

COMPUTER SIMULATION OF PROCESSES INVOLVING
MULTICOMPONENT MULTIPHASE EQUILIBRIA

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ABSTRACT

COMPUTER SIMULATION OF PROCESSES INVOLVING MULTICOMPONENT MULTIPHASE EQUILIBRIA

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A computer program applicable for simulating the chemical processes involving multicomponent multiphase equilibria was developed. The assemblage of the equilibrium phases and their compositions were determined from Gibbs energy minimization. The thermodynamic state of the system was specified by assigning the temperature and pressure.

The algorithm of the optimization routine was based on the minimization of the Gibbs energy. The minimization method was performed using the Lagrange's method of undetermined multipliers. The Lagrangian function, \mathcal{L} , was constructed in terms of the emphasized thermodynamic function, the Gibbs energy, G , which defines the state of the equilibrium of the system, and the necessary subsidiary, material balance conditions.

Selected well-known systems were simulated and the solutions were compared with a popular commercial software, F*A*C*T (Facility for the Analysis of Chemical Thermodynamics).

Keywords: Gibbs energy, minimization, optimization, Lagrange function, chemical equilibrium

ÖZ

ÇOK BİLEŞENLİ ÇOK FAZLI DENGELERİ İÇEREN İŞLEMLERİN BİLGİSAYAR BENZETİŞİMİ

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Çok bileşenli çok fazlı dengeleri içeren kimyasal süreçlerin benzetişimini yapabilen bir bilgisayar programı geliştirilmiştir. Denge fazlarının ve kompozisyonlarının belirlenmesi Gibbs enerji minimizasyonu ile sağlanmıştır. Sistemin termodinamik durumu sıcaklık ve basıncının verilmesiyle belirlenmiştir.

Optimizasyon hesapları Gibbs enerjinin minimizasyonu üzerine kuruludur. Minimizasyon işlemi, Lagrange fonksiyonunun belirsiz çarpanları yöntemi kullanılarak gerçekleştirilmiştir. Lagrange fonksiyonu, sistemin durumunu tanımlayan bahsi geçen termodinamik fonksiyon, Gibbs enerji, G , ve gerekli tamamlayıcı kütle balans şartları ile oluşturulmuştur.

Hazırlanan bilgisayar programı ile iyi bilinen sistemlerden seçilmiş örneklerin benzetişimi yapılmış ve sonuçlar popüler bir ticari program olan F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) sonuçları ile karşılaştırılmıştır.

Anahtar Kelimeler: Gibbs enerjisi, çok bileşenli, çok fazlı, bilgisayar benzetimi

To my family

I am deeply indebted to my parents.

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CHAPTER 1

INTRODUCTION

In every chemical process it is important to know the outcome of the present conditions in advance. Therefore, people are always interested in predicting the stable species in a chemical system.

In metallurgical and materials engineering processes, reliable phase diagrams are the mandatory tools which mostly are very difficult to obtain experimentally. Hence, computational phase diagrams have been developed by the Gibbs energy calculations. There are other types of diagrams such as predominance area diagrams (PADs); Kellogg diagrams and Pourbaix diagrams, the topological equivalents of the PADs, which are employed in pyrometallurgical, hydrometallurgical, electrochemical, and corrosion processes [1]. All these diagrams are results of chemical equilibrium calculations.

The advantages of using the multiphase free energy methods have also been utilized in chemical engineering [2]. In the analysis and design of a wide variety of chemical processes, knowing the chemical equilibrium compositions of the system is important [3, 4]. For example, to succeed the separation of fluid mixtures which is a fundamental aspect of chemical process design [5], the chemical and phase equilibrium between these fluids should be described with reliable thermodynamic models.

The subject discussed in this study, i.e. chemical equilibria calculations, are used in different disciplines. For example in oil recovery simulations [6] in petroleum engineering, rock formation and the conditions of the earth in geochemistry.

1.1 Statement of the Problem

Since the thermodynamic models consist of nonlinear equations, the chemical equilibrium calculation problems are mathematically described as complex systems. A considerable amount of studies, both on solving nonlinear equations and specifically concentrated on the chemical equilibrium calculations, can be found in the literature. A short bibliography of the studies which are of interest is given in the next section.

The chemical equilibria calculation studies are generally classified into two major categories on the basis of the method used to solve the problem.

The first is the equation-solving method which based on solving a set of nonlinear algebraic equations derived from equilibrium constant expressions and the mass balance equations. The work of Brinkley [7] was the first in this branch. The use of optimization methods involving the minimization of the Gibbs energy is the second fundamental and the most favored way to solve the problem formed by a nonlinear function, G , with material balance constraints. An optimization technique was first applied to a chemical equilibrium problem by White et.al [8].

The Gibbs energy minimization method is usually performed using the Lagrange method of undetermined multipliers together with the mass balance conditions of the system components as the essential constraints.

The Lagrangian function, \mathcal{L} , is constructed in terms of the thermodynamic function, the Gibbs energy, G , which defines the state of the equilibrium of the system, and the necessary subsidiary, material balance conditions:

$$\mathcal{L} = G - \sum_{j=1}^l \lambda_j \phi_j \quad (1.1)$$

in which λ_j 's are the undetermined multipliers of the Lagrangian and ϕ_j 's denote the particular mass balance equations as follows:

$$\phi_j = b_j^o - \sum_{p=1}^{NP} \sum_{c=1}^{NC} a_{cj}^p n_c^p \quad (j = 1, 2, \dots, l) \quad (1.2)$$

where the total input amount of a system component is denoted by b_j^o , and a_{cj}^p is assigned to the stoichiometric number of component j in constituent c , in the phase p . The number of moles of species c in phase p is represented by n_c^p . NC and NP refer to the number of constituents and the total number of phases, respectively. The system components are generally chosen as the chemical elements.

1.2 Literature Review

In 1947, Brinkley [7] developed a computational procedure for the calculation of the equilibrium composition of the systems which consist of many constituents. He was the first to treat the problem of the numerical solution of the nonlinear chemical-equilibrium equations for a general chemical system [9]. In this study, the thermodynamic state of the system was specified by assigning the temperature and pressure. The mathematical base of the method was the expansion of the nonlinear set of equations defining the problem in a Taylor series about an approximate set of values of the variables by neglecting terms higher than the first order.

After a few years, in 1951, Huff, Gordon and Morrell [10] described a successive approximation process that simultaneously determines both composition and temperature resulting from a chemical reaction, in their report written for National Advisory Committee for Aeronautics, NACA (predecessor of NASA). In this study, the thermodynamic state of the system was specified by assigning the pressure and either the temperature, the enthalpy, or the entropy depending on the specific process.

One of the oldest methods [8] belongs to White et.al, who considered the chemical equilibrium in an ideal gas mixture of O, H and N with the species H, H₂, H₂O, N, N₂, NH, NO, O, O₂ and OH, published in 1958. Finding the most stable mixture of species

was the problem. The method for the determination of the complex mixture of species was based on the minimization of free energy. The thermodynamic state of the system was specified by assigning the temperature and pressure. In this paper, two different computation procedures; one using a steepest descent technique applied to a quadratic fit and the other making use of linear programming, were shown. White and co-authors employed the Lagrangian of a truncated Taylor's expansion of Gibbs energy. The method, as originally presented, treated problems involving only gaseous reaction products. It was later extended first by Kubert and Stephanou [11] to include condensed reaction products. After many others, Dluzniewski and Adler presented the final form being the RAND algorithm [12].

Gordon et.al [13] presented the slightly modified form of the Huff method for computing equilibrium compositions and theoretical rocket performance of propellants in another report, prepared for NASA.

An analytical investigation of the Brinkley [7], Huff [10] and White [8] methods for chemical-equilibrium calculations was reported by Zeleznik and Gordon [9] in 1960 for NASA. The modified and extended versions of the methods were discussed in detail in this review. The Brinkley-NASA-RAND (shortly BNR) algorithm with three variations was discussed with an illustrative example for usage of the RAND variation in "Chemical reaction equilibrium analysis: Theory and algorithms" [14].

Clasen [15] and Eriksson and Rosen [16] proposed two other algorithms which were applicable to multiphase systems in 1965 and 1973 respectively. These algorithms were similar to those of White et.al in that they employed the Lagrangian of a truncated Taylor's series.

While the last two algorithms were originally restricted to ideal systems, in a subsequent paper, in 1975, Eriksson [17] described a computer program called SOLGASMIX which allows the consideration of non-idealities. The program calculates equilibria containing gases, condensed phases, and mixtures at constant total pressure and temperature.

After a while, in 1977, Theodore M. Besmann [18] reported the results of the work sponsored by the United States Energy Research and Development Administration. The author modified the program SOLGASMIX, on the basis of ideal gas law, in order to calculate equilibria at a constant total gas volume with variable total pressure. The new version of the program was called SOLGASMIX-PV.

From the very beginning of these studies, both academic and commercial computer programs have been developed and still they are being improved for extended applications and better accuracies.

1.3 Softwares in chemical equilibrium calculations

In the last decades, several softwares using the minimization methods to determine chemical equilibrium conditions were developed. The most featured and well-known programs are:

- F*A*C*T [19] (Canada)
- MTDATA [20] (United Kingdom)
- ChemSage [21] (Germany)
- Thermo-Calc [22] (Sweden)
- HSC Chemistry [23] (Finland)

F*A*C*T

F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) started as a joint project between the École Polytechnique de Montréal and McGill University in collaboration with Thermfact Inc. in 1976, for carrying out thermodynamic calculations [19]. Its promotion and development both in research and education accelerated by the foundation of the research center CRCT - Centre de Recherche en Calcul Thermochimique / Centre for Research in Computational Thermochemistry in 1984. The collaboration between the F*A*C*T group and GTT-Technologies, lead to the release of the commercial product FactSage[®], one of the largest fully integrated database computing systems in chemical thermodynamics in the world in 2001.

FactSage[®] offers the opportunity to combine a proven software for calculating chemical equilibria with a trusted thermodynamic database. It is possible to access to thermodynamic data on more than 5000 pure substances and solutions, and perform thermodynamic equilibrium calculations of multiphase, multicomponent mixtures which are present in the database.

MTDATA

Developed in the National Physical Laboratory, U.K. MTDATA [20] is a powerful analytical tool for the prediction of equilibrium phases in a given system containing many chemical elements.

