	CO2	SC2	CS2
100.00	0.00125	0.00012	0.00007	0.00058	0.00403	0.00247	0.00259	0.00338	0.20296	0.77066	0.00000	0.01361
9.00	0.00125	0.00012	0.00007	0.00058	0.00405	0.00248	0.00251	0.00339	0.20330	0.77023	0.00000	0.01365
4.00	0.00125	0.00012	0.00007	0.00058	0.00407	0.00249	0.00253	0.00340	0.20385	0.76953	0.00000	0.01373
2.33	0.00125	0.00012	0.00007	0.00058	0.00414	0.00253	0.00258	0.00342	0.20521	0.76778	0.00000	0.01395
1.50	0.00125	0.00012	0.00007	0.00058	0.00426	0.00256	0.00266	0.00339	0.20349	0.76956	0.00000	0.01369
1.00	0.00125	0.00012	0.00007	0.00058	0.00359	0.00244	0.00287	0.00333	0.20187	0.77201	0.00000	0.01348
0.82	0.00125	0.00012	0.00007	0.00058	0.00365	0.00244	0.00287	0.00337	0.20202	0.77187	0.00000	0.01345
0.67	0.00125	0.00012	0.00007	0.00058	0.00401	0.00245	0.00288	0.00338	0.20246	0.77131	0.00000	0.01352
0.59	0.00125	0.00012	0.00007	0.00058	0.00170	0.00133	0.00144	0.02314	0.05270	0.88172	0.03755	0.00000
0.43	0.00125	0.00012	0.00007	0.00058	0.00123	0.00055	0.00104	0.01957	0.04350	0.76375	0.16956	0.00001
0.33	0.00125	0.00012	0.00007	0.00058	0.00104	0.00082	0.00189	0.01581	0.03446	0.59782	0.34916	0.00000
0.25	0.00125	0.00012	0.00007	0.00058	0.00053	0.00074	0.00180	0.01240	0.02669	0.44991	0.50852	0.00000
0.11	0.00125	0.00012	0.00007	0.00058	0.00087	0.00072	0.00377	0.01722	0.01342	0.18461	0.78081	0.01156
0.01	0.00125	0.00012	0.00007	0.00058	0.00310	0.00110	0.00310	0.00011	0.00011	0.00066	0.98008	0.01674

S/N	S2	S3	S4	S5	S6	S7	S8	CC	CCS	CC2	SO2	CS2
100.00	0.00125	0.00012	0.00007	0.00058	0.00405	0.00248	0.00251	0.00339	0.20337	0.77014	0.00000	0.01366
9.00	0.00125	0.00012	0.00007	0.00058	0.00405	0.00248	0.00252	0.00339	0.20339	0.77011	0.00000	0.01367
4.00	0.00125	0.00012	0.00007	0.00058	0.00403	0.00247	0.00250	0.00339	0.20129	0.77231	0.00000	0.01361
2.33	0.00125	0.00012	0.00007	0.00058	0.00403	0.00246	0.00250	0.00338	0.20250	0.77114	0.00000	0.01355
1.50	0.00125	0.00012	0.00007	0.00058	0.00407	0.00249	0.00253	0.00341	0.20124	0.77213	0.00000	0.01373
1.00	0.00125	0.00012	0.00007	0.00053	0.00406	0.00248	0.00252	0.00340	0.20277	0.77070	0.00000	0.01368
0.67	0.00125	0.00012	0.00007	0.00058	0.00408	0.00250	0.00254	0.00340	0.20413	0.76917	0.00000	0.01378
0.54	0.00125	0.00012	0.00007	0.00058	0.00410	0.00251	0.00255	0.00341	0.20447	0.76873	0.00000	0.01383
0.43	0.00125	0.00012	0.00007	0.00058	0.00412	0.00252	0.00256	0.00342	0.20481	0.76825	0.00000	0.01389
0.33	0.00125	0.00012	0.00007	0.00058	0.00418	0.00256	0.00261	0.00344	0.20623	0.76647	0.00000	0.01411
0.25	0.00125	0.00012	0.00007	0.00058	0.00409	0.00250	0.00254	0.00341	0.20284	0.77043	0.00000	0.01379
0.18	0.00125	0.00012	0.00007	0.00058	0.00359	0.00244	0.00267	0.00337	0.20208	0.77175	0.00000	0.01346
0.11	0.00125	0.00012	0.00007	0.00058	0.00387	0.00241	0.00282	0.00349	0.11451	0.85945	0.00000	0.01345
0.01	0.00125	0.00012	0.00007	0.00058	0.00009	0.00008	0.00009	0.00009	0.00017	0.99956	0.00000	0.00892

