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AN INTERACTIVE COMPUTER PROGRAM FOR PREDOMINANCE AREA DIAGRAMS

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ABSTRACT

AN INTERACTIVE COMPUTER PROGRAM FOR
PREDOMINANCE AREA DIAGRAMS

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An interactive computer program, SKOP v.2, has been developed to construct Predominance Area Diagrams on IBM PC and compatible computers. The name SKOP is given as an abbreviation from Turkish words "Sistemlerin Kararlı Oluşum Potansiyeli". Program uses elementary thermodynamic data for computations. Entering elements that build up the system, constant temperature and diagram axes is sufficient for program to construct any diagram. Multicomponent systems, composed of maximum 6 elements, and systems that bear one or two-metals can be handled by the program. Support for non-stoichiometric and decomposing phases are also present. Program lets the user select diagram axes freely. For the plotting part, "Constrained Chemical Potential" method is applied. SKOP program serves advanced features to users such as detailed diagram examination with zooming and point tracing. Program is driven by pull-down menu system and contains a "help to user" utility. Several examples are provided to illustrate the use of the program.

Keywords: Interactive Computer Program, Predominance Area Diagram, Phase Stability, Thermodynamics

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ÖZ

PREDOMİNANT ALAN DİYAGRAMLARI İÇİN BİR BİLGİSAYAR YAZILIMI

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Predominant Alan Diyagramlarını hesaplayan, IBM PC ve uyumlu bilgisayarlarda çalışabilen bir bilgisayar yazılımı düzenlenmiştir. Program hesaplamalarda temel termodinamik değerleri kullanmaktadır. SKOP programı ismini "Sistemlerin Kararlı Oluşum Potansiyeli" cümlesindeki kelimelerin baş harflerinden almaktadır. Bir sistemin diyagramını çizebilmek için sistemi belirleyen elementlerin, sabit sıcaklığın ve diyagram eksenlerinin girilmesi yeterli olmaktadır. Program, çok elementli, maksimum 6 element, ve bir veya iki metal içeren sistemler için hesaplama yapabilmektedir. Stokiyometrik olmayan ve bozunuma uğrayan fazlar otomatik olarak hesaplamadan çıkarılabilmektedir. Program kullanıcıların diyagram eksenlerini istedikleri gibi seçmelerine izin vermektedir. Diyagram çizimi için "Sınırlı Kimyasal Potansiyel" metodu kullanılmaktadır. SKOP programı, büyültme ve nokta tarama gibi gelişmiş özellikleri bünyesinde bulundurmaktadır. Program, "Pull-Down" menü sistemiyle idare edilmekte ve içinde bir "kullanıcıya yardım" birimi bulunmaktadır. Programın kullanılışını göstermek için örnek diyagramlar verilmiştir.

Anahtar Kelimeler: Predominant Alan Diyagramı, Kellog Diyagramı, Bilgisayar Programı, Termodinamik, Faz kararlılığı

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NOMENCLATURE

a	Activity
C_p	Heat capacity at constant pressure
ΔG°_T	Standard Gibbs energy of formation at temperature T
ΔG	Gibbs energy of formation
$\Delta H^\circ_{298.15}$	Standard enthalpy of formation
ΔH°_T	Enthalpy of formation at temperature T
ΔH°_{tr}	Enthalpy change due to transformation
K	Equilibrium constant
P	Partial pressure
R	Universal Gas Constant
$S^\circ_{298.15}$	Standard entropy
ΔS°_T	Entropy of formation at temperature T
T	Temperature
T_{tr}	Transformation temperature

CHAPTER I

INTRODUCTION

1.1 Predominance Area Diagrams

The relative stabilities of reactive species in various chemical environments can be represented by diagrams in which areas or domains define the conditions for thermodynamic stability. Among the types of diagrams which have been extensively applied to high temperature systems are isothermal ones in which the axes represent relative chemical potentials (logarithm of partial pressures for gases or activities in the case of condensed phases). These type of diagrams, are called Kellog diagrams, Predominance Area diagrams, or Phase Stability diagrams. In aqueous electrochemistry & hydrometallurgy, the topological equivalent of the predominance area diagram is the Pourbaix or Eh-pH diagrams. All of the diagrams mentioned, whether they are for aqueous or non-aqueous systems, can be classified as isothermal, potential vs. potential type diagrams.

Predominance Area diagrams have found increasing applications in the analysis and interpretation of metallurgical processes [12]. One of the well known application area is in the analysis of roasting of sulphur containing minerals. In this application, roasting product can easily be determined with reference to a predominance area diagram and roasting conditions. Other applications involve analysis of hot corrosion of metals (or alloys) [23], corrosion of ceramics by corrosive fluids [30], and even composite processing [15]. In the hot corrosion of metals and ceramics, the influence of corrosive environments and interpretations of corrosion product(s) on corroding surfaces can be determined by using a predominance area diagram. The phases that could be formed during composite processing can also be

determined, to an extent, with reference to these diagrams.

Variable compositions due to solution phases or non stoichiometry ($Fe_{1-x}O$) are generally not taken into account when constructing this type of diagrams. However, applications of constant non stoichiometry to one or more of the species that form a system is possible. Introduction of variable compositions require a lot of information (e.g. solution data) and computations result in data that are very difficult to represent. For those systems where there are non-stoichiometric compounds or stable solution phases, the predominance area diagram is not the true phase diagram but rather a map of the relative stabilities [15].

The methods of calculating and utilizing the predominance area diagrams are well documented in the literature [1-10]. Kellog and Basu, Tuffley and Russell, and Ingraham have contributed significantly to our understanding of the stability relations in a variety of metallurgically important ternary systems [18]. Predominance area diagrams (PAD) are constructed essentially by computing standard Gibbs energy changes for various reactions taking place in a system by assuming equilibrium conditions. The stability areas for various species are plotted as functions of relative chemical potentials of two species involved in reactions by using standard Gibbs energy changes [12].

1.2 Applications of Predominance Area Diagrams

Predominance area diagrams are frequently used in the analysis of metallurgical processes such as roasting. Normally, roasting treatment is applied to sulfide concentrates to gain one of two objectives: to obtain an oxide product that can be converted to metal in a subsequent pyrometallurgical reduction unit or to provide a water-soluble sulfate product that can be used as a feed to a hydrometallurgical process. The chemical composition of the gas phase in the roaster has a critical influence on the type (oxide or sulfate) of product that emerges from roasting operation. Knowledge of the equilibrium constant for the various heterogeneous

equilibria involved in the system is of particular value in selecting the optimum range of operating conditions for the roasting processes [18]. These operating conditions can be precisely determined with predominance area diagrams.

These diagrams are also used extensively in the interpretation of hot corrosion. They reveal the corrosion products that will be expected to form, usually from a single metallic element over a wide range of environmental conditions expressed, for example, in terms of temperature, oxygen potential, and sulfur or sulfur dioxide potential [19]. Use of PAD in hot corrosion studies are well documented in literature [8, 19-24]. In addition, PAD can be used to determine the extent of passive film formation, which in turn be used in alloy development or in selection of service environment for a particular alloy. Similar applications can be found in the use of PAD for the analysis of corrosion of ceramics by fluids [30, 31].

In composite processing, the common three element PAD's are not used in general. For this application multi metal PAD are needed. In the production of metal-ceramic composites, chemically inert interfaces between metal and ceramic is required. The conditions that will yield such an interface can be determined by constructing a multi metal PAD that has both matrix metal and the metal of the ceramic phase as reactive elements. By this way, stable metal-ceramic pairs can be determined easily. In addition, a metal-ceramic pair can be tested for thermodynamic stability, to find out if a certain pair be used in composite production.

1.3 Application of Computers to PAD development

Manual construction of predominance area diagrams is a very time consuming process making this an ideal problem for solution with computers. Programs have been written to construct these diagrams [10-16]. Programs designed for this purpose are present and accessible at the Integrated Thermochemical Database (ITD) sites, like F*A*C*T of Canada and CSIRO of Australia (see [25, 26]). But, since most of the programs run on site

mainframes, users must connect to these host computers to obtain a diagram.

In North America, F*A*C*T of Canada is the principal system available for dial-up service on a mainframe computer. The F*A*C*T system was initiated in 1979 with the host computer being located at McGill University. Access to F*A*C*T is via Datapac, Telenet or Tymenet. The programs are interactive and user-friendly. The system is divided into 13 application programs. PREDOM program, present in the F*A*C*T site, constructs isothermal predominance area diagrams. The availability of the CSIRO system has been greatly enhanced in recent years. System initiated in 1975 in collaboration with NPL (National Physical Laboratory, U.K). Programs operate on VAX 11/750 (VMS) and other mini-computers and on IBM PC. There are nine programs along with the thermodynamic database included in the system. SYSTEM program, which operates on this site, constructs predominance area, Eh-pH (Pourbaix) and related diagrams with a flexible choice of axes variables. Other important ITD sites that have capability to draw predominance area diagrams are MTDATA (U.K), THERDAS (Germany) and THERMO-CALC (Sweden).

Operation of these programs by users at host computer site or away from that site requires a subscription. This arrangement is securing the copyright of programs and providing financial benefit to developers. Although the security of programs are guaranteed by computer centers, the cost of that is paid by users. Especially users that are far away from host computer site are charged heavily on data communications, by data switch networks, and by computer centers for subscription.

With the wide spread use of personal computers, programs that run on IBM PC and compatibles are being developed [10, 12, 13]. Although some of these programs are freely distributed , they can not offer developed features to users as mainframe programs does. For example, the program given by Ventakhalam [10] can only construct PAD of ternary systems with classical log (P_{O_2}) vs. log (P_{SO_2}) axes. Also, to use the program user must supply a high number of data including thermochemical ones. This time consuming deficiency is also seen in the PSD program [13]. PSD is a more recent

interactive program designed in the University of Kentucky, for PC and compatibles. Later, this program was adapted by the Generic Mineral Technology Center for Pyrometallurgy of University of Missouri-Rolla [32]. To use the PSD program, user must supply the number of species and name of each, the number of component atoms in each species, and the standard Gibbs energy of formation of each species in order to construct a diagram. There is no support present in PSD for non-stoichiometric and decomposing phases. Although program runs faster than other PAD constructing programs, it is heavily dependent on user interaction. PSD program works with a relatively small sized database and constructs a separate data file for each system examined. This operation results in an unorganized and crowded data sets, which affects the performance of the program.

More recently another type of application, that involves the use of full capacity of the mainframe programs with graphic capabilities of external devices are introduced. This is done either by use of a plotter attached to mainframe or by interfacing mainframe to PC and/or compatibles [33]. The only advantage of this approach is improved graphics output, users are still charged for subscription and data communications.

1.4 Aim of This Study

Main objective of the present work is to develop an interactive computer program to construct predominance area diagrams on IBM PC and compatibles. The direction taken during the course of present study was to develop a program, that will have comparable details to mainframe programs and at the same time implement the power of personal computers to ease user interactions. Therefore the program was designed to offer the following features :

- Automatic handling of all necessary thermochemical data input and calculations.
- Automatic selection of possible species that can take form for any given system.

- Support for multicomponent (3 to 6 elements) systems.
- Provision for user interaction to modify the data.
- Freedom in variable selection for axes.
- Determining diagram scale freely.
- Handling non-stoichiometric and decomposing phases.
- Support for systems having 2-metals.
- Advanced features for detailed diagram examination like zoom-in and zoom-out functions.
- Pull-Down menu system with "Help to User" utility.
- Relatively large and upgradable database.

CHAPTER II

THEORY OF PREDOMINANCE AREA DIAGRAMS

2.1 PAD Construction Principles

Construction of a predominance area diagram advances in three stages. At the first stage, possible species that can take form in the predefined system are found. At the next step standard Gibbs energy changes for various reactions taking place in the system are calculated, and at the final stage stability areas for various species are plotted as a function of partial pressures of two gases (or activities of selected condensed species) involved in the reactions by using these Gibbs energy changes. Since the lines on predominance area diagrams separate two areas of thermodynamic stabilities, their construction is based on the criteria that, Gibbs energy at a specified temperature and pressure is the lowest for a particular specie in the region where it is stable. Therefore, Gibbs energies of two species that have adjacent stability areas are equal along boundary lines that separate two region from each other.

Thus, to draw predominance area diagrams, both manual construction and computer algorithms should follow the three steps shown below:

- Define the thermodynamic system: reactions involved and constant temperature.
- Calculate standard Gibbs energy changes, ΔG°, associated with all these reactions at required temperature.
- Find stability regions using either equilibrium constants or Gibbs energy changes of reactions.

In the following sections the methods that deal with the development of a predominance area diagram will be explained with reference to the construction of log P_{O_2} vs. log P_{SO_2} diagram for Cu-O-S system at 1000°K.

2.2 Defining The System

To define the thermodynamic system, one should know elements that take part in reactions, which builds up the system, and constant temperature. After the thermodynamic system is defined completely, species (all combinations of given elements) that can be formed after possible reactions are found by tracing the thermochemical database. To find correct data from the database an algorithm called EXTRACT is designed in this study. Details of this algorithm are given in Appendix A. For Cu-O-S system the following list of species are present at 1000°K :

Name	State at 1000°K
Cu	Solid
Cu_2O	Solid
Cu_2S	Solid-3
Cu_2SO_4	Solid
CuO	Solid
$CuO \cdot CuSO_4$	Solid
CuS	Solid
$CuSO_4$	Solid

As seen from above table, if there is only one crystalline state present for a particular specie at the given temperature, this state is designated as "Solid". But if there are more than one crystalline states present for this specie, which are stable within different temperature ranges, then these states are designated with "Solid" sign together with a number showing rank of the crystalline state. This number increases with a change in the crystalline state, thus "Solid–1" means first crystalline state, "Solid–2" means second crystalline state and so on. In the case of Cu_2S, the third

crystalline state is stable at 1000°K.