MTDATA uses a carefully assessed database to perform equilibrium computations for multicomponent and multiphase systems of interest. Nearly thirty different components and five hundred phases can be considered simultaneously and complicated calculations can be carried out in a reasonable period of time. Assessment, manipulation and retrieval of the data, execution of complicated calculations and construction of binary, ternary, multicomponent, and predominance area diagrams are handled by various modules incorporated into the software. MTDATA also allows users to link MTDATA to their own software or third party commercial software packages which enables users to simulate unit operations within an industrial plant. Special derivatives of MTDATA that are user friendly are also being studied to provide the capabilities of MTDATA to non-expert users for special applications.

ChemSage

ChemSage [21] is a sophisticated database and programming interface for universities and industry. Its powerful computation ability is used to investigate many technical problems and save considerable hours of work compared to conventional approaches. ChemSage and its predecessor SOLGASMIX are used in hundreds of research centers, universities and companies worldwide to obtain reliable, quick and effective results.

ChemSage was developed from Gunnar Eriksson's SOLGASMIX Gibbs energy minimizer program. After its release by GTT-Technologies in 1987, together with

SOLGASMIX, the two programs had the greatest frequency of quotation in the literature. Today, many other similar software programs use the ChemSage 'engine' as a basis. The collaborative efforts between Thermfact/CRCT and GTT-Technologies led to the development of above mentioned FactSage[®] in 2001. FactSage[®] is the fusion of the FACT-Win/F*A*C*T and ChemSage/SOLGASMIX thermochemical packages.

ChemSage Modules allow:

- Thermodynamic property calculations of a single solution and stoichiometric condensed phases with respect to a selected reference state.
- Chemical equilibrium calculations; amounts and/or equilibrium activities of any phase constituent in the system at a defined temperature, pressure or volume.
- Calculation of precipitation temperatures when such particles are formed from the liquid.
- Multi stage reactor simulations by specifying energy and material flows between stages.
- Thermochemical data optimization using experimental findings.
- Automatic phase diagram calculations, new models and data from the field of geochemistry and geophysics and stoichiometric reaction calculations are planned to be included in the new version of ChemSage (V4).

Thermo-Calc

The Thermo-Calc software [22] is another important database and programming interface that is used to carry out thermodynamic calculations. Complicated homogeneous and heterogeneous phase equilibria can be handled by the program and property and/or phase diagrams can be plotted using the results obtained.

Both stoichiometric and non-ideal solution models and databases are totally supported by Thermo-Calc. These models and databases are used to perform calculations on thousands of materials including steels, alloys, slags, salts, ceramics, solders,

polymers, subcritical aqueous solutions, supercritical electrolyte solutions, non-ideal gases and hydrothermal fluids or organic substances. In the calculations, various temperature, pressure and compositions conditions are considered.

Some important modules like DICTRA and DIC_PARROT, which permits running simulations for diffusion controlled transformations in multicomponent systems, are also included in the Thermo-Calc program.

HSC Chemistry

HSC is a conventional software to perform thermodynamic calculations with personal computers [23]. Therefore, it has a wide area of application ranging from industry to research and education.

HSC Chemistry is a strong tool for studying the effects of multiple variables on thermodynamic equilibrium for chosen system. For instance, if the user specifies the starting materials and their amounts together with the temperature and pressure, the program calculates the amounts of the products. It is also possible to carry out heat and material balance calculations by HSC for different processes, which makes such calculations much easier when compared to any manual method. It can also draw Eh-pH-diagrams, which offers a very effective way of investigating the dissolution and corrosion behaviors of different materials.

1.4 Thermodynamic database used in the program

The applications involving chemical reactions require thermodynamic data for individual species. These data supplied in literature, generally, in tabular form which consists of data rows for certain temperatures and columns of data for common thermodynamic properties. For calculation purposes, tabulated data are converted to a compact form which is resulted from simple empirical equations. In this form, a group of thermodynamic data is condensed into a few constants which can accurately reproduce the many data points.

In the database construction, a fourth-order polynomial was used as an empirical representation of the dimensionless form of heat capacity, $C_p^o(T)/R$.

$$C_p^o(T)/R = a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4 \quad (1.3)$$

Enthalpy and entropy are obtained by integrating, $C_p^o(T)$ and $C_p^o(T)/T$, respectively, with respect to T .

$$H^o(T)/RT = -a_1T^{-2} + a_2 \ln T/T + a_3 + a_4T/2 + a_5T^2/3 + a_6T^3/4 + a_7T^4/5 + b_1/T \quad (1.4)$$

$$S^o(T)/R = -a_1T^{-2}/2 - a_2T^{-1} + a_3 \ln T + a_4T + a_5T^2/2 + a_6T^3/3 + a_7T^4/4 + b_2 \quad (1.5)$$

where b_1 and b_2 are integration constants. These equations have been found to accurately reproduce the thermodynamic quantities over a wide range of temperature.

The database used in this study is an extended version of the “*NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species*” [24]. The database originally contains data from sources:

- Data produced at Glenn Research Center
- NIST-JANAF Thermochemical Tables [25]
- Thermodynamic Properties of Individual Substances [26]
- TRC Thermodynamic Tables, NIST
- Thermochemical Data of Pure Substances [27]
- CODATA Key Values for Thermodynamics [28]
- Several J. Phys. Chem. Ref. Data journals

The database was originally build up from more than 1,200 gaseous species and nearly a thousand condensed specie temperature intervals. Nevertheless the core alone is not adequate for metallurgical models since it does not contain data for some compounds, for example those composed of Mn, S, and O₂ or Ag, S, and O₂. Hence, it was extended with data from other sources, like JANAF [25], and Barin [27] as they are some of the fundamental thermodynamic properties sources. The database format used in the present program is given in Table 1.1.

Table 1.1 The database format used in the present program.

Record	Content	Columns
1	Species name or formula Comments and data sources	1 to 16 19 to 80
2	Number of T intervals Reference date code Chemical formula – symbols (all capitals) and numbers Zero for gas; nonzero for condensed <i>(Condensed phases are numbered in increasing order by temperature)</i> Molecular weight Heat of formation at 298.15 K, J/mole	1 to 2 4 to 9 11 to 50 51 to 52 53 to 65 66 to 80
3	Temperature range Number of coefficients for $C_p^o(T)/R$ <i>(always seven)</i> T exponents in empirical equation for $C_p^o(T)/R$ <i>(always -2, -1, 0, 1, 2, 3, 4)</i> $H^o(298.15) - H^o(0)$ J/mole, <i>if available</i>	1 to 22 23 24 to 63 66 to 80
4	First five coefficients for $C_p^o(T)/R$	1 to 80
5	Last two coefficients for $C_p^o(T)/R$ Integration constants b_1 and b_2	1 to 32 49 to 80
-	Repeat 3, 4, and 5 for each interval	-

A small portion of the database is given in appendix.

1.5 Aim of this study

There are many commercial softwares capable of simulating the state of the systems involving multicomponent multiphase equilibria. Some of them are well-known and trusted works. Unfortunately, these softwares are very expensive, especially for students who want to have a tool for educational purposes. For this reason, alternative software aimed to determine chemical equilibrium conditions of systems which is not associated with financial expectations, have been developed.

CHAPTER 2

THEORY

2.1 Introduction

The second law of thermodynamics states that the entropy of an isolated system i.e. the system does not exchange energy or matter with its surroundings, always tends to increase [29]. The entropy change for any process which may be reversible or irreversible, is given as Clausius inequality [30]:

$$dS \geq \frac{dq}{T} \quad (2.1)$$

where S and q represent entropy and heat, respectively.

For an isolated system, change in entropy, obviously, will be greater than or equal to zero, $dS \geq 0$ since $dq = 0$.

At constant temperature and pressure Gibbs energy, G , and at constant pressure the enthalpy, H , are defined as:

$$G = H - TS \quad (2.2)$$

$$H = E + PV \quad (2.3)$$

where E represents the internal energy.

For an infinitesimal change in the system, the Gibbs energy change will be

$$dG = -SdT + VdP \quad (2.4)$$

Thus, for a system at constant temperature and pressure, the equilibrium condition is

$$(dG)_{T,P} = 0 \quad (2.5)$$

Therefore, Gibbs energy is at a minimum.

The detailed information can be found on many textbooks, for example those in references [29, 30].

2.2 Basic Thermodynamic Concepts

2.2.1 Standard and Reference States

The standard state is that of a system chosen as standard for reference by convention. The database used in this study was prepared in such a way that all data are for species at their standard state at the specified temperature. For gaseous species, this is the ideal gas at the standard pressure, 1 bar. The standard state for condensed substances is the pure crystalline or liquid species at the standard pressure, 1 atm. All thermodynamic properties are molar quantities.

A set of reference states for the chemical elements must be specified in order for heats of formation to be uniquely related to specific reactions. The reference state of the elements is generally taken to be the thermodynamically stable state at 298.15 K. The reference state for those elements which are in gaseous form at 298.15 K and 1 bar is taken as gaseous over the entire temperature range. For substances that are condensed at 298.15 K, the entire range is taken to be condensed having transitions to various phases.

2.2.2 Enthalpy and entropy of formation

To compute standard Gibbs energy of formation, ΔG_T^o , enthalpy of formation, ΔH_T^o , and entropy of formation, ΔS_T^o , must be determined at the given temperature, T . For any temperature, T ($T > 298.15K$), Kirchoff equation can be applied

$$\Delta H_T^o = \Delta H_{298.15}^o + \int_{298.15}^T \Delta C_P dT \quad (2.6)$$

where

$$\Delta C_P = \sum C_{P,Product} - \sum C_{P,Reactants} \quad (2.7)$$

The equation (2.6) is valid when there is no phase transformation for the species involved in a compound formation. If any phase change occurs within temperature range from 298.15K to T , the equation should be separated to include changes in C_P values and enthalpy changes associated with the phase transformations. If the product (compound) that is formed by the reaction changes its phase, corresponding enthalpy of transformation, ΔH_{tr}^o , is introduced with a positive sign. If any reactant (element), of reaction discussed, changes phase, its ΔH_{tr}^o value is introduced with a negative sign to the ΔH_T^o expression. So, for the case $T_{tr(Prod)} > T_{tr(React)}$, equation (2.6) becomes:

$$\begin{aligned} \Delta H_T^o = & \Delta H_{298.15}^o + \int_{298.15}^{T_{tr(React)}} \Delta C_{P1} dT - \Delta H_{tr(React)}^o \\ & + \int_{T_{tr(React)}}^{T_{tr(Prod)}} \Delta C_{P2} dT + \Delta H_{tr(Prod)}^o + \int_{T_{tr(Prod)}}^T \Delta C_{P3} dT \end{aligned} \quad (2.8)$$

where $T_{tr(React)}$ and $T_{tr(Prod)}$ are the transformation temperatures of the reactant and the product, respectively. $\Delta H_{tr(React)}^o$ and $\Delta H_{tr(Prod)}^o$ are enthalpy of transformations at their transformation temperatures for the reactant and the product, respectively. ΔC_{P1} , ΔC_{P2} and ΔC_{P3} are ΔC_P values for the temperature ranges over which they are integrated.