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-19: P=10 ATM.T=573 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00002	0.00000	0.00000	0.00003	0.00042	0.00026	0.00056	0.00018	0.03638	0.96215	0.00000	0.00005
9.00	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03634	0.96184	0.00000	0.00035
4.00	0.00002	0.00000	0.00000	0.00003	0.00043	0.00026	0.00057	0.00012	0.03598	0.96246	0.00000	0.00019
2.33	0.00002	0.00000	0.00000	0.00003	0.00039	0.00025	0.00052	0.00018	0.03478	0.96380	0.00000	0.00008
1.50	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00060	0.00018	0.03648	0.96167	0.00000	0.00037
1.00	0.00002	0.00000	0.00000	0.00003	0.00043	0.00026	0.00058	0.00018	0.03601	0.96224	0.00000	0.00030
0.82	0.00002	0.00000	0.00000	0.00003	0.00043	0.00026	0.00058	0.00018	0.03593	0.96228	0.00000	0.00034
0.67	0.00002	0.00000	0.00000	0.00003	0.00042	0.00026	0.00055	0.00017	0.03568	0.96288	0.00000	0.00005
0.50	0.00002	0.00000	0.00000	0.00003	0.00045	0.00030	0.00056	0.01425	0.03892	0.91888	0.02662	0.00030
0.43	0.00002	0.00000	0.00000	0.00003	0.00022	0.00017	0.00026	0.00696	0.02371	0.81278	0.15589	0.00000
0.33	0.00002	0.00000	0.00000	0.00003	0.00021	0.00016	0.00024	0.00472	0.01515	0.47487	0.50465	0.00000
0.25	0.00002	0.00000	0.00000	0.00003	0.00021	0.00016	0.00024	0.00374	0.00952	0.20734	0.77876	0.00000
0.11	0.00002	0.00000	0.00000	0.00003	0.00022	0.00017	0.00025	0.00374	0.00952	0.20734	0.77876	0.00000
0.01	0.00002	0.00000	0.00000	0.00003	0.00015	0.00013	0.00016	0.00074	0.00130	0.01640	0.97961	0.00150

S/0	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00002	0.00000	0.00000	0.00003	0.00043	0.00026	0.00058	0.00018	0.03581	0.96238	0.00000	0.00036
9.00	0.00002	0.00000	0.00000	0.00003	0.00044	0.00026	0.00059	0.00018	0.03626	0.96191	0.00000	0.00036
4.00	0.00002	0.00000	0.00000	0.00003	0.00044	0.00026	0.00058	0.00017	0.02980	0.96864	0.00000	0.00011
2.33	0.00002	0.00000	0.00000	0.00003	0.00044	0.00026	0.00059	0.00018	0.03410	0.96408	0.00000	0.00036
1.50	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03628	0.96188	0.00000	0.00037
1.00	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03635	0.96181	0.00000	0.00036
0.67	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03641	0.96175	0.00000	0.00037
0.54	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03628	0.96188	0.00000	0.00036
0.43	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00060	0.00018	0.03651	0.96164	0.00000	0.00037
0.33	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03644	0.96171	0.00000	0.00037
0.25	0.00002	0.00000	0.00000	0.00003	0.00044	0.00027	0.00059	0.00018	0.03549	0.96268	0.00000	0.00036
0.18	0.00002	0.00000	0.00000	0.00003	0.00043	0.00026	0.00057	0.00018	0.03574	0.96247	0.00000	0.00035
0.11	0.00002	0.00000	0.00000	0.00003	0.00043	0.00026	0.00058	0.00018	0.03604	0.96215	0.00000	0.00036
0.01	0.00002	0.00000	0.00000	0.00003	0.00040	0.00025	0.00052	0.00018	0.01080	0.98749	0.00000	0.00035