2.3 Standard Gibbs Energy of Formation

In the present study, elementary thermodynamic data are used for the calculation of standard Gibbs energy of formation, to make the use of program easy and to add potential to the database of the program. Standard Gibbs energy of formation of any species, ΔG°, at a constant temperature is calculated by using specific heat capacity, C_p, standard enthalpy of formation, $\Delta H^\circ_{298.15}$, and standard entropy, $S^\circ_{298.15}$. In addition, transformation temperature, T_{tr}, and enthalpy change due to transformation, ΔH°_{tr}, are incorporated when species undergo phase transformations within the temperature range between 298.15°K and the temperature for which the diagram is to be constructed. To compute standard Gibbs energy of formation, one needs to determine enthalpy of formation, ΔH°_T, and entropy of formation, ΔS°_T, at the given temperature T. If specific heat capacity is represented with the form below

$$C_p = A + B \cdot T + C \cdot T^{-2} + D \cdot T^2 \qquad (2.1)$$

Then, for any temperature T (T>298.15), Kirchoff equation can be applied

$$\Delta H^\circ_T = \Delta H^\circ_{298.15} + \int_{298.15}^{T} \Delta C_p \cdot dT \qquad (2.2)$$

where

$$\Delta C_p = \sum C_{p,Product} - \sum C_{p,Reactants} \ .$$

Above equation is valid if there is no phase transformation for the species involved in the formation of a compound. If there are phase changes within temperature range from 298.15°K to T, above equation is separated in such a way 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} is introduced with a positive sign. If any reactant (element), of reaction discussed, changes phase, its ΔH_{tr} is introduced with a negative sign to the ΔH°_T expression. Then equation (2.2) takes the form (for $T_{tr\ (Prod)} > T_{tr\ (React)}$)

$$\Delta H^\circ_T = \Delta H^\circ_{298.15} + \int_{298.15}^{T_{tr\ (React)}} \Delta C_{p_1} \cdot dT - \Delta H^\circ_{tr\ (React)} +$$

$$\int_{T_{tr\ (React)}}^{T_{tr\ (Prod)}} \Delta C_{p_2} \cdot dT + \Delta H^\circ_{tr\ (Prod)} + \int_{T_{tr\ (Prod)}}^{T} \Delta C_{p_3} \cdot dT \qquad (2.3)$$

Where

$T_{tr\ (React)}$, $T_{tr\ (Prod)}$ = transformation temperatures of reactant & product
$\Delta H^\circ_{tr\ (React)}$, $\Delta H^\circ_{tr\ (Prod)}$ = enthalpy of transformations at T_{tr}
ΔC_{p_1} , ΔC_{p_2} and ΔC_{p_3} are ΔC_p values for the temperature ranges over which they are integrated.

Following the same formalism as C_p, ΔC_p is expressed in the form

$$\Delta C_p = \Delta A + \Delta B \cdot T + \Delta C \cdot T^{-2} + \Delta D \cdot T^2 \qquad (2.4)$$

then, integration of equation (2.3) yields

$$\Delta H^\circ_T = H_\circ + \Delta A \cdot T + \frac{\Delta B}{2} \cdot T^2 - \Delta C \cdot \frac{1}{T} + \frac{\Delta D}{3} T^3 \qquad (2.5)$$

where the term $H_\circ$ is made up of $\Delta H^\circ_{298.15}$, integration constant and ΔH_{tr} values associated with phase transformations.

Similarly, entropy of formation is calculated by

$$\Delta S^\circ_T = \Delta S^\circ_{298.15} + \int_{298.15}^{T} \frac{\Delta C_p}{T} \cdot dT \qquad (2.6)$$

If there are phase changes, incorporation of entropy changes due to these transformations yield

$$\Delta S^\circ_T = \Delta S^\circ_{298.15} + \int_{298.15}^{T_{tr\ (React)}} \frac{\Delta C_{p_1}}{T} \cdot dT - \frac{\Delta H^\circ_{tr\ (React)}}{T_{tr\ (React)}} +$$

$$\int_{T_{tr\ (React)}}^{T_{tr\ (Prod)}} \frac{\Delta C_{p_2}}{T} \cdot dT + \frac{\Delta H^\circ_{tr\ (Prod)}}{T_{tr\ (Prod)}} + \int_{T_{tr\ (Prod)}}^{T} \frac{\Delta C_{p_3}}{T} \cdot dT \qquad (2.7)$$

after integrating

$$\Delta S^\circ_T = S_\circ + \Delta A \cdot \ln T + \Delta B \cdot T - \frac{\Delta C}{2} \cdot \frac{1}{T^2} + \frac{\Delta D}{2} \cdot T^2 \qquad (2.8)$$

Where the term $S_\circ$ is a constant and obtained like $H_\circ$ value.

Thermochemical data including C_p, $\Delta H^\circ_{298.15}$, $S^\circ_{298.15}$, T_{tr} and ΔH°_{tr} for Cu-O-S system is taken from a standard source [27] and listed in Tables 2.1 and 2.2 . Examination of these tables shows the presence of two C_p equations, for species: Cu, Cu_2O and $CuSO_4$, although there are no phase transformations present for these species below 1000 °K. The reason for this operation is to get a better analytical fit for C_p from the experimental data. C_p fitting details from the experimental data is given in Appendix B.

Table 2.1 C_p Ranges and Constants for Cu-O-S Bearing Species

	Range(°K)		C_p (Cal/Deg·mole)			
	T_1	T_2	A	B	C	D
Cu	298	700	5.9418	4.759980E-4	-25159.5	4.67471E-7
	700	1000	8.3928	-3.72695E-3	-260477	2.44816E-6
Cu_2O	298	900	15.6382	3.967260E-3	-166701	0
	900	1000	6.7349	1.002379E-2	2636233	0
Cu_2S	298	376	11.4953	2.315034E-2	-1394.46	0
	376	720	28.3007	-1.39058E-2	18933.6	5.33379E-6
	720	1000	20.0104	-2.99536E-4	58559.1	-1.4770E-7
Cu_2SO_4	298	1000	23.7997	1.660032E-2	22.145	0
CuO	298	1000	11.6106	1.778860E-3	-181481	0
$CuO \cdot CuSO_4$	298	1000	40.832	1.084401E-2	-938192	0
CuS	298	1000	10.6429	2.640067E-3	11.240	0
$CuSO_4$	298	700	25.2730	1.430434E-2	-529087	0
	700	1000	43.8358	-3.72184E-3	-3487093	0

Table 2.2 $\Delta H°_{298.15}$, $S°_{298.15}$, T_{tr} and $\Delta H°_{tr}$ values

	$\Delta H°_{298.15}$ Cal	$S°_{298.15}$ Cal	T_1 °K	$\Delta H°_1$ Cal	T_2 °K	$\Delta H°_2$ Cal
Cu	0	7.926	-	-	-	-
Cu_2O	-40799	22.07	-	-	-	-
Cu_2S *	-19400	27.76	376	864	720	280
Cu_2SO_4	-179588	43.599	-	-	-	-
CuO	-37299	10.179	-	-	-	-
$CuO \cdot CuSO_4$	-221700	37.599	-	-	-	-
CuS	-12690	15.89	-	-	-	-
$CuSO_4$	-184358	26.052	-	-	-	-

* Transformation temperatures are 376 °K and 720 °K.

Finally, standard Gibbs energy of formation of any specie at temperature T is

$$\Delta G^\circ_T = \Delta H^\circ_T - T \cdot \Delta S^\circ_T \qquad (2.9)$$

By replacing the value of T, numerical value for ΔG° can be determined. Calculated ΔG° values for Cu-O-S system at 1000°K are shown in Table 2.3

Table 2.3 ΔG° values of Cu-O-S bearing species

Name	ΔG°_{1000} (Cal)
Cu	0
Cu_2O	-22829
Cu_2S	-23459
Cu_2SO_4	-97674
CuO	-15867
$CuO \cdot CuSO_4$	-112030
CuS	-9576
$CuSO_4$	-94638

2.4 Finding Stability Regions

General procedures used to determine the stability regions of predominance area diagrams can be found in references [10] , [28]. After the definition of the thermodynamic system and calculation of standard Gibbs energy of formations completed, stability regions, for manual construction, are found by using the steps shown below:

- Combine the chemical reactions involving gas phases for all pairs of species. The number of such reactions will be

$$\binom{n}{2} = \frac{n!}{(n-2)! \cdot 2!}$$

where n is the number of species considered.

- Calculate "log K" values for each reaction, where K is the equilibrium constant of a reaction at the required temperature, from the relation

$$\log K = \frac{-\Delta G^\circ}{2.303 \cdot RT} \tag{2.10}$$

Where R = 1.987 Cal/deg. mole.

- Choose variables for axes of the predominance area diagram, as the partial pressures of two gases (or activities of condensed phases) that are present in the system.
- Write the equations for log K, for all the reactions in terms of variables of X and Y axes of the diagram. If we choose, for example, X axis as base 10 logarithm of partial pressures of oxygen (P_{O_2}) and Y axis as base 10 logarithm of partial pressure of sulfur dioxide (P_{SO_2}), then one can write

$$K = \frac{(P_{SO_2})^m}{(P_{O_2})^n} \tag{2.11}$$

and

$$\log K = m \cdot \log (P_{SO_2}) - n \cdot \log (P_{O_2}) \tag{2.12}$$

for all equilibria.

- Equate equations (2.10) and (2.12) to get straight line equations on $\log (P_{SO_2})$ and $\log (P_{O_2})$ axes at a particular temperature.
- Plot lines and construct the predominance area diagram for a given system at the given temperature, by determining the most stable species at different points.

Example for Manual construction:

Construction of $\log P_{O_2}$ vs $\log P_{SO_2}$ PAD for Cu-O-S system at 1000 °K will be explained below.

Construction starts with finding combinations of reactions involving

gas phases. Application of phase rule to a three component system indicates that an equilibrium among five phases has no degrees of freedom. Thus, if a gas phase is always present,

- four condensed phases can be in equilibrium with one another and a gas phase at an invariant state,
- three condensed phases can be in equilibrium with one another and a gas phase at an arbitrarily chosen temperature,
- two condensed phases can be in equilibrium with one another and a gas phase at an arbitrarily chosen temperature and an arbitrarily chosen value of P_{O_2} or P_{SO_2}, and
- one condensed phase can be in equilibrium with the gas phase at an arbitrarily chosen temperature and arbitrarily chosen values of P_{O_2} and P_{SO_2}.

As eight solid phases are present in the system, there are $\binom{8}{3} = 56$ possible equilibria involving three condensed phases and the gas phase, $\binom{8}{2} = 28$ possible equilibria involving two condensed phases and the gas phase. In addition, there are eight possible equilibria involving a single condensed phase and the gas phase. However most of the 56 four phase and the 28 three phase equilibria are metastable. In the current system, computations show that there are 14 univariant lines, where two condensed phases are in equilibrium with the gas phase, and 7 invariant points, where three condensed phases are in equilibrium with the gas phase.

At the second step, equilibrium constants of reactions that take place at 1000°K for the system of interest are found. At equilibrium one can write $\Delta G^\circ = -R \cdot T \cdot \ln K$, replacing the constants R and T=1000°K, above term yields

$$\log K = \frac{-\Delta G^\circ}{4576.061}$$

Formation reactions for this system and their equilibrium constants are given in Table 2.4.

Table 2.4 Formation reactions and their equilibrium constants

No	Reaction	log K at 1000 °K
1.	$2 \cdot Cu + \frac{1}{2} \cdot O_{2(g)} = Cu_2O$	4.9888
2.	$Cu + \frac{1}{2} \cdot O_{2(g)} = CuO$	3.4674
3.	$2 \cdot Cu + \frac{1}{2} \cdot S_{2(g)} = Cu_2S$	5.1264
4.	$Cu + \frac{1}{2} \cdot S_{2(g)} = CuS$	2.0926
5.	$2 \cdot Cu + \frac{1}{2} \cdot S_{2(g)} + \frac{5}{2} \cdot O_{2(g)} = CuO \cdot CuSO_4$	24.4817
6.	$Cu + \frac{1}{2} \cdot S_{2(g)} + 2 \cdot O_{2(g)} = CuSO_4$	20.6811
7.	$2 \cdot Cu + \frac{1}{2} \cdot S_{2(g)} + 2 \cdot O_{2(g)} = Cu_2SO_4$	21.3445
8.	$\frac{1}{2} \cdot S_{2(g)} + O_{2(g)} = SO_2$	15.0756

At the next step, equations for log K, for all the reactions in terms of the partial pressures of X and Y axis of the diagram are written. From here the equations of straight lines on log (P_{SO_2}) and log (P_{O_2}) axes at 1000 °K are found by procedure outlined in section 2.4. These equations are shown below in Table 2.5

By using equilibrium lines (A to N) and considering stable species at different points, manual construction of predominance area diagram is completed (see Fig 2.1 (a) through (l)). In these figures, diagrams on the left hand side represents the equilibrium lines extending through the diagram. These lines include both stable and metastable equilibria. Diagrams on the right hand side represents the points of intersection together with stability regions which are formed by equilibrium lines. All the constructions done above are obtained by eliminating metastable extensions of equilibrium lines [28].