Entropy of formation is calculated by:

$$\Delta S_T^o = \Delta S_{298.15}^o + \int_{298.15}^T \frac{\Delta C_P}{T} dT \quad (2.9)$$

When the phase transformations occur, incorporation of entropy changes due to these phase changes yield:

$$\begin{aligned} \Delta S_T^o = \Delta S_{298.15}^o &+ \int_{298.15}^{T_{tr(React)}} \frac{\Delta C_{P1}}{T} dT - \frac{\Delta H_{tr(React)}^o}{T_{tr(React)}} \\ &+ \int_{T_{tr(React)}}^{T_{tr(Prod)}} \frac{\Delta C_{P2}}{T} dT + \frac{\Delta H_{tr(Prod)}^o}{T_{tr(Prod)}} + \int_{T_{tr(Prod)}}^T \frac{\Delta C_{P3}}{T} dT \end{aligned} \quad (2.10)$$

2.2.3 Standard Gibbs energy of formation

The standard Gibbs energy of formation is calculated from:

$$\Delta G_T^o = \Delta H_T^o - T \Delta S_T^o \quad (2.11)$$

The program developed uses the reduced Gibbs function, G/RT , as the objective function i.e. to be minimized. Hence, the calculation is performed as:

$$\frac{\Delta G_T^\circ}{RT} = \frac{\Delta H_T^\circ}{RT} - \frac{\Delta S_T^\circ}{R} \quad (2.12)$$

The calculations for enthalpy of formation and entropy of formation (as dimensionless variations) are done directly using the nine coefficients ($a_1, a_2, \dots, a_7, b_1, b_2$) given in the database as discussed in the section 1.4. The first seven coefficients (a_1, a_2, \dots, a_7) are coming from the C_p expression, b_1 is the coefficient of enthalpy and b_2 is the coefficient of entropy terms given in equations (1.3), (1.4) and (1.5), respectively.

2.2.4 Non-standard state calculations

All the calculations in previous sections were performed at standard state, i.e. at one atmosphere pressure. In any system when the assigned pressure is different from one atmosphere, the Gibbs energy of formation should be calculated according to the procedure illustrated in Figure 2.1.

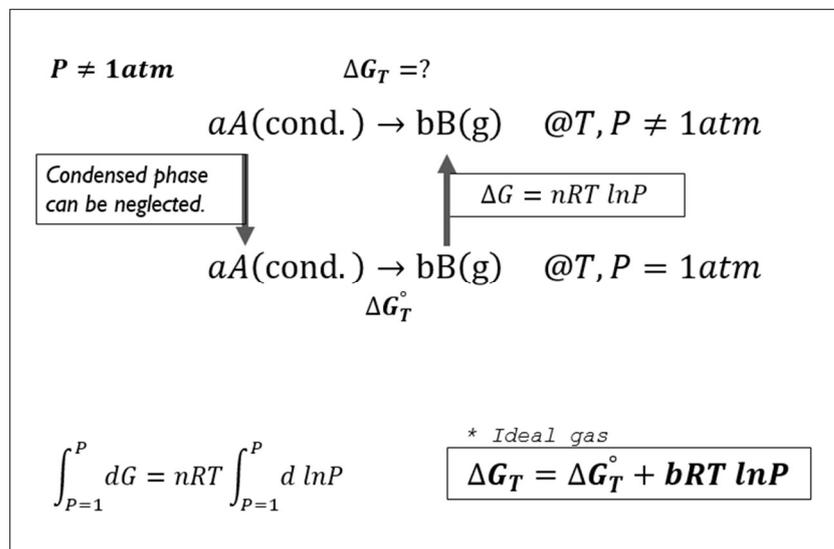


Figure 2.1 Illustration of non-standard state calculation method.

The pressure dependence of G , in the case of pure condensed phases can be given as:

$$dG = V dP, \quad T = \text{constant} \quad (2.13)$$

The change in the Gibbs energy of pure condensed phases as a result of changes in pressure is often negligible in comparison to that resulting from changes in temperature and chemical reactions [27].

CHAPTER 3

PROCEDURE

3.1 Introduction

A basic flowchart of the simulation used in this thesis is given in Figure 3.1.

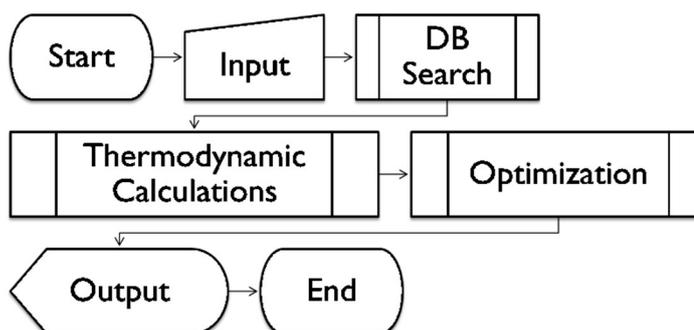


Figure 3.1 Basic flowchart of the simulation.

Any interactive computer software uses the information provided by user, process given and stored data, makes necessary calculations and gives results, in an appropriate format.

As outlined in the main flowchart in Figure 3.1, the program expects the user to define the chemical system. The system is defined by the values of temperature in Kelvins, and pressure in atmospheres and constituents as mole numbers. Although the default units are chosen as Kelvin for temperature and atmosphere for pressure, it is possible to select others from options menu. The program uses certain units implicitly and

makes necessary simple conversions if needed. Similarly, the amount of species build the system can be assigned in grams or kilograms since the molecular weights are stored in the database. For database content and structure, see Table 1.1. In addition, sample of records are given in appendix.

3.2 Database searching

After the completion of user input, the program determines the system constituents in elemental form implicitly and begins searching the database for possible species which can be present in the equilibrium state of the system. As can be seen in Table 1.1, record 2 includes the chemical formula in exploded form, i.e. the symbols and the numbers.

The database searching routine is a very straightforward process and could be handled in many other ways. Table 3.1 shows searching result of the Mg-O-Si system as an example.

Table 3.1 Possible species in Mg-O-Si system.

	Gas phase	Condensed phases
1	Mg	Mg(cr)
2	MgO	Mg(L)
3	Mg ₂	MgO(cr)
4	O	MgO(L)
5	O ₂	MgSiO ₃ (I)
6	O ₃	MgSiO ₃ (II)
7	Si	MgSiO ₃ (III)
8	SiO	MgSiO ₃ (L)
9	SiO ₂	Mg ₂ SiO ₄ (cr)
10	Si ₂	Mg ₂ SiO ₄ (L)
11	Si ₃	Si(cr)
12		Si(L)
13		SiO ₂ (a-qz)
14		SiO ₂ (b-qz)
15		SiO ₂ (b-crt)
16		SiO ₂ (L)

3.3 Thermodynamic calculations

The required thermodynamic calculations for determining equilibrium compositions were discussed in sections “1.4 Thermodynamic database used in the program” and “2.2 Basic Thermodynamic Concepts”. ΔG_T^o for all species from equation (2.12) and ΔG_T according to

$$\Delta G_T = \Delta G_T^o + b RT \ln P \quad (3.1)$$

were calculated when necessary. The last equation is for an arbitrary non-standard state reaction.

3.4 Optimization procedure

3.4.1 Defining the problem

The thermodynamic equilibrium state of a metallurgical (or chemical) system, for a given temperature and pressure, can be defined as a mathematical problem:

*Minimize Gibbs free energy of the system
subject to
the material balance and non – negativity constraints.*

For a multicomponent multiphase system, at temperature T and pressure P , the Gibbs energy, G , is the sum of all molar Gibbs energies, weighted by the respective molar amounts:

$$G = \sum_{i=1}^c n_i \mu_i \quad (3.2)$$

where C is the number of constituents, n_i is the molar amount of constituent i , μ_i is the molar chemical potential which is Gibbs energy of constituent i at constant T and P and defined as

$$\mu_i = G_i^o + RT \ln a_i \quad (3.3)$$

Postulate: Gaseous species are ideal and condensed substances are pure.

On the basis of above assumption, activities, a_i , are equal to the partial pressures, P_i , for the gaseous species, and unity for the condensed substances.

$$a_i = \begin{cases} P_i = (n_i/N)P, & \text{for gaseous species} \\ 1, & \text{for condensed substances} \end{cases} \quad (3.4)$$

where N and P are the total number of moles of the gaseous species and the total pressure, respectively.

Since the activities differ for gaseous and condensed substances, it is necessary to rewrite the right-hand side of the equation (3.2) as the sum of two summations, one for gaseous, and the other for condensed phases.

$$G = \sum_{i=1}^m n_i^g (G_i^o + RT \ln a_i)^g + \sum_{i=1}^s n_i^c (G_i^o)^c \quad (3.5)$$

The gaseous and condensed phases were marked with the indices g and c , respectively, while the summation limits m and s denote the number of substances in the gas and condensed phases that are assumed to be present at equilibrium, respectively.

The new objective function, (G/RT) was obtained by dividing equation (3.5) by (RT) .

$$G/RT = \sum_{i=1}^m n_i^g [(G^o/RT)_i^g + \ln P + \ln(n_i^g/N)] + \sum_{i=1}^s n_i^c (G^o/RT)_i^c \quad (3.6)$$

Note that optimum solution of $c * f(x)$ is the same as that of $f(x)$ for any real number c , as illustrated in Figure 3.2.

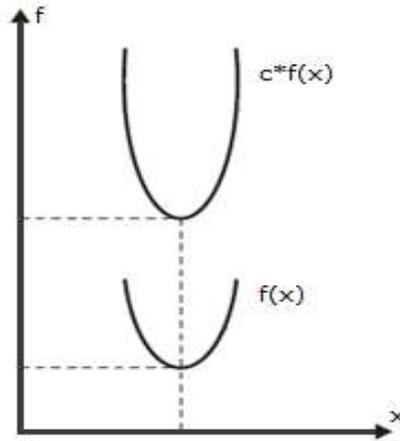


Figure 3.2 Optimum solution of $c*f(x)$.