EQUILIBRIUM GAS PHASE MOLE FRACTIONS FOR THE S-C-O SYSTEM
TABLE-20: P=10 ATM,T=673 K

C/O	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00062	0.00006	0.00003	0.00029	0.00203	0.00124	0.00146	0.00250	0.14991	0.83603	0.00000	0.00684
9.00	0.00062	0.00006	0.00003	0.00029	0.00202	0.00123	0.00145	0.00250	0.14963	0.83646	0.00000	0.00671
4.00	0.00062	0.00006	0.00003	0.00029	0.00204	0.00125	0.00147	0.00251	0.15031	0.83558	0.00000	0.00686
2.33	0.00062	0.00006	0.00003	0.00029	0.00203	0.00124	0.00146	0.00250	0.15018	0.83696	0.00000	0.00563
1.50	0.00062	0.00006	0.00003	0.00029	0.00204	0.00125	0.00147	0.00251	0.15034	0.83589	0.00000	0.00651
1.00	0.00062	0.00006	0.00003	0.00029	0.00199	0.00122	0.00143	0.00248	0.14877	0.83766	0.00000	0.00644
0.82	0.00062	0.00006	0.00003	0.00029	0.00197	0.00121	0.00142	0.00237	0.14008	0.84031	0.00000	0.00664
0.67	0.00062	0.00006	0.00003	0.00029	0.00200	0.00122	0.00144	0.00247	0.14877	0.83736	0.00000	0.00674
0.53	0.00062	0.00006	0.00003	0.00029	0.00114	0.00067	0.00055	0.02141	0.04880	0.89170	0.03513	0.00000
0.43	0.00062	0.00006	0.00003	0.00029	0.00081	0.00061	0.00067	0.01547	0.03863	0.76580	0.17139	0.00661
0.33	0.00062	0.00006	0.00003	0.00029	0.00078	0.00060	0.00065	0.01524	0.03302	0.60095	0.34874	0.00001
0.25	0.00062	0.00006	0.00003	0.00029	0.00065	0.00050	0.00055	0.01165	0.02522	0.45308	0.50835	0.00000
0.11	0.00062	0.00006	0.00003	0.00029	0.00058	0.00047	0.00050	0.00649	0.01280	0.20343	0.77872	0.00000
0.01	0.00062	0.00006	0.00003	0.00029	0.00040	0.00035	0.00036	0.00139	0.00190	0.01665	0.97856	0.00000

S/C	S2	S3	S4	S5	S6	S7	S8	CO	COS	CO2	SO2	CS2
100.00	0.00062	0.00006	0.00003	0.00029	0.00202	0.00123	0.00145	0.00249	0.14953	0.83648	0.00000	0.00680
9.09	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.00250	0.14781	0.83953	0.00000	0.00547
4.00	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.00249	0.14946	0.83656	0.00000	0.00679
2.33	0.00062	0.00006	0.00003	0.00029	0.00201	0.00123	0.00145	0.00249	0.14929	0.83673	0.00000	0.00675
1.50	0.00062	0.00006	0.00003	0.00029	0.00205	0.00125	0.00147	0.00251	0.15066	0.83514	0.00000	0.00691
1.00	0.00062	0.00006	0.00003	0.00029	0.00203	0.00124	0.00146	0.00250	0.14991	0.83603	0.00000	0.00684
0.67	0.00062	0.00006	0.00003	0.00029	0.00202	0.00124	0.00146	0.00251	0.14319	0.84275	0.00000	0.00683
0.54	0.00062	0.00006	0.00003	0.00029	0.00203	0.00124	0.00146	0.00250	0.15015	0.83574	0.00000	0.00686
0.43	0.00062	0.00006	0.00003	0.00029	0.00205	0.00125	0.00147	0.00251	0.15058	0.83523	0.00000	0.00690
0.33	0.00062	0.00006	0.00003	0.00029	0.00204	0.00125	0.00147	0.00251	0.15045	0.83538	0.00000	0.00685
0.25	0.00062	0.00006	0.00003	0.00029	0.00204	0.00125	0.00147	0.00251	0.15028	0.83558	0.00000	0.00688
0.18	0.00062	0.00006	0.00003	0.00029	0.00199	0.00122	0.00143	0.00248	0.14861	0.83757	0.00000	0.00671
0.11	0.00062	0.00006	0.00003	0.00029	0.00200	0.00122	0.00144	0.00248	0.14892	0.83720	0.00000	0.00674
0.01	0.00062	0.00006	0.00003	0.00029	0.00028	0.00023	0.00025	0.00031	0.00105	0.99112	0.00000	0.00676