Table 2.5 Equations of univariant equilibrium lines

Line	Equilibrium	Equation
A.	Cu - Cu_2O - Gas Phase	$\log P_{O_2} = -9.9776$
B.	Cu - Cu_2S - Gas Phase	$\log P_{SO_2} = \log P_{O_2} + 9.9492$
C.	Cu_2O - Cu_2S - Gas Phase	$\log P_{SO_2} = 1.5 \cdot \log P_{O_2} + 14.938$
D.	Cu_2O - $CuSO_4$ - Gas Phase	$\log P_{SO_2} = -0.75 \cdot \log P_{O_2} - 3.1111$
E.	Cu_2S - $CuSO_4$ - Gas Phase	$\log P_{SO_2} = -3 \cdot \log P_{O_2} - 21.1602$
F.	$CuSO_4$ - $CuO \cdot CuSO_4$ - Gas Phase	$\log P_{SO_2} = -0.5 \cdot \log P_{O_2} - 1.8049$
G.	Cu_2O - $CuO \cdot CuSO_4$ - Gas Phase	$\log P_{SO_2} = -\log P_{O_2} - 4.4173$
H.	Cu_2O - CuO - Gas Phase	$\log P_{O_2} = -3.892$
I.	CuO - $CuO \cdot CuSO_4$ - Gas Phase	$\log P_{SO_2} = -0.5 \cdot \log P_{O_2} - 2.4713$
J.	Cu_2S - CuS - Gas Phase	$\log P_{SO_2} = \log P_{O_2} + 16.0168$
K.	CuS - $CuSO_4$ - Gas Phase	$\log P_{O_2} = -9.2942$
L.	Cu_2S - Cu_2SO_4 - Gas Phase	$\log P_{O_2} = -8.10905$
M.	Cu_2SO_4 - $CuSO_4$ - Gas Phase	$\log P_{SO_2} = -\log P_{O_2} - 4.9421$
N.	Cu_2SO_4 - Cu_2O - Gas Phase	$\log P_{SO_2} = -0.5 \cdot \log P_{O_2} - 1.2801$

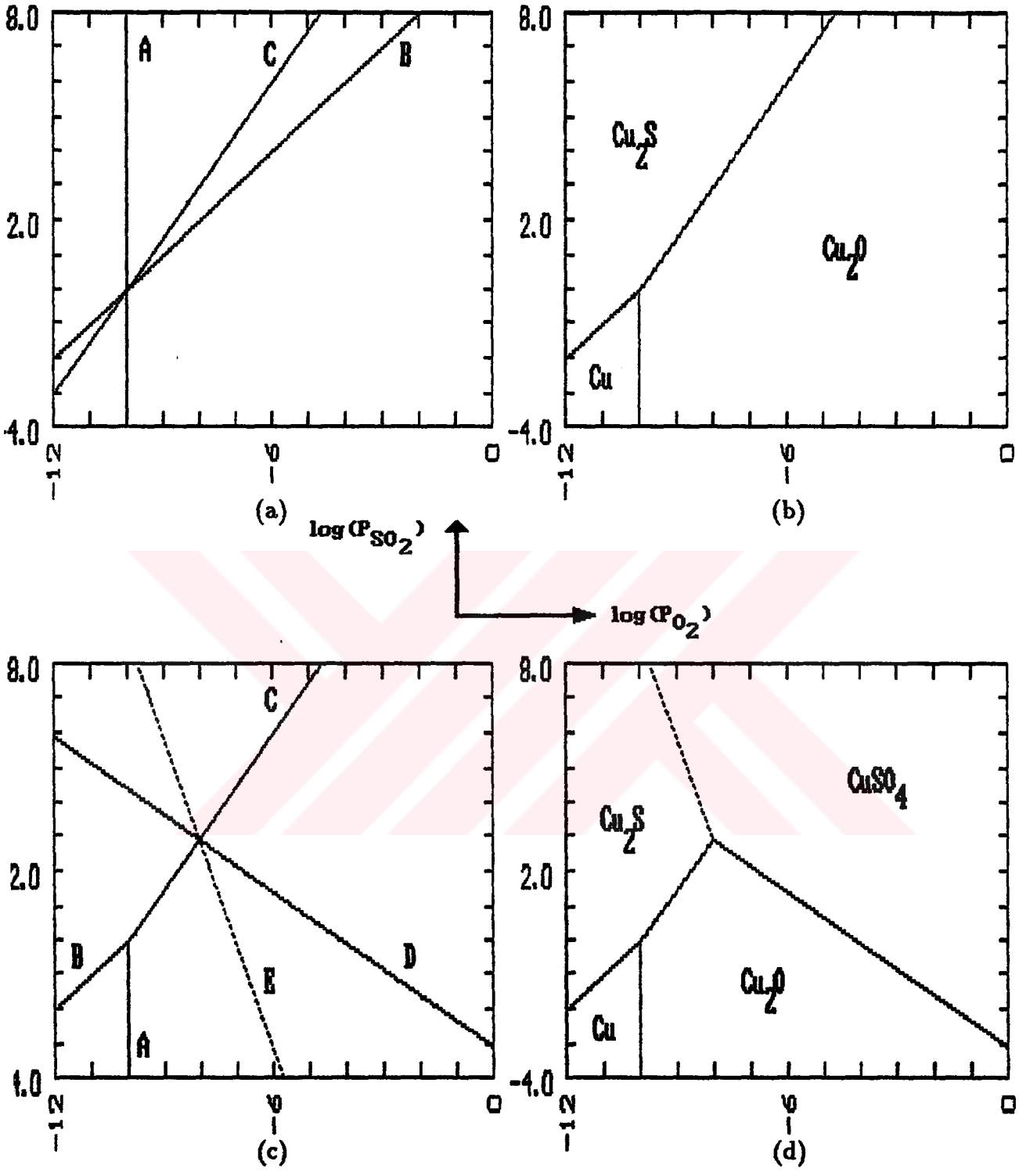


Figure 2.1 Manual Construction of PAD for Cu-O-S system

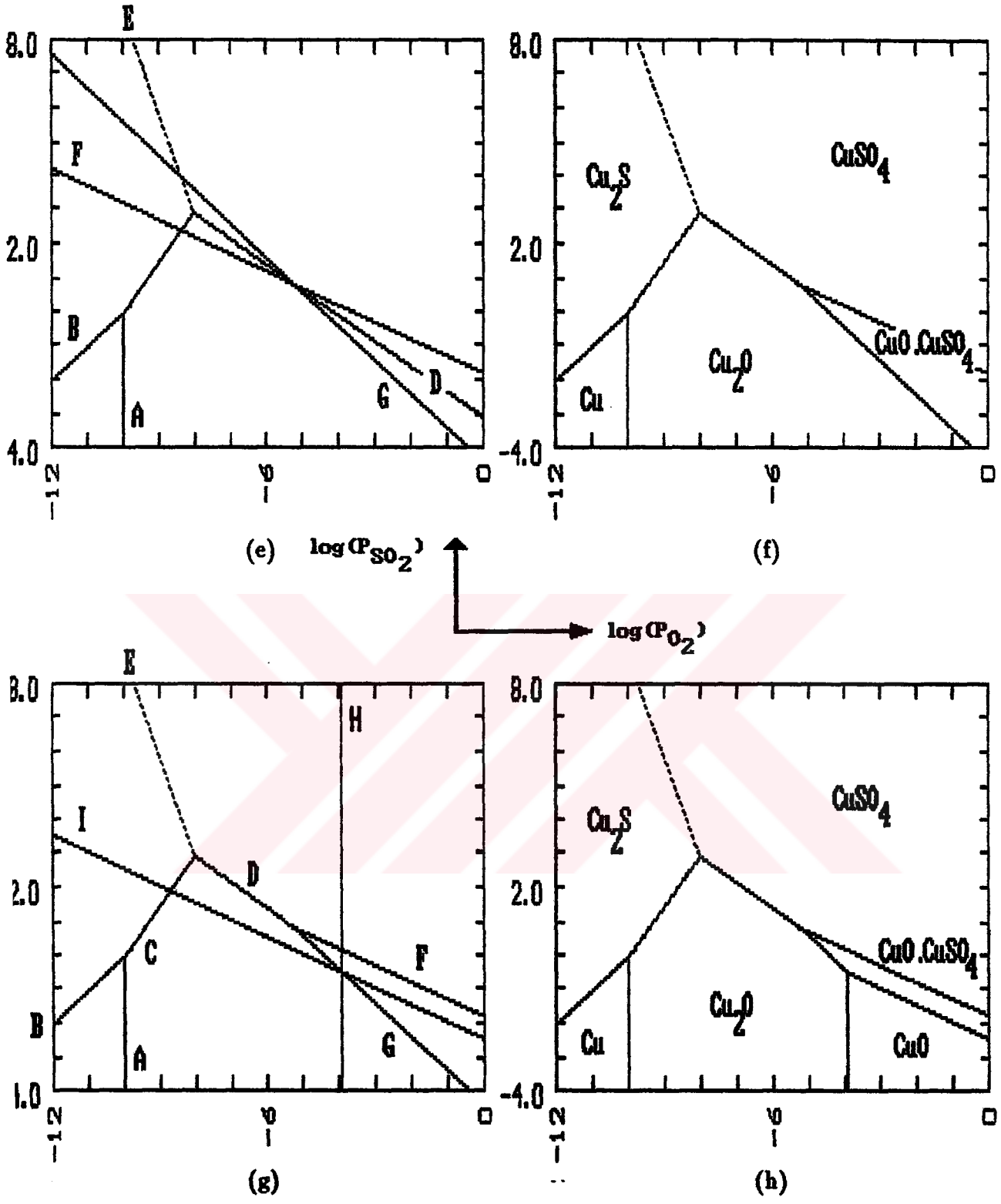


Figure 2.1 (cont'd)

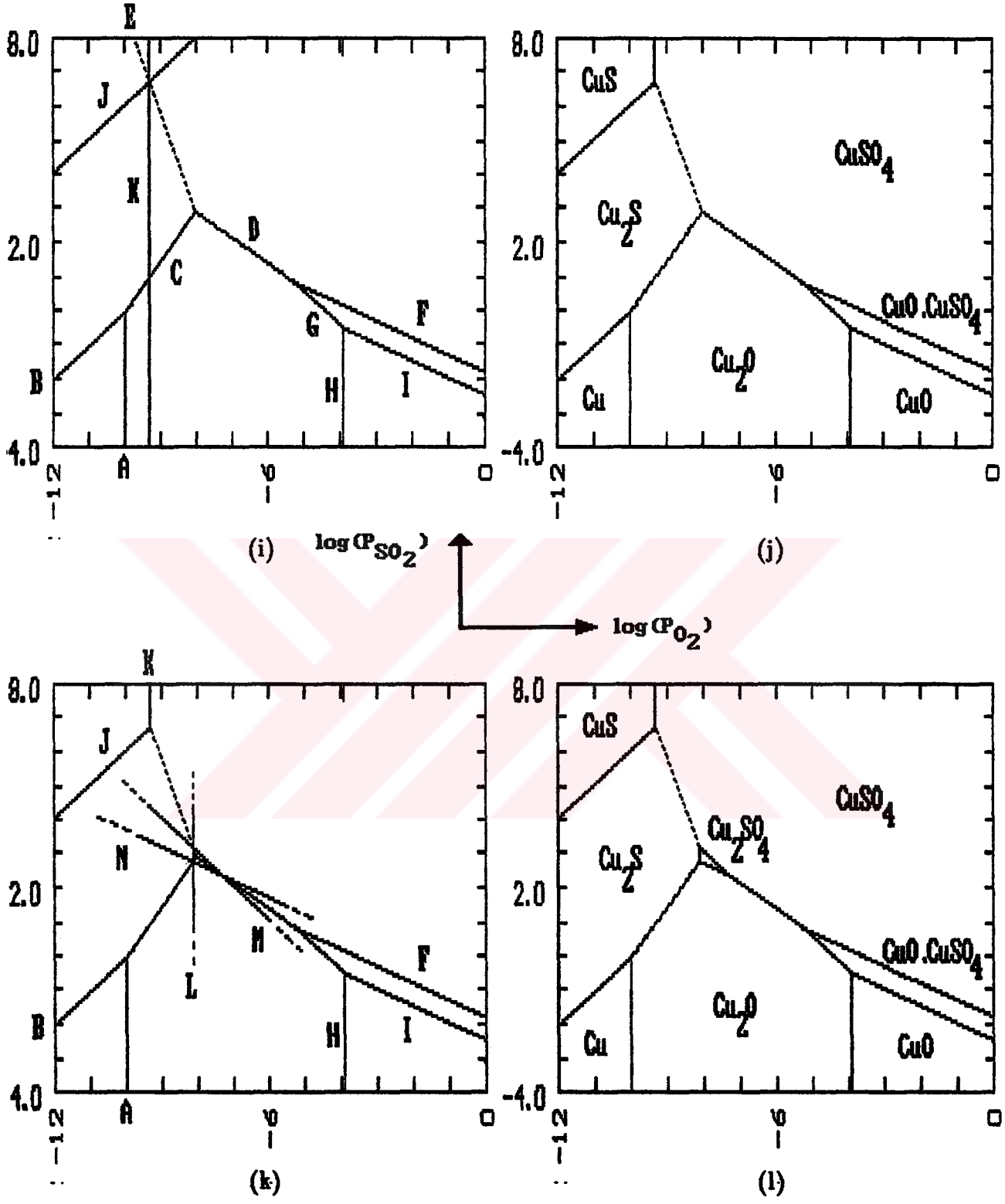


Figure 2.1 (cont'd)

CHAPTER III

CONSTRUCTION OF PAD BY COMPUTER

3.1 Introduction

Although the general strategy of predominance area diagram construction is the same for manual and computer calculation, both methods differ from each other in several ways. These differences can be summarized as follows:

1. All the reactions that can take place in the system are known in manual construction, whereas computer calculation must re-determine them.
2. Manual calculation uses univariant lines and invariant points to find stability regions but present computer program uses Gibbs energy of formation and grid point calculation to determine stability areas.
3. Changes in axes selection do not affect the manual calculation strategy, but computer program must use a new algorithm depending on the diagram type.