Admittedly, the mole numbers must be non-negative, i.e. a substance may exist in finite amount or does not appear in the system. The non-negativity constraint was not included in the problem formulation at this point and it was checked systematically during the iteration processes. Therefore, the only constraint taken into account for the problem formulation was the mass balance. The mass balance relations as constraint functions $h_j(n^g, n^c)$ can be written as

$$\sum_{i=1}^m a_{ij}^g n_i^g + \sum_{i=1}^s a_{ij}^c n_i^c - b_j = 0 \quad (j = 1, 2, \dots, k) \quad (3.7)$$

where a_{ij} represents the number of atoms of the j th element in a molecule of the i th substance, b_j is the total number of moles of the j th element, and k is the total number of elements. The gaseous and condensed phases were marked by the superscripts g and c , respectively.

Lagrange's method of undetermined multipliers was applied to the problem as follows:

$$\frac{\partial(G/RT)}{\partial n_i^g} - \lambda \frac{\partial(h)}{\partial n_i^g} = 0 \quad (i = 1, 2, \dots, m) \quad (3.8)$$

$$\frac{\partial(G/RT)}{\partial n_i^c} - \lambda \frac{\partial(h)}{\partial n_i^c} = 0 \quad (i = 1, 2, \dots, s) \quad (3.9)$$

Substituting objective and constraint functions into equations (3.8) and (3.9) gave

$$(G^o/RT)_i^g + \ln P + \ln(n_i^g/N) - \sum_{j=1}^k \lambda_j a_{ij}^g = 0 \quad (i = 1, 2, \dots, m) \quad (3.10)$$

$$(G^o/RT)_i^c - \sum_{j=1}^k \lambda_j a_{ij}^c = 0 \quad (i = 1, 2, \dots, s) \quad (3.11)$$

where λ_j are Lagrangian multipliers.

The equations (3.7) and (3.10) were expanded in a Taylor series in the first degree about an arbitrary point $(x_1^g, x_2^g, \dots, x_m^g; x_1^c, x_2^c, \dots, x_s^c)$ for linearization and the following equations (3.12) and (3.13) were obtained.

$$\sum_{i=1}^m a_{ij}^g x_i^g + \sum_{i=1}^s a_{ij}^c x_i^c - b_j + \sum_{i=1}^m a_{ij}^g (n_i^g - x_i^g) + \sum_{i=1}^s a_{ij}^c (n_i^c - x_i^c) = 0 \quad (3.12)$$

$(j = 1, 2, \dots, k)$

$$(G^o/RT)_i^g + \ln P + \ln(x_i^g/X) - \sum_{j=1}^k \lambda_j a_{ij}^g + (n_i^g/x_i^g) - (N/X) = 0 \quad (3.13)$$

$(i = 1, 2, \dots, m)$

where $X = \sum_{i=1}^m x_i^g$.

From equation (3.13) n_i^g can be calculated as:

$$n_i^g = -x_i^g [(G^o/RT)_i^g + \ln P + \ln(x_i^g/X)] + x_i^g \left[(N/X) + \sum_{j=1}^k \lambda_j a_{ij}^g \right] \quad (i = 1, 2, \dots, m) \quad (3.14)$$

The first part of the above equation is the negative of the Gibbs energy change due to the specie i in the gas phase and it can be assigned to a new term f_i as applied by White [8] and Eriksson [31].

$$f_i = x_i^g [(G^o/RT)_i^g + \ln P + \ln(x_i^g/X)] \quad (i = 1, 2, \dots, m) \quad (3.15)$$

Equation (3.14) was shortened by combining the equations (3.14) and (3.15).

$$n_i^g = -f_i + x_i^g \left[(N/X) + \sum_{j=1}^k \lambda_j a_{ij}^g \right] \quad (i = 1, 2, \dots, m) \quad (3.16)$$

The summation of equation (3.15) gives the equation (3.17) which is gas phase contribution of the total Gibbs energy change and can be calculated by summing up equations (3.16) over i .

$$\sum_{j=1}^k \lambda_j \sum_{i=1}^m x_i^g a_{ij}^g = \sum_{i=1}^m f_i \quad (3.17)$$

Substitution of the equation (3.16) into the equation (3.12) gives

$$\begin{aligned} \sum_{i=1}^m a_{ij}^g \left\{ -f_i + x_i^g \left[\frac{N}{X} - 1 + \sum_{j=1}^k \lambda_j a_{ij}^g \right] \right\} + \sum_{i=1}^s a_{ij}^c n_i^c \\ = \left(\sum_{i=1}^m a_{ij}^g x_i^g - b_j \right) \quad (j = 1, 2, \dots, k) \end{aligned} \quad (3.18)$$

For the right hand side of the equation (3.18), a quantity C_j , which was defined first by Levine [32] and later used by Eriksson [31], was also introduced here as a correction term which serves in cases where the initial guess of the mole numbers does not satisfy the mass balance relations.

$$C_j = \sum_{i=1}^m a_{ij}^g x_i^g - b_j \quad (j = 1, 2, \dots, k) \quad (3.19)$$

Some simple arithmetic operations on the equation (3.18) with the new term C_j yield a new equation:

$$\begin{aligned} \sum_{r=1}^k \lambda_r u_{jr} + \left(\frac{N}{X} - 1\right) \sum_{i=1}^m a_{ij}^g x_i^g + \sum_{i=1}^s a_{ij}^c n_i^c \\ = \sum_{i=1}^m a_{ij}^g f_i - C_j \quad (j = 1, 2, \dots, k) \end{aligned} \quad (3.20)$$

where

$$u_{jr} = \sum_{i=1}^m a_{ij}^g a_{ir}^g x_i^g \quad (j, r = 1, 2, \dots, k) \quad (3.21)$$

Finally, a linear system of $(s + 1 + k)$ unknowns, and a set of linear equations with the same size were formed by the equations (3.11), (3.17) and (3.20).

3.4.2 Formulation of the Problem

In order to code the above mentioned mathematical operations in a suitable form for iteration processes, it was necessary to sum up them and convert all the required equations to matrices. The values λ_j 's in equation (3.17) are unknowns.

Let the term

$$\left(\sum_{i=1}^m x_i^g a_{ij}^g \right) = D_j$$

to have easy to read equations. Then, the expanded form of the above equation is

$$\lambda_1 D_1 + \lambda_2 D_2 + \dots + \lambda_k D_k = \sum_{i=1}^m f_i$$

and it gives the matrix below

$$[D_1 \quad D_2 \quad \cdots \quad D_k] \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_k \end{bmatrix} = \left[\sum_{i=1}^m f_i \right] \quad (3.22)$$

Similarly, recall the equation (3.11) in which the λ_j 's are the unknowns. The expanded and matrix forms of this equation are:

$$\begin{aligned} \lambda_1 a_{11}^c + \lambda_2 a_{12}^c + \cdots + \lambda_k a_{1k}^c &= (G^o/RT)_1^c \\ \lambda_1 a_{21}^c + \lambda_2 a_{22}^c + \cdots + \lambda_k a_{2k}^c &= (G^o/RT)_2^c \\ &\vdots \\ \lambda_1 a_{s1}^c + \lambda_2 a_{s2}^c + \cdots + \lambda_k a_{sk}^c &= (G^o/RT)_s^c \end{aligned}$$

$$\begin{bmatrix} a_{11}^c & a_{12}^c & \cdots & a_{1k}^c \\ a_{21}^c & a_{22}^c & \cdots & a_{2k}^c \\ \vdots & \vdots & & \vdots \\ a_{s1}^c & a_{s2}^c & \cdots & a_{sk}^c \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_k \end{bmatrix} = \begin{bmatrix} (G^o/RT)_1^c \\ (G^o/RT)_2^c \\ \vdots \\ (G^o/RT)_s^c \end{bmatrix} \quad (3.23)$$

Note that s may or may not be equal to k .

Finally, the equation (3.20) was recalled.

Let $[(N/X) - 1] = \phi, (\sum_{i=1}^m a_{ij}^g x_i^g) = D_j$ and $(\sum_{i=1}^m a_{ij}^g f_i - C_j) = E_j$ to have easy to read equations. Then, the expanded form of equation (3.20) is:

$$\begin{aligned}
(\lambda_1 u_{11} + \dots + \lambda_k u_{1k}) + \phi D_1 + (a_{11}^c n_1^c + a_{21}^c n_2^c + \dots + a_{s1}^c n_s^c) &= E_1 \\
(\lambda_1 u_{21} + \dots + \lambda_k u_{2k}) + \phi D_2 + (a_{12}^c n_1^c + a_{22}^c n_2^c + \dots + a_{s2}^c n_s^c) &= E_2 \\
&\vdots \\
(\lambda_1 u_{k1} + \dots + \lambda_k u_{kk}) + \phi D_k + (a_{1k}^c n_1^c + a_{2k}^c n_2^c + \dots + a_{sk}^c n_s^c) &= E_k
\end{aligned}$$

and the group of equations can be written in a matrix form as:

$$\begin{bmatrix} u_{11} & u_{12} & \dots & u_{1k} & D_1 & a_{11}^c & a_{21}^c & \dots & a_{s1}^c \\ u_{21} & u_{22} & \dots & u_{2k} & D_2 & a_{12}^c & a_{22}^c & \dots & a_{s2}^c \\ \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & & \vdots \\ u_{k1} & u_{k2} & \dots & u_{kk} & D_k & a_{1k}^c & a_{2k}^c & \dots & a_{sk}^c \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_k \\ \phi \\ n_1^c \\ n_2^c \\ \vdots \\ n_s^c \end{bmatrix} = \begin{bmatrix} E_1 \\ E_2 \\ \vdots \\ E_k \end{bmatrix} \quad (3.24)$$

By combining three matrices given in the equations (3.22), (3.23) and (3.24), the problem matrix is constructed as:

$$\begin{bmatrix} a_{11}^c & a_{12}^c & \dots & a_{1k}^c & 0 & 0 & 0 & 0 & 0 & 0 \\ a_{21}^c & a_{22}^c & \dots & a_{2k}^c & 0 & 0 & 0 & 0 & 0 & 0 \\ \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ a_{s1}^c & a_{s2}^c & \dots & a_{sk}^c & 0 & 0 & 0 & 0 & 0 & 0 \\ D_1 & D_2 & \dots & D_k & 0 & 0 & 0 & 0 & 0 & \phi \\ u_{11} & u_{12} & \dots & u_{1k} & D_1 & a_{11}^c & a_{21}^c & \dots & a_{s1}^c & n_1^c \\ u_{21} & u_{22} & \dots & u_{2k} & D_2 & a_{12}^c & a_{22}^c & \dots & a_{s2}^c & n_2^c \\ \vdots & \vdots & & \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots \\ u_{k1} & u_{k2} & \dots & u_{kk} & D_k & a_{1k}^c & a_{2k}^c & \dots & a_{sk}^c & n_s^c \end{bmatrix} \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_k \\ \phi \\ n_1^c \\ n_2^c \\ \vdots \\ n_s^c \end{bmatrix} = \begin{bmatrix} (G^o/RT)_1^c \\ (G^o/RT)_2^c \\ \vdots \\ (G^o/RT)_s^c \\ \sum_{i=1}^m f_i \\ E_1 \\ E_2 \\ \vdots \\ E_k \end{bmatrix} \quad (3.25)$$

3.4.3 Iterative procedure

The linear system of $(s + 1 + k)$ unknowns, given in the equation (3.25) should be solved to find the equilibrium composition of the system and the level of success is highly dependent on the initial estimates.