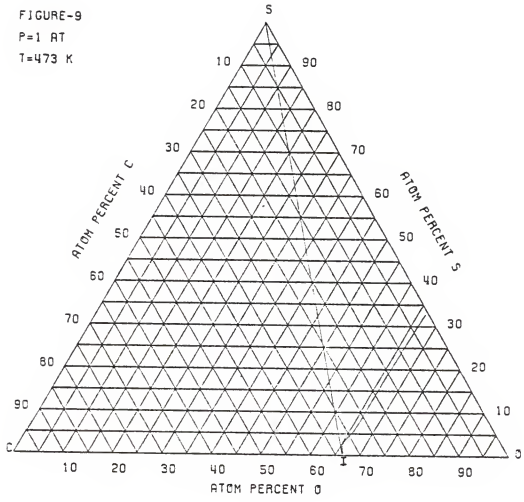


FIGURE-9
P=1 AT
T=473 K
S
C
O
ATOM PERCENT C
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90
1

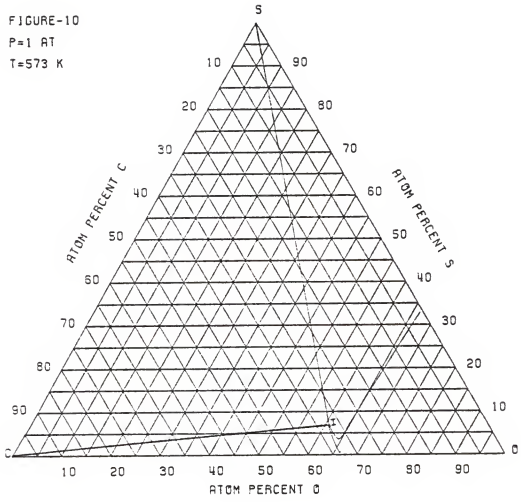
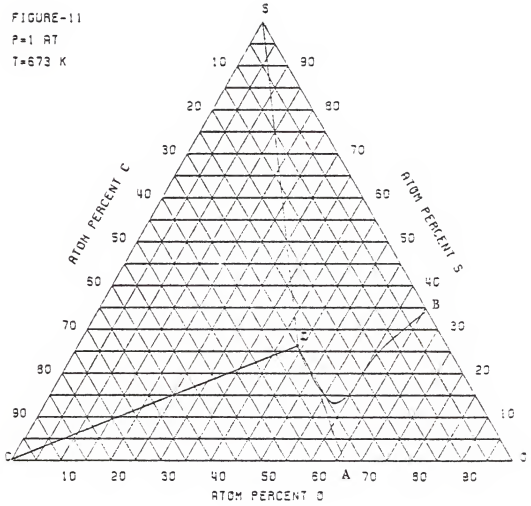


FIGURE-10
P=1 AT
T=573 K
S
C
O
ATOM PERCENT C
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90