Construction of Predominance Area Diagrams with computer can be summarized by the following series of steps:

- Choose axes of the predominance area diagram, as the base 10 logarithm of partial pressures of two gases or activities of condensed phases that are present in the system.
- Calculate Gibbs energies of formation, ΔG , of all the species at the specified coordinates on the diagram. For any species $M_zA_jB_kC_lD_m$ formed, one can write

$$M + \frac{j}{z \cdot s} A_{s_{(g)}} + \frac{k}{z \cdot t} B_{t_{(g)}} + \frac{l}{z \cdot u} C_{u_{(g)}} + \frac{m}{z} D = \frac{1}{z} M_z A_j B_k C_l D_m \qquad (3.1)$$

For the reaction (3.1) Gibbs energy of formation is calculated as

$$\Delta G = \Delta G^\circ + RT \cdot \ln \frac{{}^{a}M_z A_j B_k C_l D_m^{\frac{1}{z}}}{a_M \cdot P_{A_s}^{\frac{j}{z \cdot s}} \cdot P_{B_t}^{\frac{k}{z \cdot t}} \cdot P_{C_u}^{\frac{l}{z \cdot u}} \cdot a_D^{\frac{m}{z}}} \qquad (3.2)$$

Where

${}^{a}M_z A_j B_k C_l D_m$ = activity of the specie $M_z A_j B_k C_l D_m$

P_{A_s} , P_{B_t} , P_{C_u} = partial pressures of gases A_s, B_t and C_u respectively

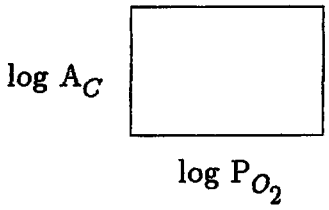
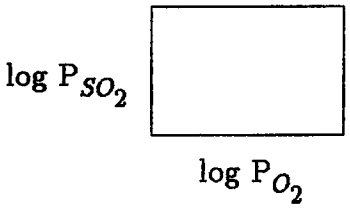
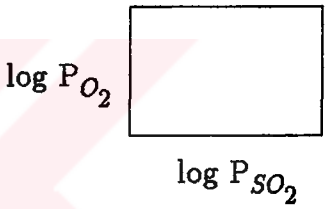
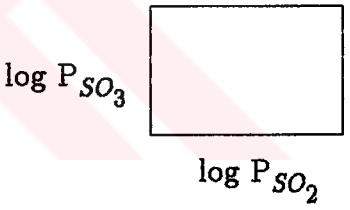
a_M , a_D = activities of reactant metal and specie D

- Determine the most stable specie at any specified coordinate of the diagram. Selection is based on the criteria that the specie that has the lowest Gibbs energy of formation is the most stable.
- Stabilities of species are continuously tested along horizontal and vertical axes. Whenever two successive tests reveal two different species as stable phases, it is decided that a phase boundary lies between those two coordinates.
- This procedure is repeated until the whole diagram is covered.

3.2 Selection of Axes

As mentioned above, axes selection plays an important role in diagram construction. Diagram axes (freely chosen by the user) can be partial pressures (or activities in case of condensed phases) of elements, compounds or algebraic combination of the two. The term element is used to indicate species with only one type of element. For every different type of diagram a new computation method must be followed. Possible diagram types present and related examples are shown below in Table 3.1 .

Table 3.1 Possible PAD Types and Related Examples

Diagram Type	Y- axis X- axis	Example
A	Element* - Element*	
B	Compound - Element*	
C	Element* - Compound	
D	Compound - Compound	

* The term element is used to indicate species with only one type of element

SKOP v.2 program only deals with diagram types A,B and C. There is no support for D type diagrams at present. However, information about those diagrams can be obtained by constructing other types of diagrams for a series of conditions.

3.3 Gibbs Energy of Formation

Suppose that a reactive metal, M, is present in a gaseous environment,

composed of A,B and C elements together with condensed phase D at a constant temperature T. For any specie $M_zA_jB_kC_lD_m$ formed, chemical equilibrium given in equation (3.1) can be written.

Gibbs energy of formation for $M_zA_jB_kC_lD_m$ at temperature T is given in equation (3.2). If activity of reactive metal, a_M, is taken as unity, equation (3.2) can be reorganized as

$$\Delta G = \Delta G^\circ - RT \cdot \ln \left(P_{A_s}^{\frac{j}{z \cdot s}} \cdot P_{B_t}^{\frac{k}{z \cdot t}} \cdot P_{C_u}^{\frac{l}{z \cdot u}} \cdot a_D^{\frac{m}{z}} \right) + RT \cdot \ln \left(a_{M_zA_jB_kC_lD_m}^{\frac{1}{z}} \right) \quad (3.3)$$

and rearrangement yields

$$\Delta G = \Delta G^\circ - RT \cdot \left(\frac{j}{z \cdot s} \ln P_{A_s} + \frac{k}{z \cdot t} \ln P_{B_t} + \frac{l}{z \cdot u} \ln P_{C_t} + \frac{m}{z} \ln a_D \right) + RT \cdot \ln \left(a_{M_zA_jB_kC_lD_m}^{\frac{1}{z}} \right) \quad (3.4)$$

The term

$$\frac{j}{z \cdot s} \ln(P_{A_s}) + \frac{k}{z \cdot t} \ln(P_{B_t}) + \frac{l}{z \cdot u} \ln(P_{C_u}) + \frac{m}{z} \ln(a_D) \quad (3.5)$$

is the main unknown of the equation (3.4) and will be called as "Pressure term" within the context of this thesis. All the computations regardless of diagram type is based on the calculation of this pressure term. Since PAD construction algorithm uses Gibbs energy of formation (3.4) at the different coordinates of the diagram, pressure term always changes.

3.4 Determination of the Pressure Term

General strategy in finding the pressure term (PT) at any point on the diagram is very straightforward. Depending on the type of diagram and number of unknowns, (P_{A_s}, P_{B_t} , etc.) different procedures are applied. If there are only two unknowns, they are determined either directly or indirectly

from the coordinates of points at which Gibbs energy change is being calculated. Direct determination is done with the help of diagram coordinates, when any axis of the diagram is chosen as an element (specie with only one element). Indirect determination of unknown(s) is done, if the axis involves a compound. In this case an equilibrium between elements that make up the compound has to be considered. If there are more than two unknowns, only two of them are determined from the coordinates, the remaining terms are requested from the user. These procedures will be explained for different types of diagrams with reference to M-A-B-C-D system.

3.4.1 Type A Diagram

In this type, diagram is constructed as a function of base 10 logarithm of partial pressures (or activities in the case of condensed phases) of two species each with only one type of element. If one denotes X and Y to be horizontal and vertical axes respectively and if partial pressures of A_t and B_t are variables for these axes, then

$$X = \log (P_{A_s})$$

and

$$Y = \log (P_{B_t})$$

Then unknowns in PT (equation(3.5)) can be

$$\ln(P_{A_s}) = 2.303 * X$$
$$\ln(P_{B_t}) = 2.303 * Y$$
$$\ln(P_{C_u}) = \text{Supplied by the user}$$
$$\ln(a_D) = \text{Supplied by the user}$$

Pressure term (equation (3.5)) at any point on the diagram now can be easily calculated by using above values.

3.4.2 Type B Diagram

In this type, the variable for X axis is partial pressure or activity of a specie that has only one type of element, and the variable for Y axis is partial pressure or activity of a compound that contains the element used to define the variable for X axis. Again X and Y axes represent base 10 logarithms of partial pressures for gases or activities of condensed phases. For example, if partial pressures of B_t and AB_t gases are taken as variables for horizontal and vertical axes respectively. Then

$$X = \log (P_{B_t})$$

and

$$Y = \log (P_{AB_t})$$

The value from X axis can be used directly in the pressure term, because

$$\ln (P_{B_t}) = 2.303 * X$$

But to determine unknown P_{A_s} (or $\ln (P_{A_s})$) , an equilibrium between A_s–B_t–AB_t has to be considered. This equilibrium is

$$\tfrac{1}{s} \cdot A_{s_{(g)}} + B_{t_{(g)}} = AB_{t_{(g)}}$$

Using standard Gibbs energy of formation for AB_t

$$\Delta G^\circ_{AB_t} = -RT \cdot \ln(K)$$

Replacing equilibrium partial pressures

$$\Delta G^\circ_{AB_t} = -RT \cdot \ln \left(\frac{P_{AB_t}}{P_{A_s}^{\frac{1}{s}} \cdot P_{B_t}} \right)$$

Rearrangement yields

$$\frac{P_{AB_t}}{P_{A_s}^{\frac{1}{s}} \cdot P_{B_t}} = e^{\left(\frac{-\Delta G^\circ_{AB_t}}{RT} \right)} \qquad (3.6.a)$$

$$\frac{P_{A_s}^{\frac{1}{s}} \cdot P_{B_t}}{P_{AB_t}} = e^{\left(\frac{\Delta G^\circ_{AB_t}}{RT}\right)} \qquad (3.6.b)$$

from here

$$P_{A_s}^{\frac{1}{s}} = e^{\left(\frac{\Delta G^\circ_{AB_t}}{RT}\right)} \cdot \frac{P_{AB_t}}{P_{B_t}} \qquad (3.6.c)$$

Then

$$\ln(P_{A_s}) = s \cdot \left(\frac{\Delta G^\circ_{AB_t}}{RT} + \ln\left(\frac{P_{AB_t}}{P_{B_t}}\right) \right) \qquad (3.7.a)$$

or

$$\ln(P_{A_s}) = s \cdot \left(\frac{\Delta G^\circ_{AB_t}}{RT} + \ln(P_{AB_t}) - \ln(P_{B_t}) \right) \qquad (3.7.b)$$

Replacing the values from coordinates

$$\ln(P_{AB_t}) = 2.303 * Y$$

Then

$$\ln(P_{A_s}) = s \cdot \frac{\Delta G^\circ_{AB_t}}{RT} + s \cdot 2.303 \cdot Y - s \cdot 2.303 \cdot X \qquad (3.7.c)$$

The remaining unknowns ($\ln(P_{C_u})$ and $\ln(a_D)$) have to be supplied by the user to complete the list of unknowns.

3.4.3 Type C Diagram

This type is just the reverse of type B diagrams. In this case partial pressure of an element (single element specie) is the variable for Y axis and partial pressure of a gas compound (that contains the element present at the Y axis) is the variable for X axis. Again, in the case of condensed phases

activities are used instead of partial pressures. If partial pressures of B_t and AB_t gases are taken as variables for vertical and horizontal axes respectively. Then

$$X = \log (P_{AB_t})$$

and

$$Y = \log (P_{B_t})$$

In this case the value of Y axis can be used directly in the pressure term, because of

$$\ln (P_{B_t}) = 2.303 * Y$$

Then, to determine the other unknown P_{A_s} (or $\ln(P_{A_s})$), equation (3.7.c) can be used by simply interchanging X and Y. Then

$$\ln (P_{A_s}) = s \cdot \frac{\Delta G^\circ_{AB_t}}{RT} + s \cdot 2.303 \cdot X - s \cdot 2.303 \cdot Y \qquad (3.8)$$

The remaining unknowns have to be supplied by the user.

3.5 Plotting

Final point of the construction of Predominance Area Diagrams is the drawing step. The plotting procedure that will be presented here is known as the "Constrained Chemical Potential" method, first proposed by Bale, Pelton and Thompson [11] and then modified for multi-component systems by Bale [15] . The strategy of the procedure is briefly outlined below.

- Scan every different location (point with different partial pressures) on the predominance area diagram to find the most stable specie at those locations.

- To find the most stable specie, compute the pressure term and calculate Gibbs energy of formation for each specie at those locations.

- Monitor stable species for any change. If a change of stable specie occurs, mark that location as a part of stability area border.

Before discussing algorithms used to plot PAD, some technical information will be given to make reader familiar with screen set-up data.

3.5.1 Definitions

Since predominance area diagrams are displayed on PC monitors, type and characteristics of monitors and graphics cards highly affect the plotting algorithm. All these in turn affect the diagram quality also. Figure 3.1 shows a skeleton diagram demonstrating the important variables, rectangle that surrounds the diagram represents the screen border.

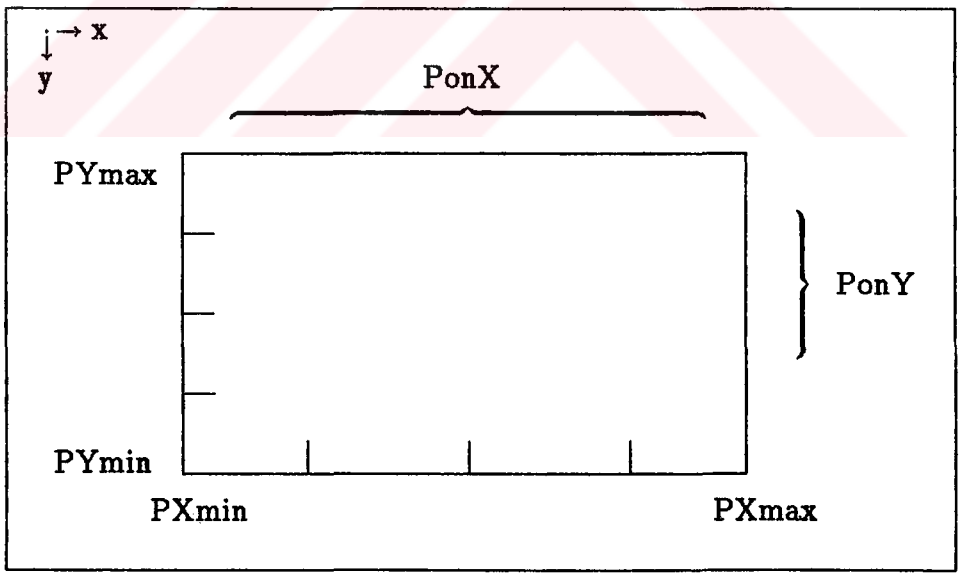


Figure 3.1 A Skeleton PAD

Variables shown in Figure 3.1 are

PXmin: minimum on X axis
PXmax: maximum on X axis
PYmin: minimum on Y axis
PYmax: maximum on Y axis
PonX: number of points (screen pixels) on X axis
PonY: number of points (screen pixels) on Y axis

Except PonX and PonY, all the pressure limits (logarithmic) are given by the user. Number of points (screen pixels) on both axes, PonX and PonY, depends on the monitor (graphics card) type. Pre-defined values of PonX and PonY for different graphics card types are given in Table 3.2 .