A program routine, given in Figure 3.3, based on equilibrium constant calculation was used to assign initial values for molar amounts of the gaseous species, $x_1^g, x_2^g, \dots, x_m^g$.

<p>Choose $x_1^g, x_2^g, \dots, x_k^g$, such that $x_i^g \leq c * K_i^{-1}$, where K_i is the equilibrium constant of the reaction below:</p> $x_i^g(\text{gas}) = x_i^c(\text{condensed})$ $K_i = \frac{a_{x_i^c}}{P_{x_i^g}} \quad \text{where,} \quad P_{x_i^g} = \frac{x_i^g}{X} P$ <p>For a system which involves any amount of x_i^c, and one mole of total gaseous phase, under one atmosphere constant pressure:</p> $a_{x_i^c} = 1 \quad \text{and} \quad P_{x_i^g} = x_i^g \quad \Rightarrow \quad x_i^g = K_i^{-1}$ <p>Then, the maximum amount of x_i^g which can exist in such a system is equal to K_i^{-1}.</p> <p>Calculate $x_{k+1}^g, x_{k+2}^g, \dots, x_m^g$, from equilibrium constants for reactions in which these gaseous compounds are formed from all gaseous species, $x_1^g, x_2^g, \dots, x_k^g$.</p>
--

Figure 3.3 Routine for estimating the amounts of the gaseous species initially.

The constant c , as multiplier of equilibrium constant, was used in the routine to avoid having a large number for the initial guess of the total gas amount.

The problem matrix given in equation (3.25) was solved using the initial estimates. The molar amounts of condensed phases, assumed to exist $(n_1^c, n_2^c, \dots, n_s^c)$ were obtained directly while that of the gaseous species $(n_1^g, n_2^g, \dots, n_m^g)$ were calculated from equation (3.16), using the values λ_j ($j = 1, 2, \dots, k$).

When all n_i^g values obtained were positive, they were used as the set of initial estimate for next iteration. If negative n_i^g values were calculated, the correction process, based on Eriksson's approach [31], given in Figure 3.4 was applied to obtain the new guess set which satisfies the non-negativity constraint. Then, the substances having an amount less than a user defined value, cut-off limit, were excluded from the subsequent iterations.

$$\text{if } n_i^g < (\text{cut - off limit}), \quad n_i^g = 0$$

<p>For all $n_i^g < 0$, calculate a correction factor α_i, such that</p> $\alpha_i^g = \frac{x_i^g}{x_i^g - n_i^g}$ <p>which is always positive and less than unity.</p> $\alpha = 0.99 * \alpha_{min}$ <p>Recalculate all x_i^g values and use them as the new estimate set of the next iteration.</p> $(x_i^g)_{new} = x_i^g + \alpha (n_i^g - x_i^g)$

Figure 3.4 Routine for the application of non-negativity constraint.

The cut-off limit can be selected by user from a predefined list which consists nine values, i.e. 1E-05, 1E-06, 1E-10, 1E-15, 1E-20, 1E-30, 1E-50, 1E-70.

The program was set to solve problem matrix without checking for singularity at the initial step. The singularity of the matrix, i.e. its determinant is zero, was checked when this step failed. The following routine, given in Figure 3.5, was applied when a singular matrix appeared.

<pre> for j = 1 to k , add trace amount (1E - 4 * b_j) of the specie try to solve the problem if not succeeded cancel the last operation and try with the next substance. </pre>
--

Figure 3.5 Routine for singular matrix correction operation.

The procedure was started with a number of condensed phases assumed to be present. As the iterations continue, these substances were changed on the basis of non-negativity criterion. For example, if mole number of a substance goes to more negative values, this specie was excluded from the condensed phase list. Furthermore, to add a condensed species i , which was not previously included as a possible species, the requirement was that its inclusion would satisfy the equation (3.26).

$$(G^o/RT)_i^c - \sum_{j=1}^k \lambda_j a_{ij}^c < 0 \quad (3.26)$$

In the cases where the problem could not be solved, some inert gas, like argon, which does not affect the system reactions was added to the assemblage. The mole number of the gas added was calculated depending on the total amount of the system constituents. If the problem could be solved in this way, the resultant composition given to user as the output of the system equilibrium was argon free, i.e. originally defined system.

One of the unknowns, ϕ , defined as;

$$\phi = [(N/X) - 1]$$

gives a good clue for convergence of the solution. The N/X is the ratio for the correct total number of moles of gaseous species to the estimated one. As ϕ goes to zero, correct solution is going to be approached.

For a satisfactory accuracy of the resultant composition, a ϕ value less than 1E-10 was considered reasonable. The overall algorithm for optimization process used in this study is given in Figure 3.6.

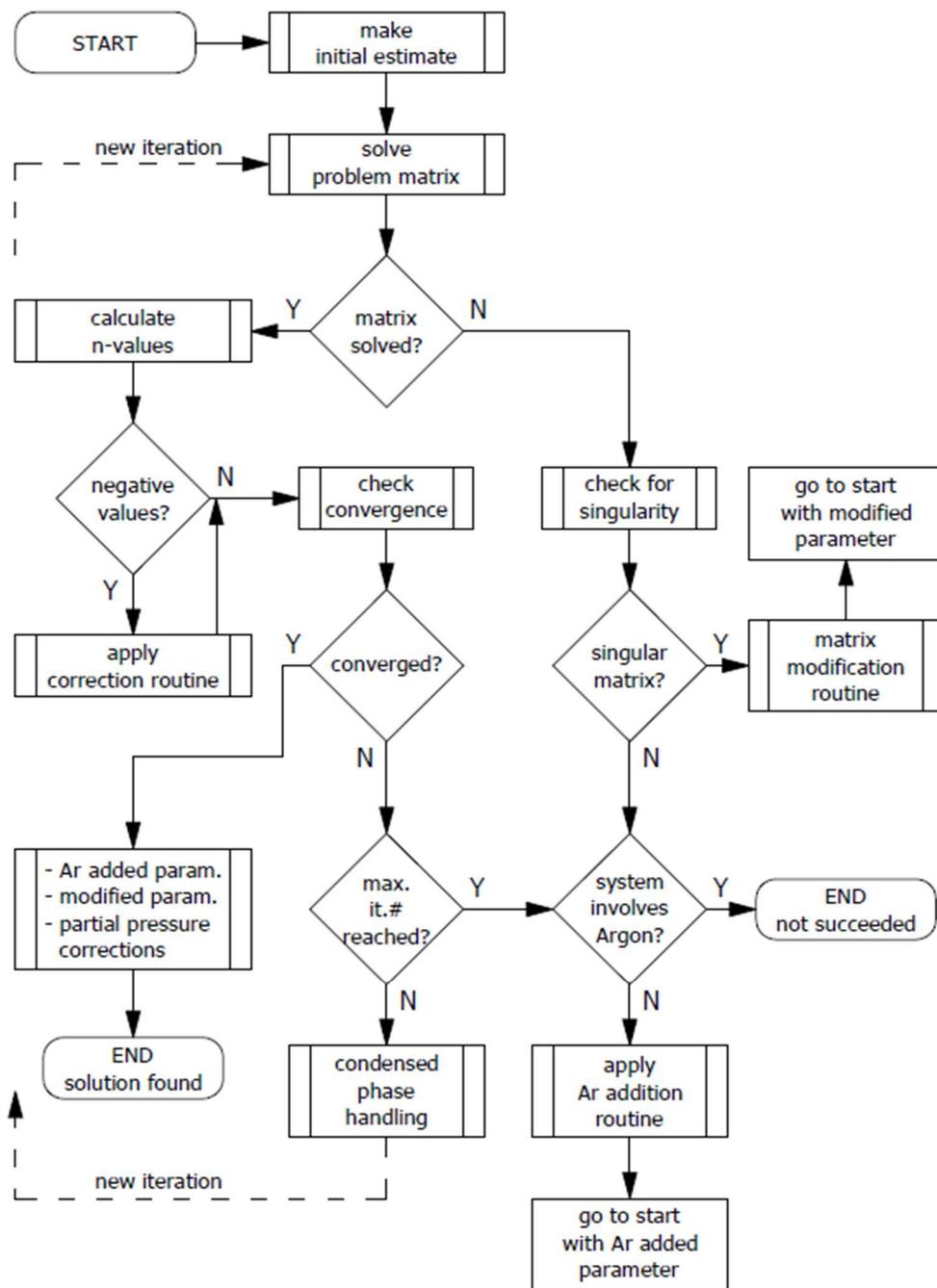


Figure 3.6 The overall algorithm of optimization process.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Computations of Chemical Reaction Equilibria

As the pioneers of the developments in chemical equilibrium calculations, White et.al, [8] determined the composition of the mixture of the gaseous species resulted from the combustion of a mixture of hydrazine and oxygen at 3500 K and 750 psi (~51 atm). A comparison for the calculated chemical equilibrium composition for the above combustion problem was obtained using the present program several decades later. The comparison of numbers of moles of the gaseous species calculated in this work with those produced by the web version of a well-known commercial software is given in Table 4.1. The partial screenshots of the programs used are given in Figures 4.1 and 4.2.

At this point, it is important to note that F*A*C*T emphasizes that Equilib-Web is for demonstration purposes only and does not have all the features of the complete Equilib module of their commercial software package.

The result obtained from the program developed in this study was satisfactory, as listed below. The total number of moles of gas was calculated as 3.27417 moles while the commercial software (web version) gives it as 3.2721. Therefore, the difference was only 0.06% which was probably because the thermodynamic databases used by the programs were not the same. Admittedly, the differences in the values of the thermodynamic properties, calculated using databases, may result in different chemical equilibrium composition states.