FIGURE-11
P=1 AT
T=673 K



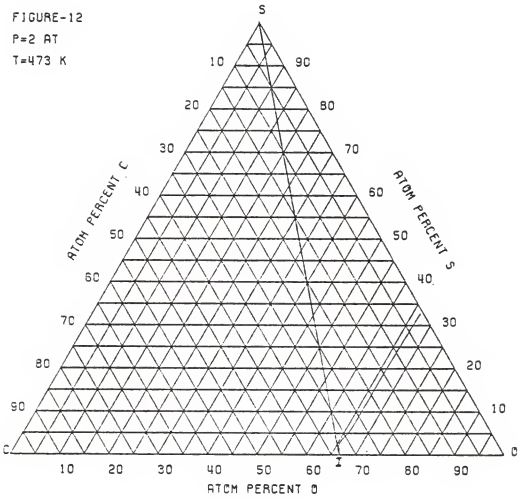


FIGURE-12
P=2 AT
T=473 K
S
C
O
ATOM PERCENT C
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90

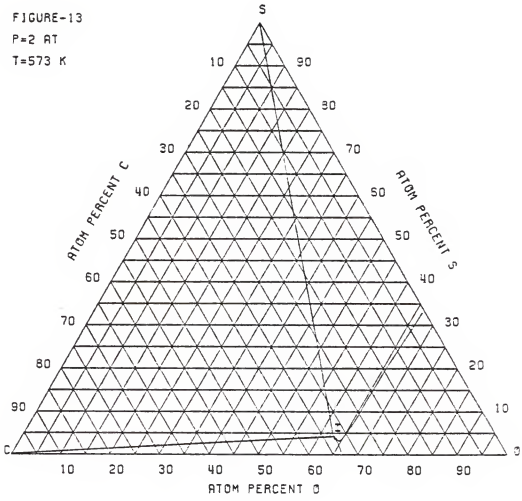


FIGURE-13
P=2 AT
T=573 K
S
C
O
ATOM PERCENT C
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90

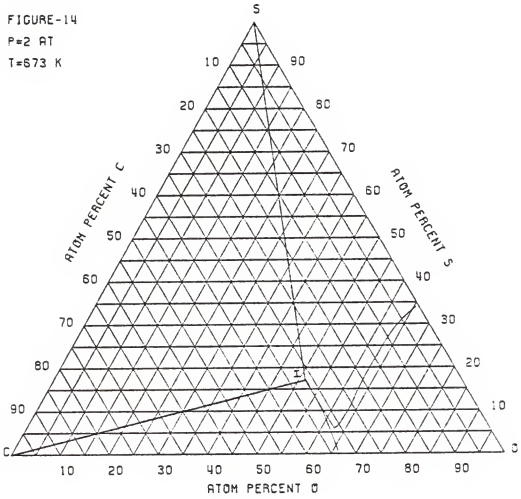


FIGURE-14
P=2 AT
T=673 K
S
10
90
20
80
30
70
40
60
50
50
60
40
70
30
80
20
90
10
C
O
ATOM PERCENT C
ATOM PERCENT S
10 20 30 40 50 60 70 80 90
ATOM PERCENT O

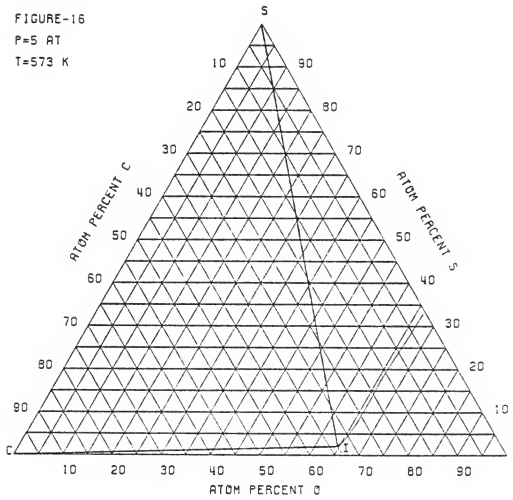


FIGURE-16
P=5 AT
T=573 K
S
10
20
30
40
50
60
70
80
90
ATOM PERCENT C
ATOM PERCENT S
C
C
10
20
30
40
50
60
70
80
90
ATOM PERCENT O