Table 3.2 PonX and PonY Values for Different Monitor/Graphics Card Types.

Monitor Type	PonX	PonY
CGA	200	120
MCGA	360	390
EGA	360	240
EGA 64	360	240
HERCULES	360	240
ATT 400	360	315
VGA	360	390

Increment units on both axes are defined as

$$IncPX = (PXmax - PXmin) / (PonX - 1) \quad (3.9.a)$$

$$IncPY = (PYmax - PYmin) / (PonY - 1) \quad (3.9.b)$$

Where IncPX and IncPY are the unit increments per screen pixel on X and Y axes respectively.

3.5.2 Plotting Algorithms

There are three different approaches to construct the diagram:

1- Basic Method: Searching all the locations on the diagram to find stability regions.

2- Constant Interval (CI) Algorithm: Scanning with a constant interval (more than one unit increment), until the change of stable specie occurs. After the detection of a change of stable specie; coming back one interval and setting search space to unit increment. Continuing to scan until program faces with the stable specie change.

3- Variable Interval (VI) Algorithm: Scanning with a variable interval (more than one unit increment), if any change of stable specie occurs. After the detection of a change of stable specie; coming back one interval, setting search space to half difference and continuing to scan. Procedure is repeated until search space reaches to unit increment and change in stable specie occurs.

3.5.2.1 Basic Method

This method is the simplest approach of PAD construction. Computation of pressure term and determination of Gibbs energy of formation of all the species at all coordinates (all pixels) of the diagram is the basis of this method. Illustration of points (pixels) at where computations are done is shown in Figure 3.2. After the computations for all species at a point is done, the specie with the lowest Gibbs energy of formation is accepted as the most stable specie at that point. If computations at two subsequent points of a row yield different species as the most stable, the point at which the new specie appears is marked with a dot to separate stability regions. Calculation starts from the top-left corner of the diagram and proceeds parallel to X axis with the unit increment, IncPX, when one row of Y axis is accomplished, algorithm turns back to PXmin position and the same procedure continues on the next

row of Y axis. The current Y value for the next row of Y-axis is obtained by increasing previous value by IncPY. Precise diagram plotting is the advantage of this method, but algorithm takes a long time to complete the diagram. Number of computations done is PonX * PonY and it increases with increasing monitor size.

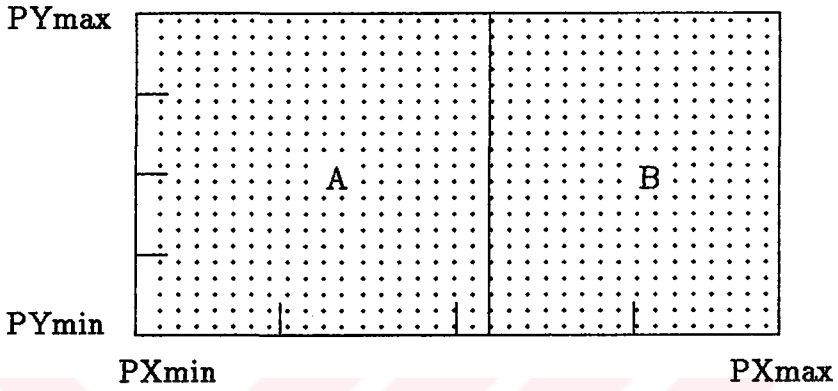


Figure 3.2 Demonstration of Basic Method

3.5.2.2 Constant Interval (CI) Algorithm

In this algorithm, scanning is done with constant intervals. Searching starts from the top-left corner, similar to the basic method, with an interval length IL. In CI algorithm, numerical values that are larger than unit increment (IncPX) are assigned to IL (IL > IncPX). Scanning is continued like the basic method until two subsequent points yield different species as the most stable specie (points 2 and 3 in Figure 3.3 (a)). As soon as program faces with this stability change, algorithm turns back to the previous point (point 2) and sets IL to unit increment (see Figures 3.3 (b)). Scanning is continued until the phase boundary is located precisely (see Figure 3.3 (c)). After exact position of the phase boundary is determined, search increment, IL, is increased again to the previous value. The procedure is continued until the whole diagram is covered.

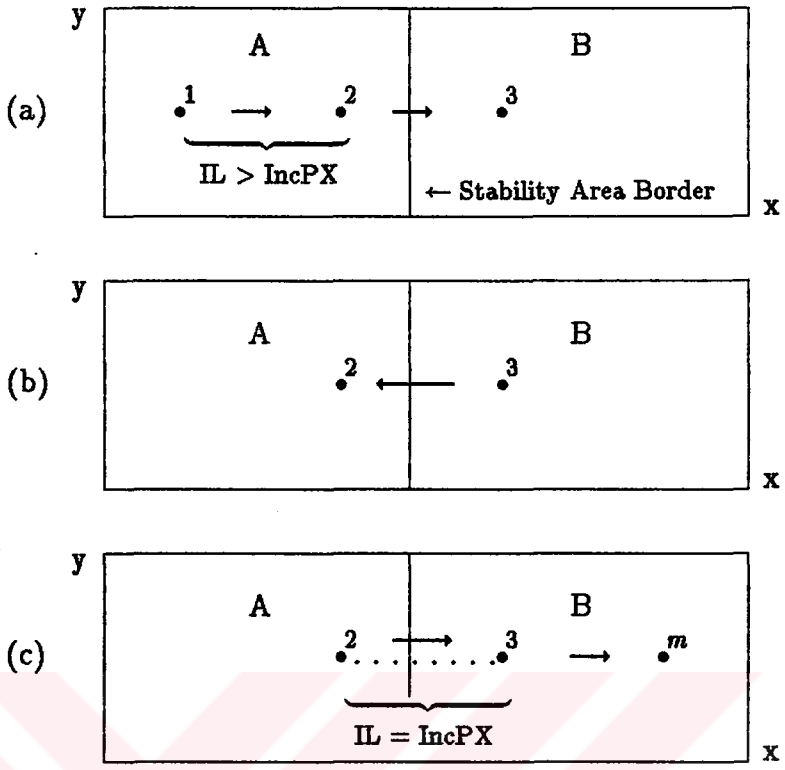


Figure 3.3 Demonstration of CI algorithm.

3.5.2.3 Determination of Optimum IL Value

Since the unit increments on X and Y axes are defined as IncPX and IncPY respectively, an optimum IL value has to be determined for proper diagram computation. Number of points along one row (constant Y) is defined as

$$NPC = \frac{PonX}{IL} + NUL \cdot IL \qquad (3.10)$$

Where

NPC = number of points along one row
PonX = number of points on X axis
NUL = number of univariant lines along current row
IL = interval length

Graphical representation of equation (3.10), for PonX=200 and NUL=1 to 4, is shown in Figure 3.4. As it can be seen from this figure, all of the four curves pass through minima at certain IL values.

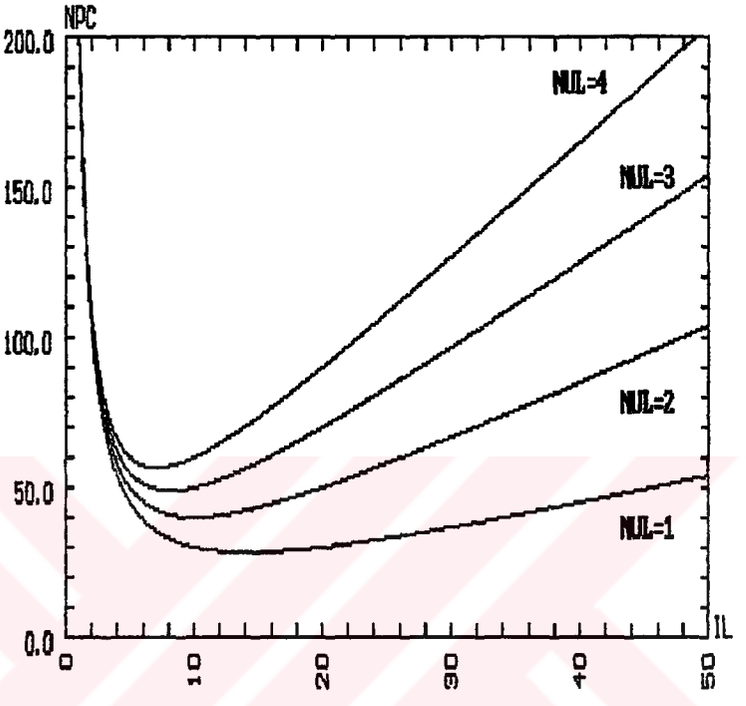


Figure 3.4 Graphical Representation of Equation (3.10) for Different NUL Values.

These minima can be determined from the first derivative of equation (3.10) with respect to variable IL. Taking PonX and NUL as constant, the first derivative becomes

$$\frac{d\,\mathrm{NPC}}{d\,\mathrm{IL}} = -\frac{\mathrm{PonX}}{\mathrm{IL}^2} + \mathrm{NUL} \qquad (3.11)$$

Equating equation (3.11) to zero yields the optimum value of IL as

$$\mathrm{IL} = \sqrt{\frac{\mathrm{PonX}}{\mathrm{NUL}}} \qquad (3.12)$$

Optimum values of IL, for PonX=200 and NUL=1 to 4, are given below

NUL	Optimum Point	IL
4	7.07	7
3	8.16	8
2	10.00	10
1	14.14	14

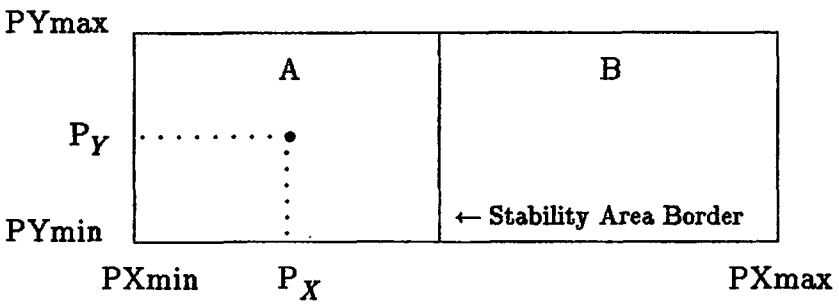
Since number of univariant lines (stability borders) at one row cannot be known before the scan, algorithm selects the NUL value determined in the previous row for the computation. To compute the first row, algorithm accepts NUL to be 4. CI algorithm runs faster than basic method, but there are still many unnecessary calculations that slows down the process.

3.5.2.4 Variable Interval (VI) Algorithm

General strategy of this algorithm is theoretically similar to CI algorithm, but VI algorithm advance with variable increments, instead of constant ones. General outline of VI algorithm, known also as half interval or divided differences method [11], is summarized below in a series of steps together with the illustrative figures and definitions.

Definitions:

P_X = Current pointer on X axis
P_Y = Current pointer on Y axis
P_{last} = Variable pointer on X axis
Stable = Current stable specie
$Stable_{last}$ = Previous stable specie



Algorithm:

Step 1 $P_Y = PYmax$
$Stable_{last} = Stable$

Step 2 Repeat
$P_X = PXmin$
$P_{last} = PXmin$
$IL = PXmax - P_{last}$

Step 3 Repeat
Find Pressure Term
Find Stable Specie at Location (P_X , P_Y)

Step 4 If Stable <> $Stable_{last}$

Step 5 then If IL <> IncPX

$$\text{then} \begin{pmatrix} IL = \dfrac{PXmax - P_{last}}{2} \\ P_X = P_{last} \end{pmatrix}$$

Step 6 else If IL = IncPX

$$\text{then} \begin{pmatrix} \text{Mark Location} \\ Stable_{last} = Stable \\ P_{last} = P_X \\ IL = PXmax - P_X \end{pmatrix}$$

Step 7 else $\begin{pmatrix} P_{last} = P_X \\ Stable_{last} = Stable \end{pmatrix}$

Step 8 $P_X = P_X + IL$
Until P_X reaches to PXmax

Step 9 $P_Y = P_Y - IncPY$
Until P_Y reaches to PYmin

Step 10 Write Stable Area Names
End

As it can be seen from the procedure given above, VI algorithm proceeds by using half differences. Thus, procedure starts with large increments and after any stability change found, algorithm turns back to the previous point and step size is reduced to half of the previous step size. This way, step size becomes unit increment near stability area border and with this method, position of border can be found precisely. Graphical illustration of the VI algorithm is given in Figures 3.5 (a) through 3.5 (g). This algorithm runs considerably faster than basic method and CI algorithm and it gives the best performance if number of univariant lines (stability area borders) at one row are less than 2. SKOP v.2 program uses the VI algorithm.