Table 4.1 Comparison of the system – hydrazine combustion.

Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
Total Gas		3.27417	3.2721	0.06%
Gaseous species mole fractions				
H₂O		0.47770	0.47919	-0.31%
N₂		0.29762	0.29745	0.06%
H₂		0.08789	8.8327E-02	-0.49%
OH		0.06578	6.2772E-02	4.79%
H		0.02455	2.4442E-02	0.44%
O₂		0.02080	2.1313E-02	-2.41%
NO		0.01552	1.6258E-02	-4.54%
O		9.9515E-03	1.0020E-02	-0.68%
HO₂	HOO	9.7519E-05	1.4047E-04	-30.58%
HNO		1.7415E-05	1.6663E-05	4.51%
N		1.6909E-05	1.6790E-05	0.71%
H₂O₂	HOOH	1.6426E-05	1.4671E-05	11.96%
NO₂		1.5117E-05	1.3710E-05	10.26%
NH		8.5370E-06	4.3443E-06	96.51%
NH₂		4.7507E-06	3.9350E-06	20.73%
N₂O		4.0032E-06	3.7295E-06	7.34%
NH₃		3.7226E-06	3.9637E-06	-6.08%
HNO₂	1.7514E-06 HONO(g ²) 1.5276E-06 HONO(g)	2.9748E-06	3.2790E-06	-9.28%
O₃		7.9898E-08	4.9824E-08	60.36%
N₂H₂	HNNH	1.2213E-09	9.9571E-10	22.66%
HNO₃	HONO2	5.5729E-10	4.9719E-10	12.09%
N₃		2.2054E-10	1.1977E-09	-81.59%
NO₃		1.6377E-10	1.7285E-10	-5.25%

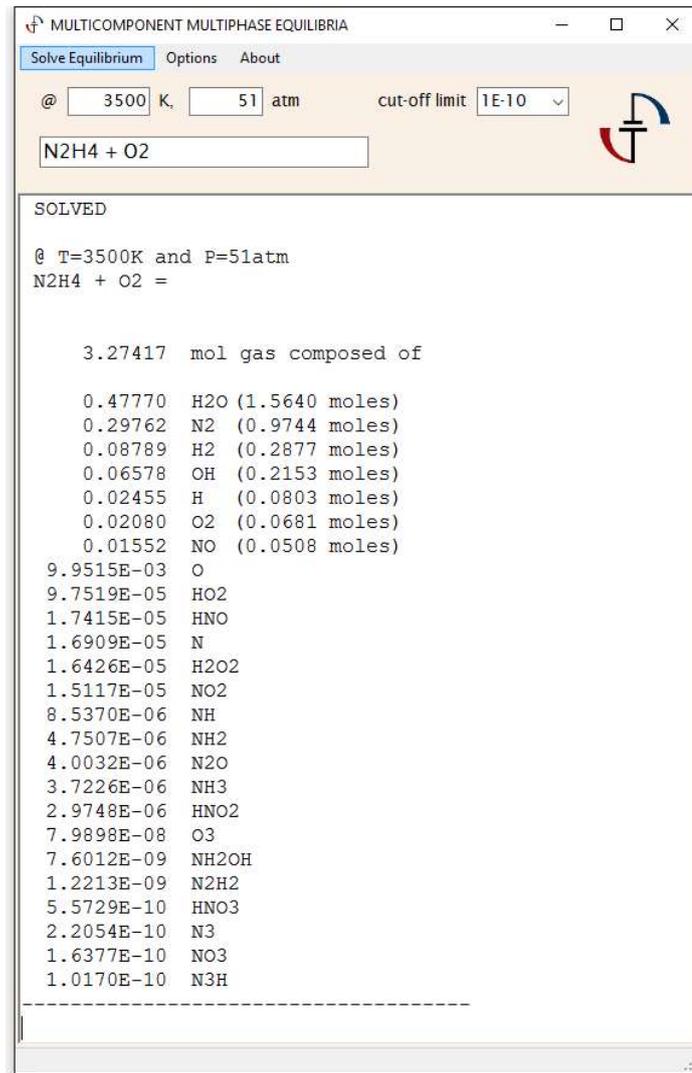


Figure 4.1 Hydrazine combustion problem solved by the present program.

There exist species having relatively large percentage differences in partial pressures in Table 4.1 (like NH). The difference is about 96%, and the partial pressure of NH has an order of 10^{-5} atm. Although it is a very small part of the gas phase resulted from the combustion and may be neglected for practical purposes, yet it should be noted that the difference was not the result of an erroneous calculation. The possible source of the differences will be discussed in next section with reference to sample calculations.

Equilib-Web Results

Equilib-Web is for demonstration purposes only. Many of the features of the complete **Equilib** module of the **FactSage™** package have been diluted – please refer to the Equilib-Web disclaimer.

Equilib-Web is accessing the FactSage 6.4 package. The compound data are taken from FactPS – the FACT pure substances database (2013).

FACT Format

N2H4 + O2 =

```
3.2721      mol   gas_ideal
(64.044 gram, 3.2721 mol, 18.426 litre, 3.4757E-03 gram.cm-3)
(3500 K, 51 atm,      a=1.0000)
( 0.47919          H2O
+ 0.29745          N2
+ 8.8327E-02       H2
+ 6.2772E-02       OH
+ 2.4442E-02       H
+ 2.1313E-02       O2
+ 1.6258E-02       NO
+ 1.0020E-02       O
+ 1.4047E-04       HOO
+ 1.6790E-05       N
+ 1.6663E-05       HNO
+ 1.4671E-05       HOOH
+ 1.3710E-05       NO2
+ 4.3443E-06       NH
+ 3.9637E-06       NH3
+ 3.9350E-06       NH2
+ 3.7295E-06       N2O
+ 1.7514E-06       HONO (g2)
+ 1.5276E-06       HONO (g)
```

```
+ 0          mol   N2O4_solid
(3500 K, 51 atm, S1, a=4.1056E-20)
```

Cut-off limit for gaseous fractions/phase activities = 1.00E-20

Figure 4.2 Equilib-Web [33] screenshot (partial) – hydrazine combustion.

A group of systems which were discussed in detail by Sultan [34], were taken as examples to simulate oxidation of iron in different oxidizing environments. All the systems listed below were studied at two different temperatures, i.e. 450 and 500°C. It was observed that the equilibrium compositions calculated using present program were very close to those found by F*A*C*T. The oxidizing environments were;

- Oxidation in air (Fe + O₂ + 3.76 N₂)
- Oxidation in CO₂ + N₂ (Fe + CO₂ + 3.76 N₂)
- Oxidation in CO₂+H₂O (Fe + CO₂ + 2 H₂O)

The partial screenshots showing calculated equilibrium compositions of products simulating oxidation of iron in air at 450°C by the program developed in this study and the F*A*C*T system are shown in Figures 4.3 and 4.4 respectively. The comparison of numbers of moles of species calculated in this work with those produced by the web version of F*A*C*T system is given in Table 4.2.

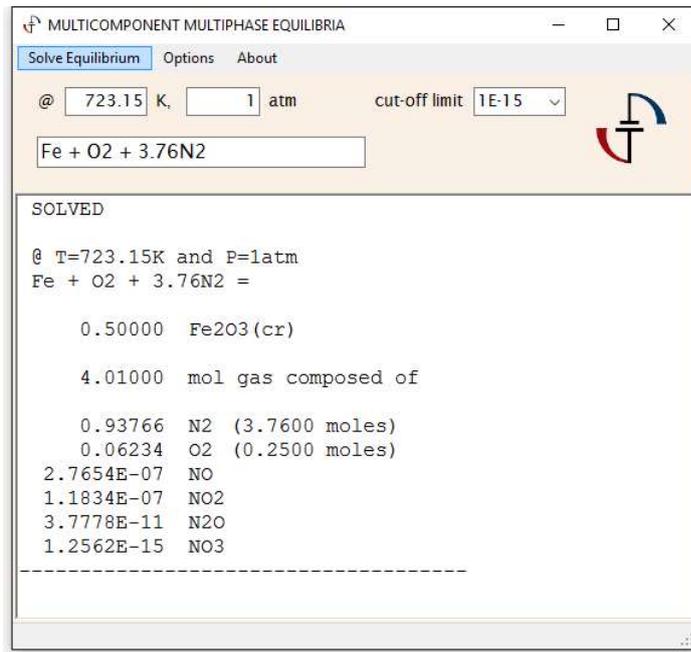


Figure 4.3 Oxidation of iron in air simulated by the program developed in this study.

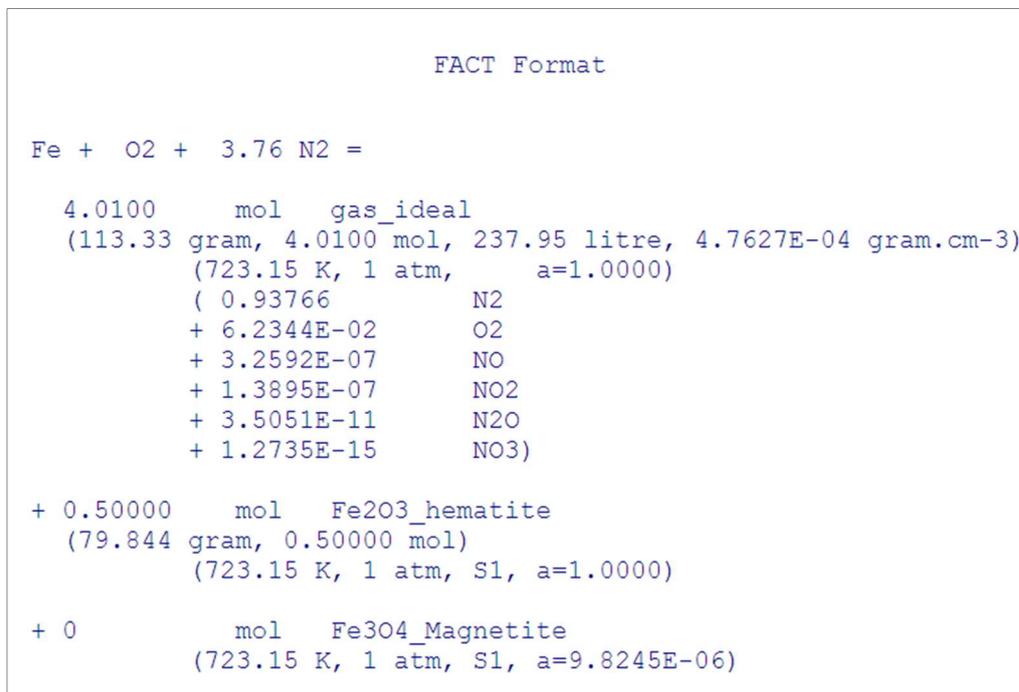


Figure 4.4 Oxidation of iron in air simulation by F*A*C*T [33] (FactSage 7.0).