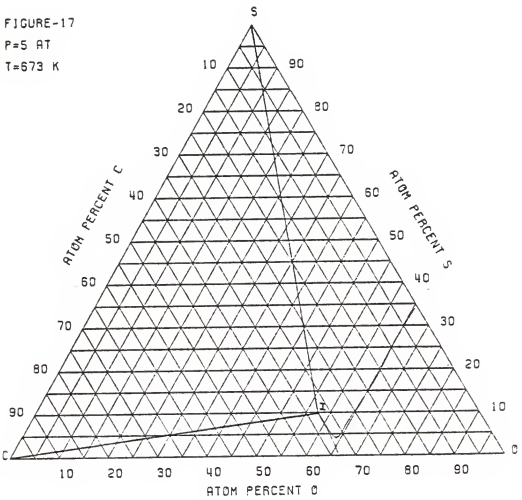


FIGURE-17
P=5 AT
T=673 K
S
C
O
ATOM PERCENT C
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90

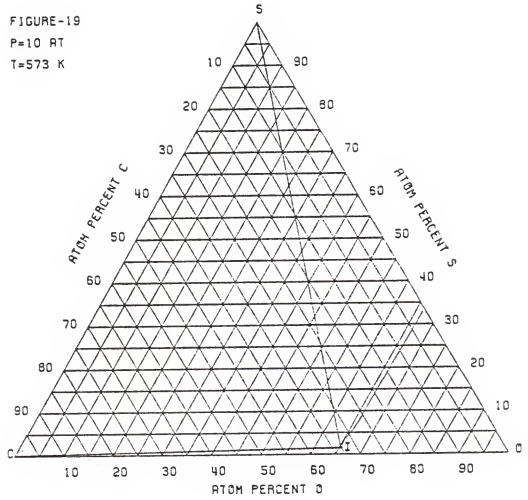


FIGURE-19
P=10 AT
T=573 K
S
10
90
20
80
30
70
40
60
50
50
60
40
70
30
80
20
90
10
C
O
ATOM PERCENT C
ATOM PERCENT S
10 20 30 40 50 60 70 80 90
ATOM PERCENT O

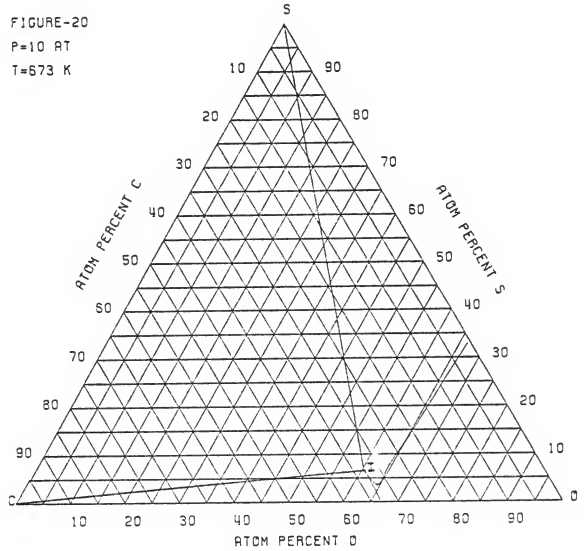


FIGURE-20
P=10 AT
T=673 K
S
C
O
ATOM PERCENT C
ATOM PERCENT S
ATOM PERCENT O
10
20
30
40
50
60
70
80
90

NOMENCLATURE

A_i - Abbreviation for $C_i + \ln \frac{n_i}{n}$

a_{ji} - Number of atoms of j-th element in one molecule of the i-th component

B_i - Abbreviation for $n_i A_i$

b_j - Total number of atoms of j-th element in the system

C - Components of the system, in the sense of the phase rule

c - Number of components present in the system

c_i - Abbreviation for $\frac{\mu_i^0}{RT} + \ln P$, for the i-th species in the gas-phase

d_i - Abbreviation for $\frac{\mu_i^0}{RT}$, for the i-th species in the condensed phase