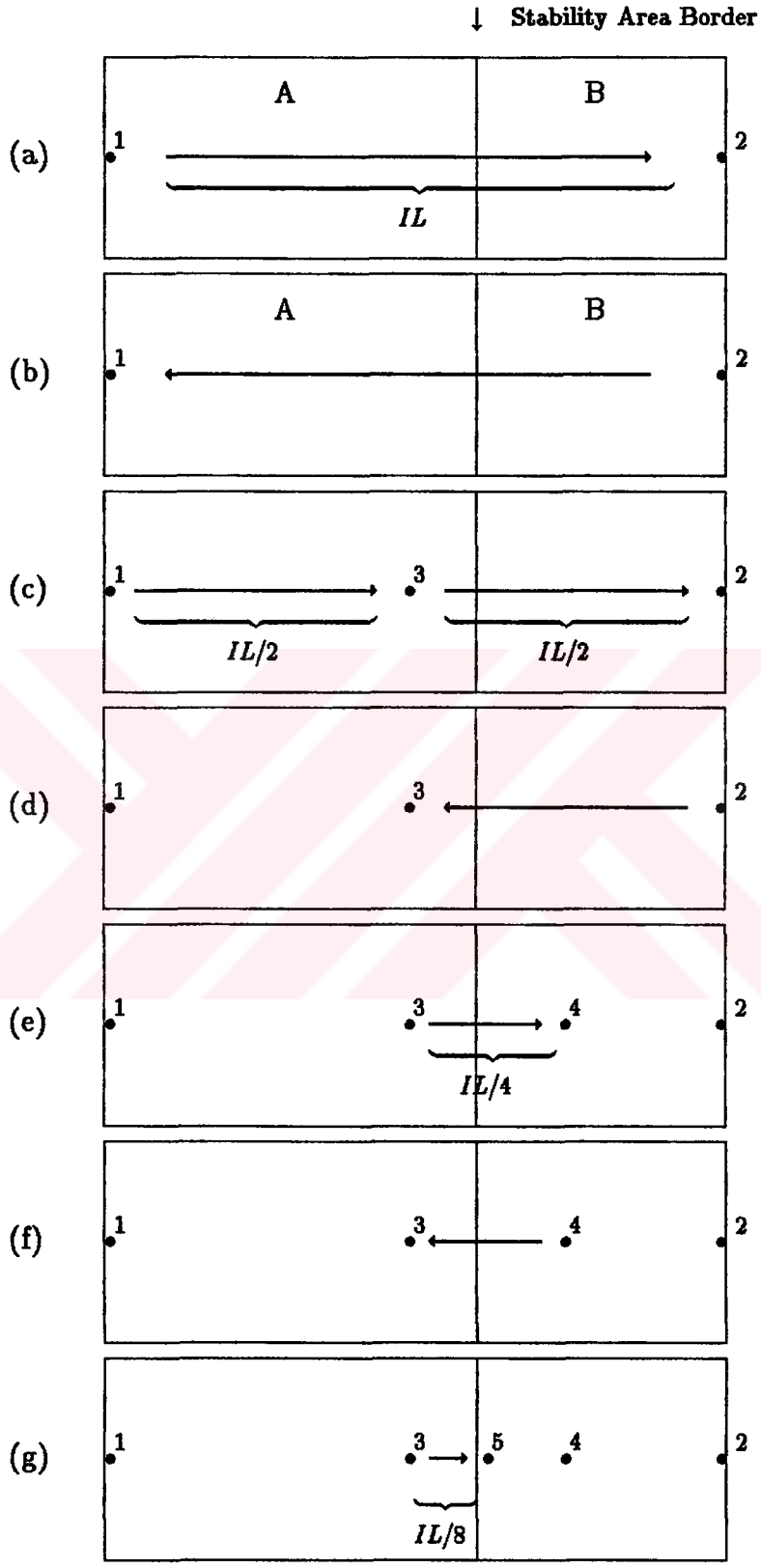


Figure 3.5 Graphical Illustration of VI algorithm

CHAPTER IV

USE OF THE PROGRAM

4.1 Features of the Program and System Requirements

SKOP v.2 program is written for IBM PC and compatibles. Program is developed under DOS 5.00 with Turbo PASCAL 6.0 language. Since Turbo PASCAL language permits user to divide the source code into sections named as "units", the program is made up of three support units together with the main part to simplify the program development and error detection easier. Names of these units and their functions are shown below.

- BIRUNI-D4 – General menu support unit
- ANALYZE-2 – Initialization and computation support unit
- GRAPHIC-2 – General graphic support unit
- SKOP – Main program

There are 87 routines, procedures or functions, present in these units. Total size of the source code is about 160 KB, and it extends over 5100 lines .

Hardware/software requirements for SKOP v.2 program are:

RAM:	Min. 512 KB
Graphics Card/Monitor:	CGA, EGA, MCGA, HGC, VGA
Input Device:	Keyboard
Magnetic Media:	One Floppy Drive (5.25" or 3.5")
	Hard Disk is Recommended
Printer:	Dot matrix printer, 9 or 24 pin
DOS:	4.01 or higher

Files on the disk:

SKOP.EXE	SKOP v.2 program
SKOP.MIF	Menu information file
SKOP.DAT	Thermochemical data file
SKOP.HLP	Detailed Help file
* .BGI	Graphic interface files

If any of the above files can not be found in the current directory, SKOP program terminates with giving an error code.

General features of the SKOP program are shown below:

- SKOP v.2 program constructs Predominance Area Diagrams using thermodynamic data.
- Entering elements that builds up the system and the constant temperature is sufficient to compute a diagram. There is no need for user to recognize any system before using it.
- Systems that are composed of maximum 6 elements can be handled by the SKOP in two different ways. User can select the components either in the form of 1 base-metal + 2 to 5 elements or in the form of 2 base-metals + 2 to 4 elements.
- All possible species that can take form and their standard formation Gibbs energies are determined from the database scan. There is no need for user to interfere with the database.
- User can change standard formation Gibbs energy of any desired species.
- Any species can be excluded from computation.
- Constant activity values can be given to species that are in solution.
- Computations are done for both stoichiometric and non-stoichiometric phases. Decomposing species at a given temperature can be excluded from calculations.
- User can select diagram axes freely.
- "Constrained Chemical Potential" method together with "Variable Increment" algorithm is used to find stability areas.
- User can be profited by the detailed investigation utilities supported by

the program like zooming and tracing.

- SKOP v.2 program is driven by "Pull-Down" menu system and it contains a help utility for users.

SKOP program does not have a graphics printing utility. To print diagrams that are constructed by the program, user can use either "GRAPHICS" command or a utility program that integrates text with graphics, like "INSET". User can refer to any DOS manual for efficient use of GRAPHICS command. INSET program is recommended for use instead of GRAPHICS command, due to its extensive support over all kinds of printers and graphics hardware.

4.2 About Pull-Down Menu System

SKOP v.2 program is driven by "Pull-Down" menu system. To handle the program, user deals with a relatively small number of key combination compared to other menu types. Direction <←→↑↓>, <Enter> and <Esc> keys are the only keys necessary to command the program. User uses direction keys to move the highlighted bar to choose the desired command and pressing the <Enter> key executes that command. The same way, any sub-menu can be activated by direction keys plus <Enter> key pair. <Esc> key is used to exit from any menu and/or program. At any menu, user can get detailed help about the current menu and/or program by pressing <F1> key. Program also helps user with message boxes that gives information about current command and/or sub-menu.

After booting up any PC or compatible, SKOP program can be loaded and run by typing SKOP at the DOS prompt. After program is loaded, SKOP first tries to find menu information file SKOP.MIF to construct the menu tree. If SKOP can't find this file, program returns to DOS by giving a run- time error. After loading SKOP successfully, program initializes the pre-defined variables, prepares the main menu and awaits for the user. Menu structure of the SKOP program is given in Figure 4.1.

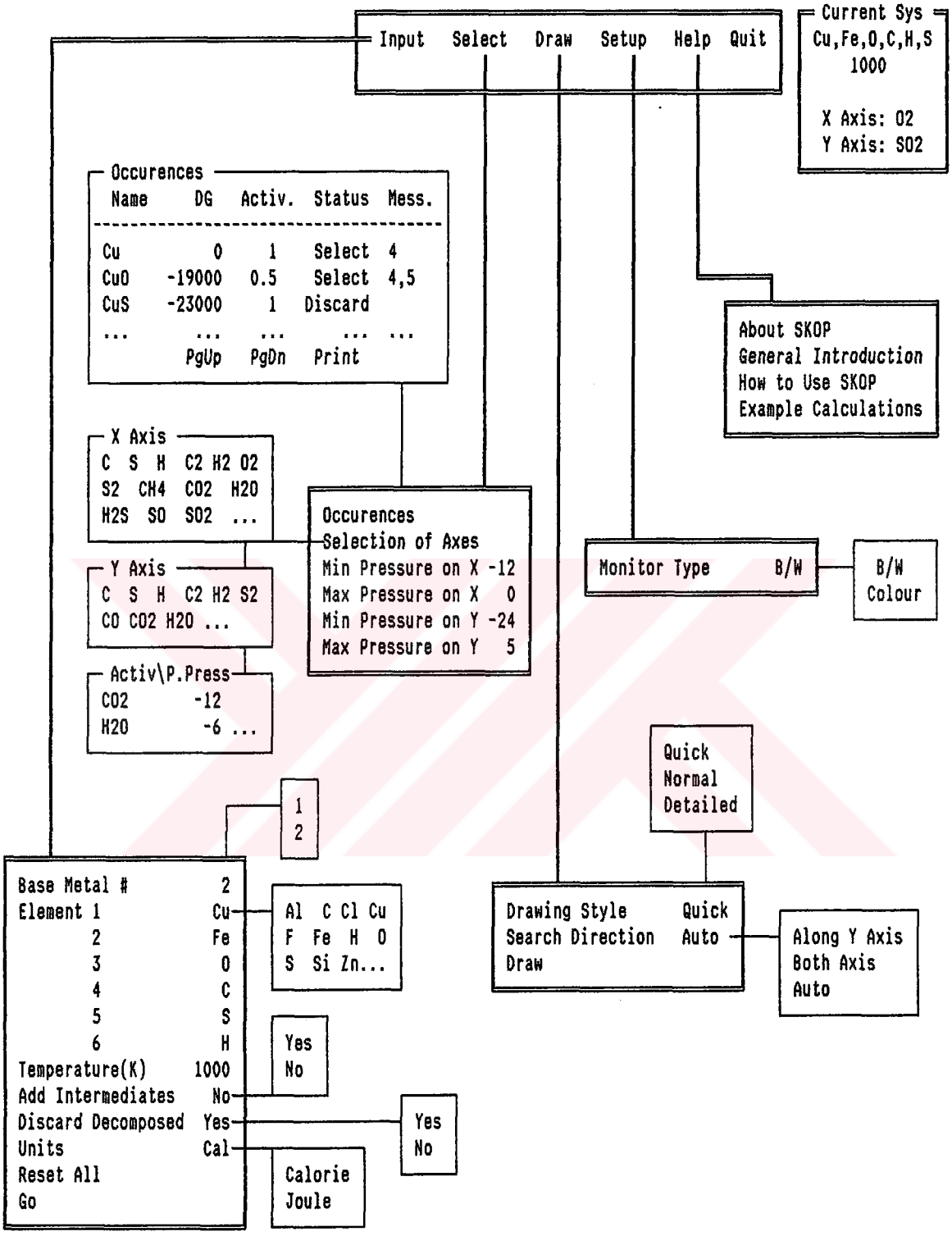


Figure 4.1 Menu Structure of SKOP v.2

4.3 Defining The System

To draw any predominance area diagram, user has to choose the components (elements) that build up the system and constant temperature. SKOP program accepts the components with metal phase priority, thus, metal phases should always be given before non-metal components.

System definition commands exist in the first menu item of the main menu, which is the "Input" sub-menu. To activate this sub-menu, user moves highlighted bar over "Input" command and presses <Enter>, this operation invokes the "Input" window to be open, as seen in Figure 4.2.

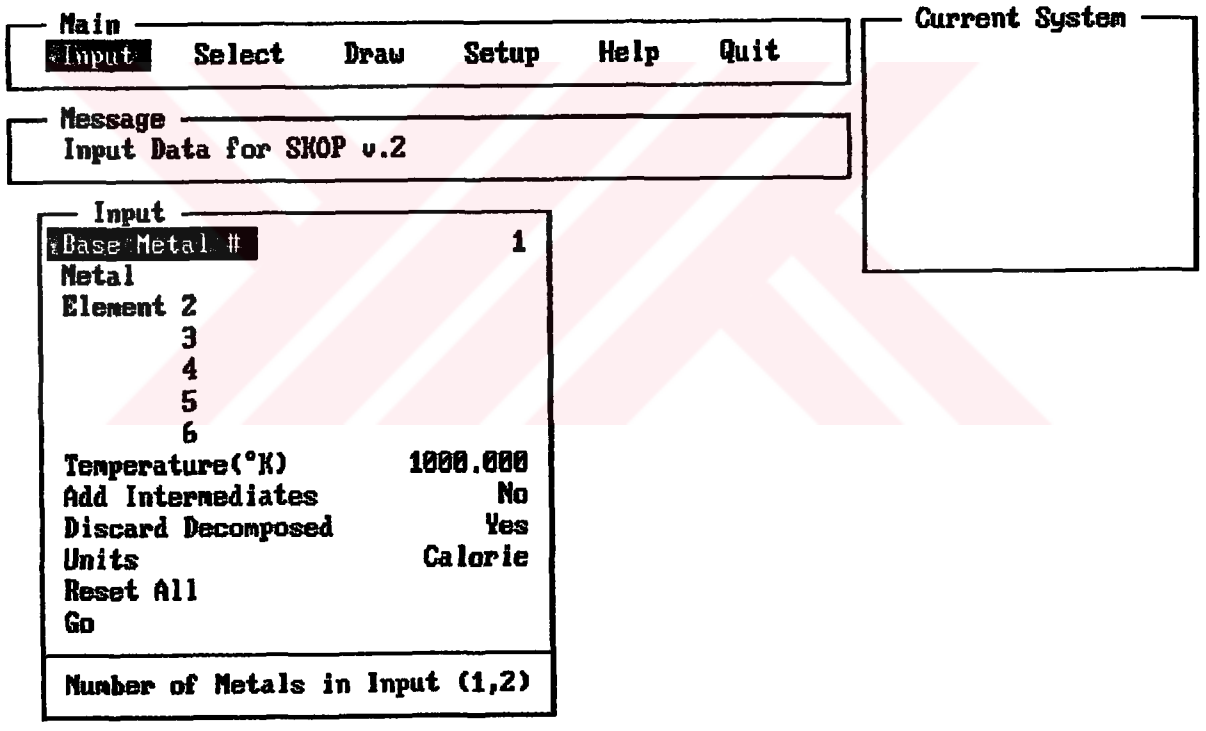


Figure 4.2 INPUT Sub-Menu Window.