Table 4.2 Comparison of the system – oxidation of iron in air at 450°C.

Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
Fe ₂ O ₃ (cr)	Fe2O3_hematite	0.50000	0.50000	0.00%
Total Gas		4.01000	4.0100	0.00%
Gaseous species mole fractions				
N ₂		0.93766	0.93766	0.00%
O ₂		0.06234	6.2344E-02	-0.01%
NO		2.7654E-07	3.2592E-07	-15.15%
NO ₂		1.1834E-07	1.3895E-07	-14.83%
N ₂ O		3.7778E-11	3.5051E-11	7.78%
NO ₃		1.2562E-15	1.2735E-15	-1.36%

The comparison of numbers of moles of species calculated in this work with those produced by the web version of F*A*C*T system simulating oxidation of iron in CO₂+3.76N₂ at 450°C is given in Table 4.3. Similar comparison for oxidation of iron in CO₂+2H₂O at 450°C is given in Table 4.4.

Table 4.3 Comparison of the system – oxidation of iron in CO₂+3.76N₂ at 450°C.

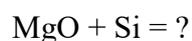
Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
C(gr)	C_Graphite	0.65216	0.6524	-0.04%
Fe ₃ O ₄ (cr)	Fe3O4_Magnetite	0.33333	0.33333	0.00%
Total Gas		4.10784	4.1076	0.01%
Gaseous species mole fractions				
N ₂		0.91532	0.91538	-0.01%
CO ₂		0.07762	7.7677E-02	-0.07%
CO		7.0614E-03	6.9462E-03	1.66%
C ₃ O ₂		1.1916E-20	1.0600E-20	12.42%

Table 4.4 Comparison of the system – oxidation of iron in CO₂+2H₂O at 450°C.

Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
Fe ₃ O ₄ (cr)		0.33333	0.33333	0.00%
Total Gas		2.53498	2.5330	0.08%
Gaseous species mole fractions				
H ₂ O		0.45861	0.45946	-0.18%
CO ₂		0.29058	0.29072	-0.05%
H ₂		0.14691	0.14574	0.80%
CO		0.01218	1.1880E-02	2.53%
CH ₄		0.09172	9.2193E-02	-0.51%
C ₂ H ₆		3.6749E-07	4.2659E-07	-13.85%
HCOOH		2.1346E-08	2.0123E-08	6.08%
C ₂ H ₄		1.2861E-09	1.2464E-09	3.19%
HCHO,formaldehy	H2CO	1.2606E-09	4.2808E-09	-70.55%
CH ₃ OH		9.1121E-10	9.3107E-10	-2.13%

One of the most popular systems to simulate is the Pidgeon process which is very famous silicothermic process used for metallic magnesium production. The process has three stages and the last stage is the silicothermic reduction of MgO by ferrosilicon performed under vacuum at a temperature of about 1400 K. For simplicity, the reaction is written as:

- Silicothermic reduction of MgO by silicon, at T = 1400 K, P = 1E-4atm



The comparison of numbers of moles of species calculated in this work with those produced by the web version of F*A*C*T system simulating silicothermic reduction of MgO by silicon at 1400 K under 1E-4 atm is given in Table 4.5.

Table 4.5 Comparison of the system – Pidgeon process.

Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
Mg₂SiO₄(cr)	Mg2SiO4_forsterite	0.22735	0.22680	0.24%
Si(cr)	Si_solid	0.68203	0.68038	0.24%
Total Gas		0.63593	0.63923	-0.52%
Gaseous species mole fractions				
Mg		0.85750	0.85479	0.32%
SiO		0.14249	0.14520	-1.87%
Si		8.2352E-06	8.2568E-06	-0.26%
Mg₂		2.7086E-08	2.7268E-08	-0.67%
Si₂		2.6249E-08	1.9517E-08	34.49%
Si₃		4.6178E-09	4.7780E-09	-3.35%
SiO₂		1.4695E-10	1.5216E-10	-3.42%

This system was used as an example for discussing the source of the differences in the partial pressures calculated in this study and those given by F*A*C*T.

The next example was chosen from copper metal production processes. The pure metal production procedure involves several steps. The selected stage to simulate was the roasting of enriched copper ore. The roasting of chalcocite which is one of the important copper ore minerals was studied for 973 K and the program screenshot is given in Figure 4.5.

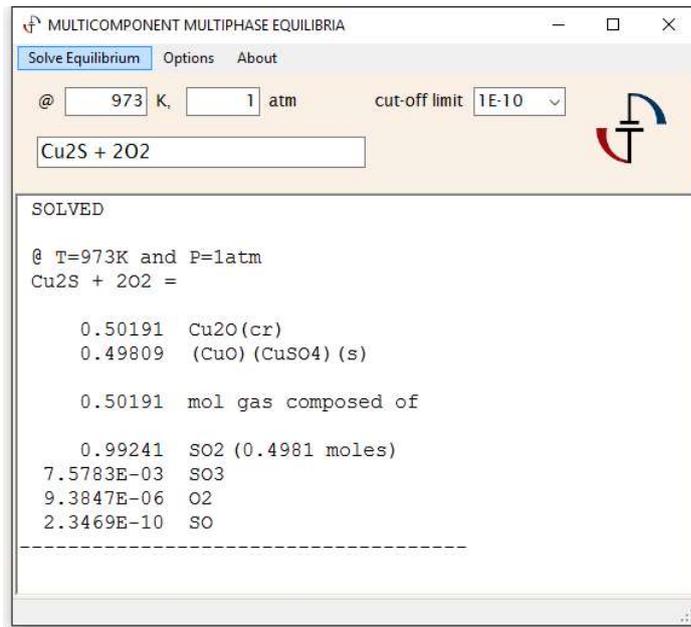


Figure 4.5 Simulation of chalcocite, Cu_2S , roasting at 973 K.

The comparison of the equilibrium state of the system calculated in this work with that produced by the web version of F*A*C*T is given in Table 4.6.

The roasting processes can be discussed with reference to the predominance area diagrams, PADs, which are also constructed by chemical equilibrium calculations. A computer program SKOP [1] developed at METU, the Department of Metallurgical and Materials Engineering, was used to observe the consistency of the simulation with the PAD of the current example given in Figure 4.6. The equilibrium O_2 and SO_2 partial pressures, given in Figure 4.5 and their logarithms are given below for comparison with the PAD:

$$P(\text{O}_2) = 9.3847\text{E} - 06 \Rightarrow \log P(\text{O}_2) = -5.028$$

$$P(\text{SO}_2) = 0.99241 \Rightarrow \log P(\text{SO}_2) = -0.003$$

Table 4.6 Comparison of the system – copper sulfide roasting at 973 K.

Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
Cu₂O(cr)		0.50191	0.50190	0.00%
(CuO)(CuSO₄)(s)		0.49809	0.49810	0.00%
Total Gas		0.50191	0.50191	0.00%
Gaseous species mole fractions				
SO₂		0.99241	0.99243	0.00%
SO₃		7.5783E-03	7.5613E-03	0.23%
O₂		9.3847E-06	9.1302E-06	2.79%
SO		2.3469E-10	2.2775E-10	3.05%

Cu-O-S (973K)

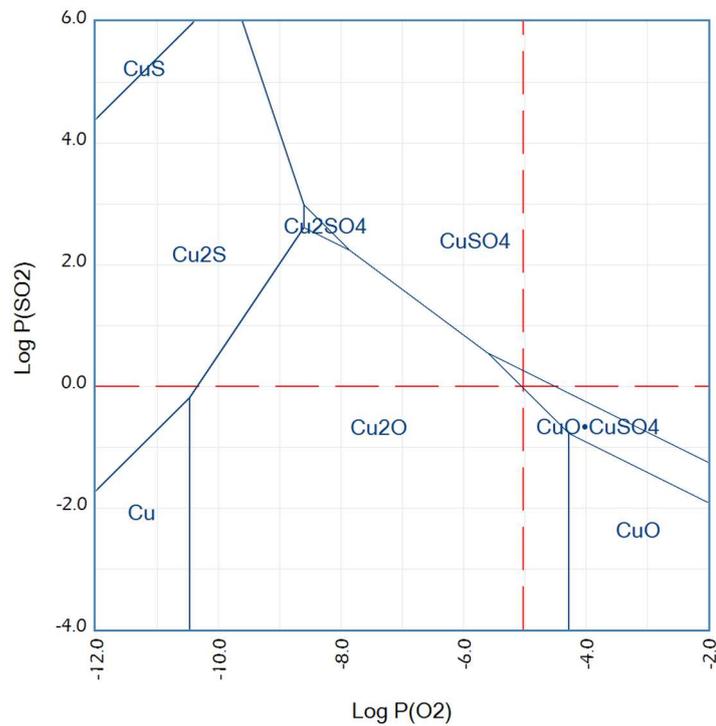


Figure 4.6 PAD for Cu-O-S at 973 K produced by SKOP [35, 36].

The dashed lines in Figure 4.6 show the logarithm of partial pressures of O₂ and SO₂ calculated by the present simulation program. The intersection of these lines defines the state of the system simulated. According to the simulation, two condensed species Cu₂O(cr) and (CuO)(CuSO₄)(s) co-exist together with the gas phase composition. Therefore, the point of intercept in the PAD given above should lie on the univariant line which separates Cu₂O(cr) and (CuO)(CuSO₄)(s). A very small deviation observed in the diagram may be attributed to slightly smaller total pressure of O₂ and SO₂ gases and differences data.

The last example was chosen to calculate equilibrium composition of WO₃ in CaCl₂ containing molten salts at high temperatures [37]. The results both from this study and F*A*C*T showed that significant amount of volatile tungsten oxychloride (WO₂Cl₂) was liberating under given conditions, i.e. at 1173 K and 1atm pressure. The comparison of simulation results shows identical values for the major constituents as given in Table 4.7.

Table 4.7 Comparison of the system – equilibrium composition of WO₃ in CaCl₂ containing molten salts at 1173 K.