E - Elements in the system, in the sense of the phase rule

F - Number of degrees of freedom

- Objective function

f_i - Fugacity of pure i-th species, at total system pressure P, and temperature T

$\hat{f}_i$ - Fugacity of i-th species in the system

m - Number of elements in the system

N - Number of components in the system, in the sense of the phase rule

n - Total number of moles in the gas phase

n_i - Number of moles of i-th species in the system

P - Number of phases, in the sense of the phase rule

- Pressure of the system

R - Number of independent reactions, in the sense of the phase rule

- Gas constant

$r_{j\ell}$ - Abbreviation for $\sum_i a_{ji} a_{\ell i} n_i$ for all components i, in the gas phase

S - Number of additional restrictions, in the sense of the phase rule

s - Number of non-gaseous components of the system

T - Temperature of the system

v_{ci} - Specific volume of the i-th non-gaseous component

y_i - Mole fraction of the i-th gaseous component

Greek

Δ - Abbreviation for $n^{\nu+1} - n^{\nu}$

Δ_i - Abbreviation for $n_i^{\nu+1} - n_i^{\nu}$

δ - Specified limit of relative change in mole number, for convergence criterion

λ - Fraction of calculated travel, so that mole numbers are positive and free energy is not increasing

μ_i - Chemical potential of the i-th species

μ_i^0 - Chemical potential of the i-th species, in standard state, referred to elements

π_j - Lagrangian multiplier associated with atomic balance for the j-th element

Subscripts

i,ℓ - For the i-th species in the system

j - For atomic species

Superscripts

0 - To denote standard state

$\nu,\nu+1$ - Number of iteration

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APPENDIX

The free energy data for most of the components included in the previous equilibrium calculations were taken from the JANAF thermochemical tables, published by the Thermal Research Laboratory of the Dow Chemical Company.

Free energy data for the sulphur species S_2, S_3, S_4, S_5, S_6, S_7 and S_8 were taken from the articles by Detry (5) and Berkowitz (6). For temperatures not included in the previous sources, the free energy data were calculated by means of the formula (11):

$$\Delta G = \Delta H_0 - 2.303\Delta a T \log T - \frac{1}{2}\Delta b T^2 + \frac{1}{2}\Delta c \frac{1}{T} + IT$$

where ΔH_0, Δa, Δb, Δc and I are constants for each component of a system, and which were available (11), or were calculated by means of the existing data and the above equation.

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CALCULATION OF COMPLEX CHEMICAL EQUILIBRIUM IN SYSTEMS CONTAINING ONE OR MORE CONDENSED PHASES

by

JOHN G. FIMERELLIS

Diploma, Polytechnic School of Athens, 1977

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

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Department of Chemical Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1979

The objectives of this work have been:

1) To derive and use the general technique of heterogeneous complex chemical equilibrium calculations based on free energy minimization as the core of a computer program which can be used to solve the majority of the chemical equilibrium problems.
2) To use this program in order to study chemical equilibrium in the Sulphur-Hydrogen-Oxygen and Sulphur-Carbon-Oxygen systems.

The range of the temperature is from 200° to 400°C (the atmospheric boiling point for sulfur is 444.6°C), the range of the pressure from 1 to 10 atm, and elemental ratios vary from 0.01 to 100.00.

The results of the equilibrium calculations were plotted on triangular diagrams for both systems.

For the Sulphur-Hydrogen-Oxygen system a single deposition boundary was found corresponding to the condensed phase of liquid sulphur.

For the sulphur-carbon-oxygen system two deposition boundaries were found in general, corresponding to the condensed phases of liquid sulphur and solid carbon and having only one point of intersection which represents the gas-phase equilibrium composition of any system which contains both liquid sulphur and solid carbon at equilibrium.