Now, user can use the INPUT sub-menu routines. Necessary steps do define any system is shown below, together with order definitions. To give a more realistic demonstration, Fe-O-S-Cl-C-H system at 900°K will be

constructed. The axes of the diagram will be $\log(P_{O_2})$ and $\log(P_{SO_2})$. In the following steps, the word "select" means to activate any command by direction keys plus <Enter> key pair.

- If number of metals in the component stream is higher than one, select "Base Metal #" command. At each selection, the number that follows the command changes between one and two (Figure 4.2).
- Enter base element, which is a metal, by selecting "Metal" command. When this command is selected, a window opens near the command and awaits user to select desired element from the list (see Figure 4.3). User can only work with elements that are listed. This list can be enlarged by adding more data to database. But the user is not allowed to modify the database at present.
- Other elements that builds up the system can be selected by using "Element *m*" command, where *m* can change from 2 to 6. Elements are chosen from a pre-defined list as done in previous step. SKOP program permits user to define systems that can be composed of maximum six elements including the base metal.
- Constant temperature of the PAD, in degrees Kelvin, can be defined with "Temperature" command. A default value of 1000 °K is preset for this item. User can enter temperatures in the range of 298 - 2000 degrees Kelvin.
- If current system is a two-metal PAD and user wants to include intermediate (two-metal) phases to the computation then, "Add Intermediates" command is selected. Default value of this item is "No".
- Species that are decomposing at the given temperature can be included or excluded from the computations by "Discard Decomposed" command. Default value of this item is "Yes".
- Although default computation unit is "Calorie", user can change it to "Joule" by selecting the "Units" command.
- System definition section is completed with "Go" command (see Figure 4.4). This command invokes SKOP to find all possible species that can take form together with physical states and their standard Gibbs energies of formation at the given temperature. If this command is not used, program can not proceed with given system.

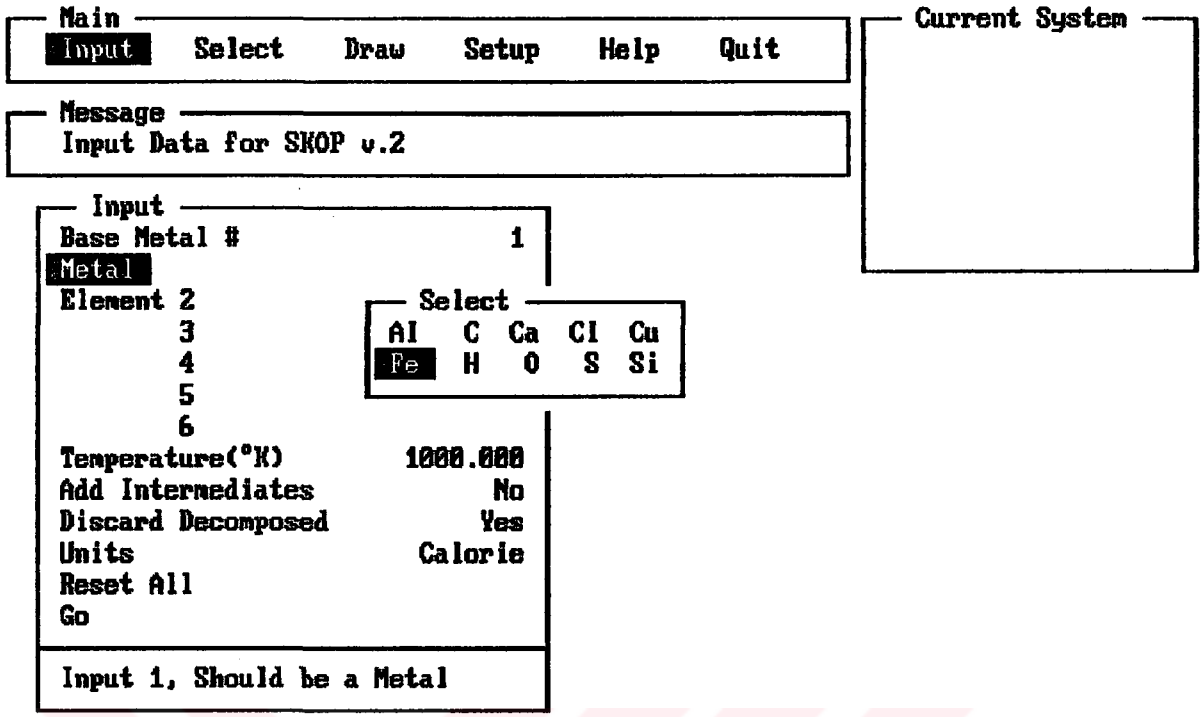


Figure 4.3 Selecting Base-Metal.

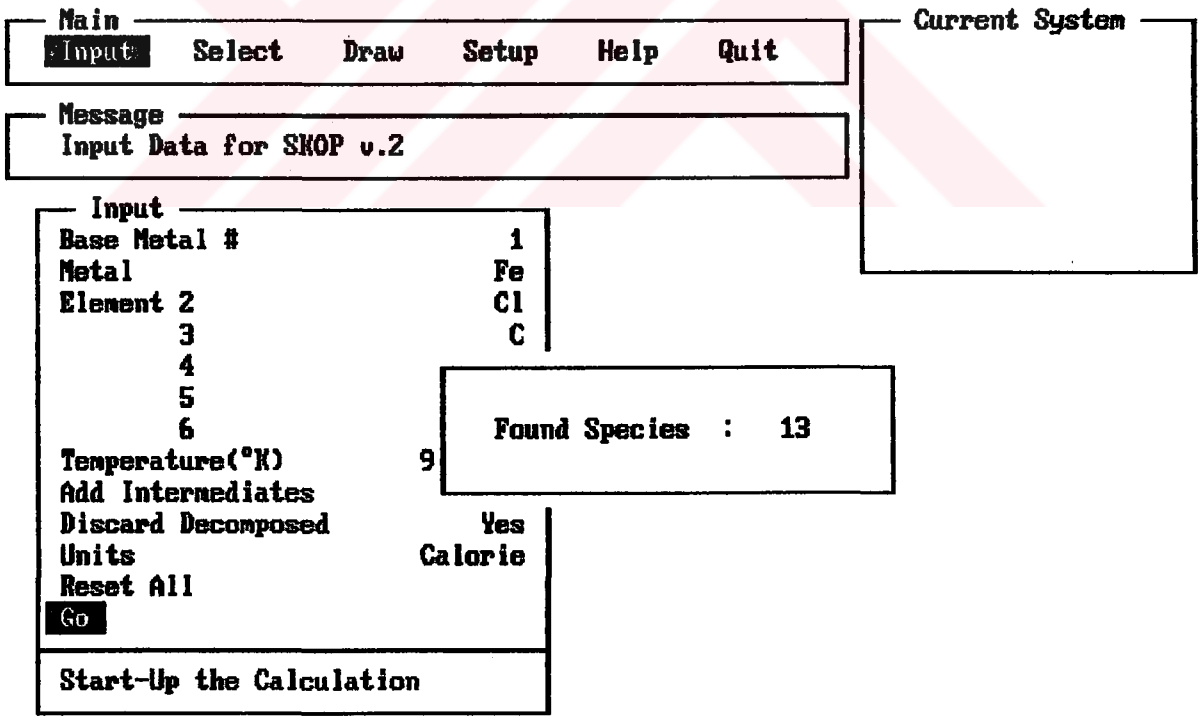


Figure 4.4 Completing System Definition.

- "Reset All" command can be used to clear the current system data and reset the program for next system.

When "Go" command is activated, SKOP program first opens the data file, SKOP.DAT, where chemical symbols and basic thermodynamic properties of selected species are present. If this file can not be found, program terminates and returns to DOS by giving a run-time error.

SKOP program permits user to change any selection (component, temperature, etc.) in the sub-menu, at any time, except "Base Metal #" option, which becomes permanent when component selection is done. User can annul any system definition operation by using "Reset All" command.

After system definition and database search is completed, "Input" window is closed automatically. Program writes components and constant temperature to the information box, named as "Current System", existing at the top-right portion of the main menu.

4.4 Selecting Species and Diagram Axes

After system definition is completed successfully with "Go" command, next operation of constructing a PAD diagram is to activate the "Select" sub-menu (Figure 4.5). This sub-menu serves user with three functions. First function; user can include or exclude desired species, change standard Gibbs energy of formation and/or activity of any specie. Second; user selects axes of diagram from a given list of species. Third; user sets logarithmic pressure limits on both X and Y axes. Operation steps are shown below:

- If any specie(s), found from database, will be excluded from the calculation or properties of any specie(s) will be changed, then select "Occurrences" command. After selecting this command, an information window is opened (see Figure 4.6) which shows the following list of information

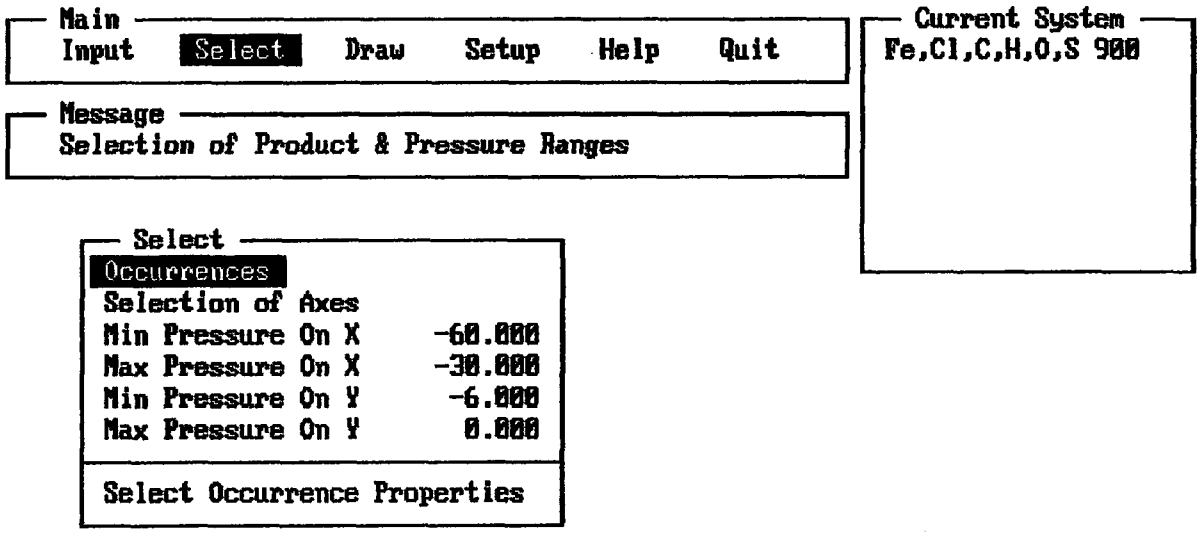


Figure 4.5 "Select" Sub-Menu.