Specie	F*A*C*T Notation	This study	F*A*C*T	Difference
(CaO)(WO3)(cr)	(CaO)(WO3)_Scheelite	0.50000	0.50000	0.00%
CaCl ₂ (L)	CaCl2_liquid	0.50000	0.50000	0.00%
Total Gas		0.50000	0.50000	0.00%
Gaseous species mole fractions				
WO ₂ Cl ₂		0.99999	0.99999	0.00%
CaCl ₂		5.9614E-06	3.6558E-06	63.07%
Cl		8.9442E-07	4.2146E-06	-78.78%
Cl ₂		6.3588E-08	1.4306E-06	-95.56%
WOCl ₄	OWCl4	1.0747E-08	1.3580E-08	-20.86%

Although simulations were in complete agreement on the condensed phases formed, total amount of the gas phase and the major part of the gas, there were inconsistencies in partial pressures of the gases that were very small in quantity. The differences were considered to be due to missing W containing species from the present database. The database used in this study did not contain even scheelite ((CaO)(WO₃)) originally. It was added to the database using the tabular data taken from F*A*C*T Compound-Web. But the rest of the data for missing substances which contain tungsten were not added to the present database yet. Although the database did not contain all the possible species which can exist in equilibrium, the system was simulated satisfactorily in terms of the major constituents.

4.2 Discussions on Deviations of Compositions

The majority of the results, i.e. the chemical equilibrium states, of the systems examined in this study were verified by F*A*C*T system. There are some inconsistencies which will be explained in detail.

One of the examples was the silicothermic reduction of MgO to simulate Pidgeon process. The largest difference was nearly 35% in the partial pressure of Si₂(g). All other values; mole numbers of the condensed phases, and partial pressures of the gaseous species were almost identical to those calculated by F*A*C*T (see Table 4.5).

The equilibrium partial pressure of a gaseous species can be calculated from the equilibrium constant of evaporation or sublimation process depending on the state of condensed substance. Therefore, the deviations of the calculated partial pressures completely depend on the available data, because computations involve simple mathematical operations. The equilibrium constant of equation (4.1) is calculated as 1.2143E+09 from the present database.

$$Si(g) = Si(cr) \quad (4.1)$$

Since activity of pure solid silicon is unity, the partial pressure of the gaseous silicon for equation (4.1) is;

$$P_{Si} = 8.2352E - 10 \text{ atm}$$

From the ratio of partial pressure to the total pressure of the system (1E-4 atm), mole fraction of gaseous silicon in the gas phase can be determined as 8.2352E-06. Similarly, it was calculated as 8.2568E-06 using data supplied ($\Delta G^o = -243,455.0 \text{ J}$) by F*A*C*T Reaction-Web [33].

The relatively large difference was observed in partial pressure of $Si_2(g)$. The equilibrium constant of the below reaction (4.2) was calculated simply using the equations (1.4) and (1.5) with the given coefficients in the database.



The equilibrium partial pressure of $Si_2(g)$ was then calculated as 2.6249E-12 atm from equation (4.3). Therefore, the mole fraction of $Si_2(g)$ calculated as 2.6249E-08 verified the simulation result. Similarly, using data provided by F*A*C*T Reaction-Web, equilibrium mole fraction of $Si_2(g)$ was calculated as 1.9517E-08.

$$P(Si_2) = K_{reaction(4.2)} * P_{Si}^2 \quad (4.3)$$

The equilibrium mole fractions given above and their corresponding percentage differences are the same as the values given in Table 4.5. Therefore, the differences between the simulation results of the present program and F*A*C*T, especially in the partial pressures of gaseous species that are small, was explained with reference to the differences in the data used.

The database portions used for these two partial pressure calculations were given in appendix.

CHAPTER 5

CONCLUSION

A computer program which is capable of simulating the chemical processes involving multicomponent multiphase equilibria, at a thermodynamic state specified by assigned temperature and pressure, was developed.

The algorithm of the optimization routine of the program is based on the minimization of the Gibbs energy because the Gibbs energy of a system at a given temperature and pressure must be a minimum as the second law of thermodynamics states.

The minimization method is performed using the Lagrange's method of undetermined multipliers together with the material balance conditions of the system components as subsidiary constraints.

Finally, some known systems were simulated using the program introduced and the solutions were verified with a well-known commercial software F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) [19]. The results reveal that the computations were in a very good agreement with the F*A*C*T results for the calculation of the amounts of the condensed phases. When the gaseous species are concerned, the correspondence was generally less than 1% if the partial pressure of the gas was higher than 10^{-2} . For smaller partial pressures, the difference between present study and F*A*C*T increased. This was explained with reference to the different databases used. It was proposed that a relatively small variation in the thermodynamic properties of a species may cause a large percent difference in equilibrium calculations, especially when very small concentrations are concerned.

5.1 Recommendations for future work

Use of a database which contains as many as possible substances of the simulated system is the top priority to achieve success in chemical equilibrium calculations. Hence, the database used in this study will be enlarged with data accessible from available different trusted sources.

In addition, an option to select database (or data for certain substances) used would be very functional in studies done for comparison purposes.

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APPENDIX

Database Formats

	1	2	3	4	5	6	7	8			
	1234567890123456789012345678901234567890123456789012345678901234567890123456789012345678901234567890										
1	Si(cr)	Cubic. Ref-Elm. Gurvich,1991 pt1 p236 pt2 p220.									
2	2 tps91 SI	1.00	0.00	0.00	0.00	0.00	1	28.0855000	0.000		
3	200.000	298.1507	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	3217.471
4	-2.323538208E+04	0.000000000E+00	2.102021680E+00	1.809220552E-03	0.000000000E+00						
5	0.000000000E+00	0.000000000E+00									-7.850635210E+02-1.038427318E+01
6	298.150	1690.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	3217.471
7	-5.232559740E+04	0.000000000E+00	2.850169415E+00	3.975166970E-04	0.000000000E+00						
8	0.000000000E+00	0.000000000E+00									-1.042947234E+03-1.438964187E+01
1	Si	Hf:Cox,1989. NIST Eata version1.1 [Online]1997. GorEon,1999.									
2	3 g 8/97 SI	1.00	0.00	0.00	0.00	0.00	0	28.0855000	450000.000		
3	200.000	1000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	7550.258
4	9.836140810E+01	1.546544523E+02	1.876436670E+00	1.320637995E-03	-1.529720059E-06						
5	8.950562770E-10	-1.952873490E-13									5.263510310E+04 9.698288880E+00
6	1000.000	6000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	7550.258
7	-6.169298850E+05	2.240683927E+03	-4.448619320E-01	1.710056321E-03	-4.107714160E-07						
8	4.558884780E-11	-1.889515353E-15									3.953558760E+04 2.679668061E+01
9	6000.000	20000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	7550.258
10	-9.286548940E+08	5.443989890E+05	-1.206739736E+02	1.359662698E-02	-7.606498660E-07						
11	2.149746065E-11	-2.474116774E-16									-4.293792120E+06 1.086382839E+03
1	Si2	Gurvich,1991 pt1 p240 pt2 p225.									
2	2 tps91 SI	2.00	0.00	0.00	0.00	0.00	0	56.1710000	580195.524		
3	200.000	1000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	10296.124
4	1.237596221E+04	-1.024904376E+02	4.354848520E+00	1.281063335E-03	-2.531991623E-06						
5	2.265694244E-09	-7.001290140E-13									6.906942850E+04 3.251125200E+00
6	1000.000	6000.0007	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	0.0	10296.124
7	1.370060657E+06	-4.207060040E+03	9.337432890E+00	-2.749217168E-03	9.586345960E-07						
8	-1.372449748E-10	6.765028100E-15									9.510884540E+04-3.168385190E+01
		1	2	3	4	5	6	7	8		
	1234567890123456789012345678901234567890123456789012345678901234567890123456789012345678901234567890										

Figure A.1 Data samples from the database used in the present program.

Silicon (Si)				Si ₁ (cr)			
Enthalpy Reference Temperature = $T_r = 298.15$ K				Standard State Pressure = $p^\circ = 0.1$ MPa			
T/K	$J \cdot K^{-1} mol^{-1}$			$kJ \cdot mol^{-1}$			
	C_p°	S°	$-(G^\circ - H^\circ(T_r))/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
0	0.	0.	INFINITE	-3.218	0.	0.	0.
100	7.268	3.833	33.351	-2.952	0.	0.	0.
200	15.636	11.665	20.531	-1.773	0.	0.	0.
250	18.221	15.446	19.138	-0.923	0.	0.	0.
298.15	20.000	18.820	18.820	0.	0.	0.	0.
300	20.050	18.943	18.820	0.037	0.	0.	0.
350	21.276	22.132	19.069	1.072	0.	0.	0.
400	22.142	25.032	19.636	2.159	0.	0.	0.
450	22.803	27.680	20.385	3.283	0.	0.	0.
500	23.330	30.110	21.237	4.436	0.	0.	0.
600	24.154	34.440	23.086	6.812	0.	0.	0.
700	24.803	38.212	24.983	9.260	0.	0.	0.
800	25.359	41.562	26.850	11.769	0.	0.	0.
900	25.874	44.579	28.655	14.331	0.	0.	0.
1000	26.338	47.329	30.387	16.942	0.	0.	0.
1100	26.778	49.860	32.044	19.598	0.	0.	0.
1200	27.196	52.208	33.627	22.297	0.	0.	0.
1300	27.614	54.401	35.142	25.037	0.	0.	0.
1400	28.033	56.463	36.592	27.820	0.	0.	0.
1500	28.451	58.411	37.982	30.644	0.	0.	0.
1600	28.870	60.261	39.317	33.510	0.	0.	0.
1685.000	29.225	61.765	40.412	35.979	CRYSTAL <-> LIQUID		
1700	29.288	62.024	40.602	36.418	50.177	0.447	0.014
1800	29.706	63.710	41.839	39.368	-49.947	3.418	-0.099
1900	30.125	65.327	43.033	42.359	-49.675	6.376	-0.175
2000	30.543	66.883	44.187	45.393	-49.361	9.318	-0.243
2100	30.962	68.383	45.303	48.468	-49.006	12.243	-0.305
2200	31.380	69.833	46.386	51.585	-48.608	15.151	-0.360
2300	31.798	71.237	47.436	54.744	-48.169	18.039	-0.410
2400	32.217	72.600	48.456	57.945	-47.688	20.908	-0.455
2500	32.635	73.923	49.448	61.187	-47.165	23.755	-0.496
PREVIOUS: December 1962				CURRENT: December 1966			
Silicon (Si)				Si ₁ (cr)			
Download table in tab-delimited text format.							

Figure A.2 Tabulated data sample from JANAF Thermochemical tables [38].