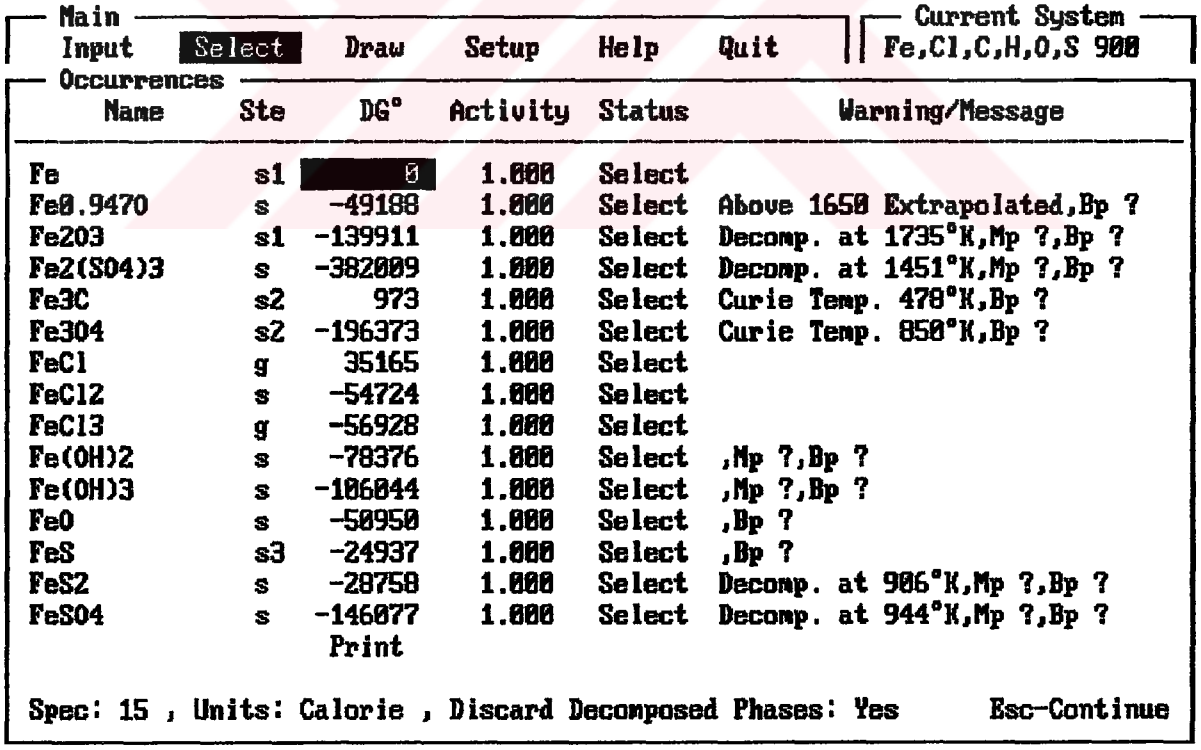


Figure 4.6 "Occurrences" Window.

- chemical symbol of possible species that can take form,
- physical states (solid, liquid, gas) at given temperature,
- standard Gibbs energy of formation values at given temperature,
- activities,
- current status (included/excluded from computation). The word "Select" indicates that the related species is included.
- messages about species.

The first two items of this window can not be changed by the user. Standard Gibbs energy of formation and activity values for any specie can be modified by selecting the value that is going to be changed and entering the new value. Status option can be changed between "Select" and "Discard" or vice versa by selecting the corresponding status row. Warning/Message part gives information about related species, meaning of abbreviations of this column are:

[S298 ?] – S°_{298} data does not exist,
[Mp ?] – melting point does not exist,
[Bp ?] – boiling point does not exist,
[Cp Range ?] – no C_p range present,
[Extrapolated] – C_p range exceeded, extrapolation is done,
[Decomposes] – decomposition occurs .

When desired changes are done, user can exit from this window by pressing <Esc> key.

- If the user does not want to change any occurrence, standard Gibbs energy of formation or activity, "Occurrences" section can be bypassed.
- With the "Selection of Axes" command, user can choose species, whose partial pressures or activities are going to be used as variables for the axes of PAD. When this command is executed, program opens a window that contains species that do not have the base metal in their formulae (found from the database). Then program awaits user to select desired species for X and Y axes (see Figure 4.7) for the system at hand.

After axis selection completed, constant values for relative chemical

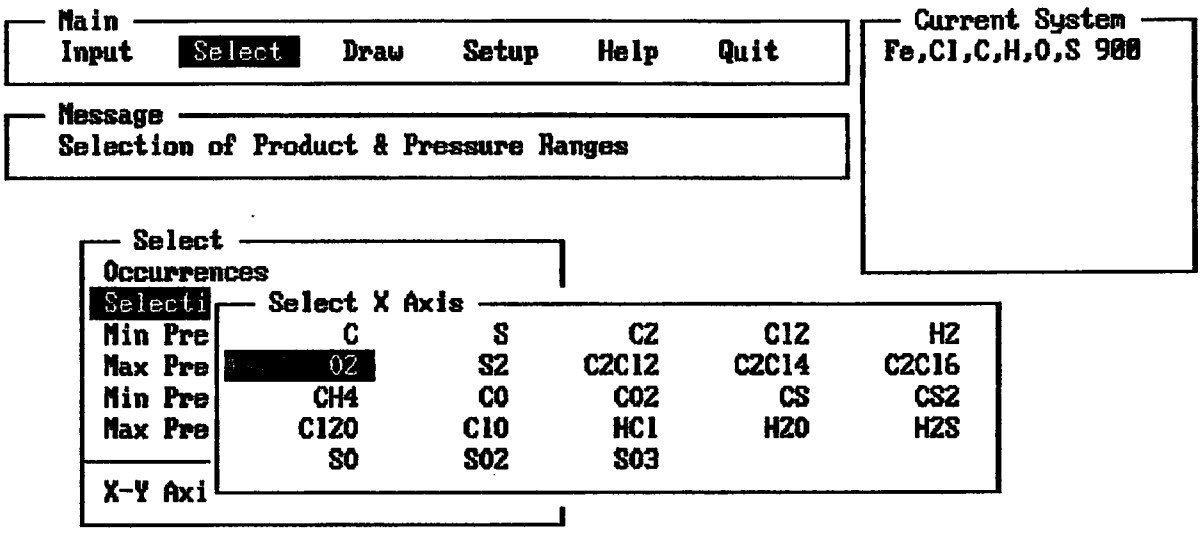


Figure 4.7 Axis Selection.

potentials (partial pressures for gas phases, activities for condensed phases) of components are supplied to satisfy Gibbs phase rule. This is not necessary if system contains 3 elements including 1 metal or 4 elements including 2 metals. SKOP permits user to give these relative chemical potentials of components in different forms. Thus, user can enter chemical potential of a component itself as well as a species (representative term) bearing the related component.

For Fe-O-S-Cl-C-H system, if O_2 and SO_2 are selected for X and Y axes (log P_{O_2} and log P_{SO_2} are taken as horizontal and vertical axes respectively), than Gibbs phase rule states that relative chemical potentials of 3 species bearing Cl_2, H_2 and C should be supplied to construct the indicated PAD. Numerical values of relative chemical potentials supplied for this example are: $a_C = 0.01$, $P_{Cl_2} = 10^{-12}$ atm and $P_{H_2O} = 0.01$ atm. Notice that H_2O is used as a representative term for H_2 (see Figures 4.8 and 4.9).

After axis selection is done and necessary chemical potentials are entered, program opens a confirmation window which summarizes all the selections done by the user (Figure 4.10).

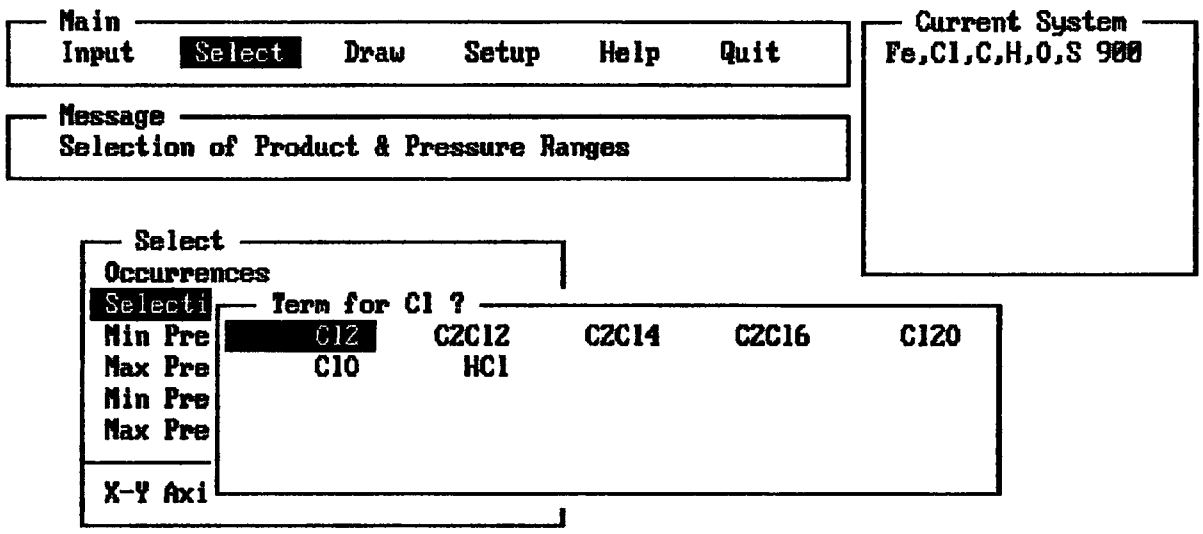


Figure 4.8 Representative Term Selection for Cl.

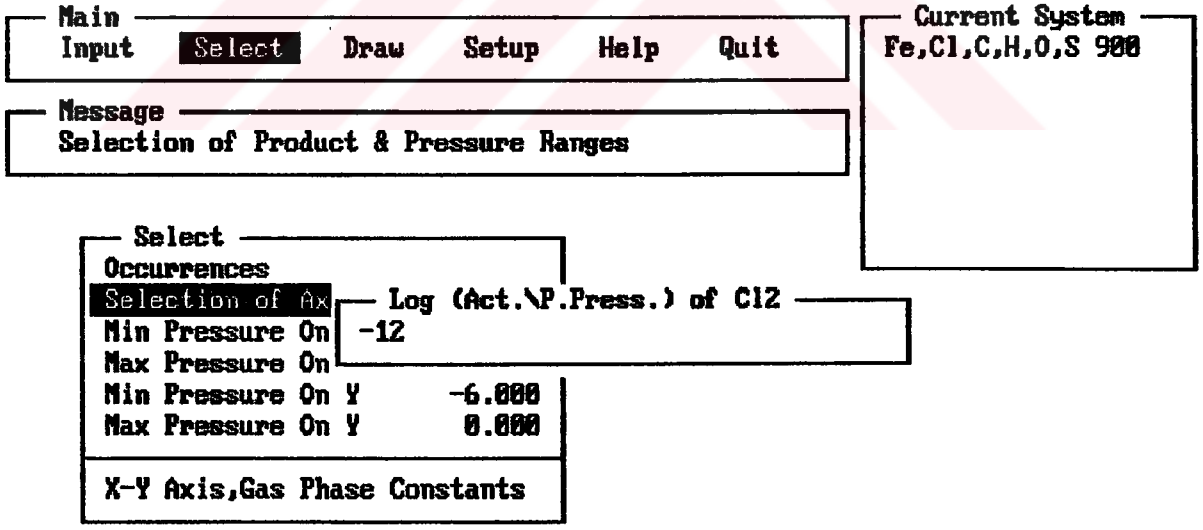


Figure 4.9 Entering Partial Pressure of Cl_2.

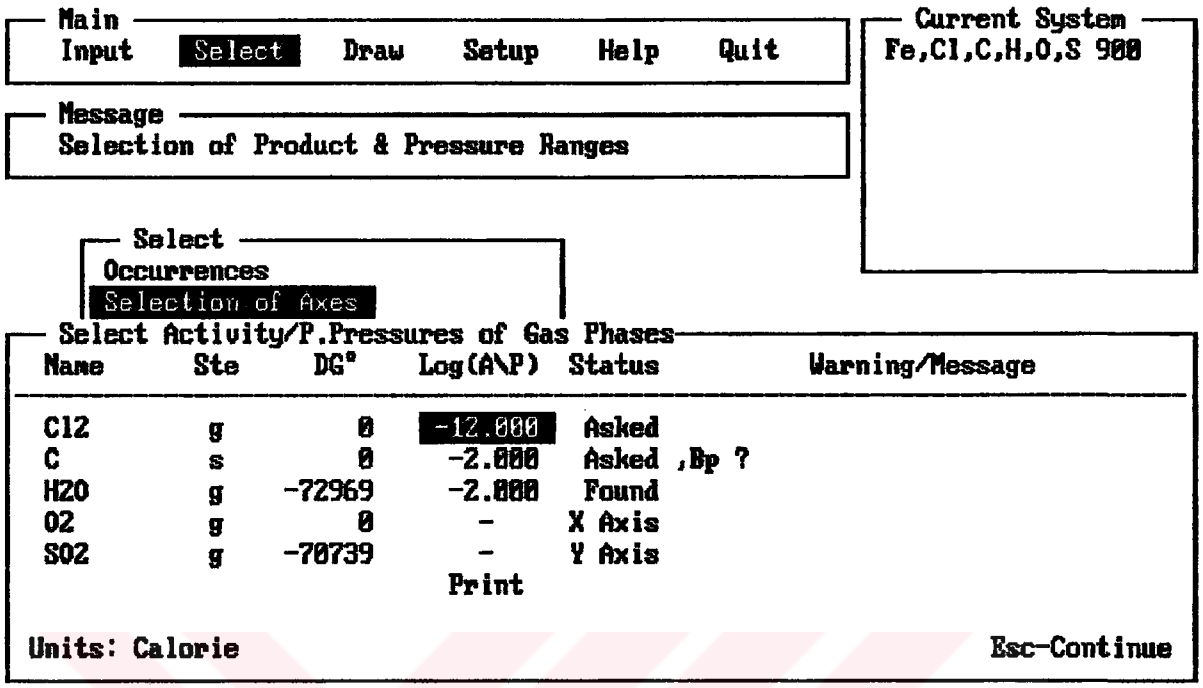


Figure 4.10 Confirmation Window.

- Next 4 items of the "Select" sub-menu handle entry of lower and upper limits of X and Y axes. Axes of the diagram are base 10 logarithms of partial pressures (and/or activities) of species selected by the user. Although there are default values present for these limits, user can freely modify them. Modification is done by selecting an item and supplying the new value. Program does not permit invalid entries like giving a "Minimum value" that is numerically larger than the "Maximum value" (see Figure 4.11).
- After exiting from this sub-menu, SKOP writes current axes selection to "Current System" box.

4.5 Drawing the Diagram

The last operation for a successful PAD creation is the plotting step. "Draw" sub-menu handles two functions for different plotting qualities. First

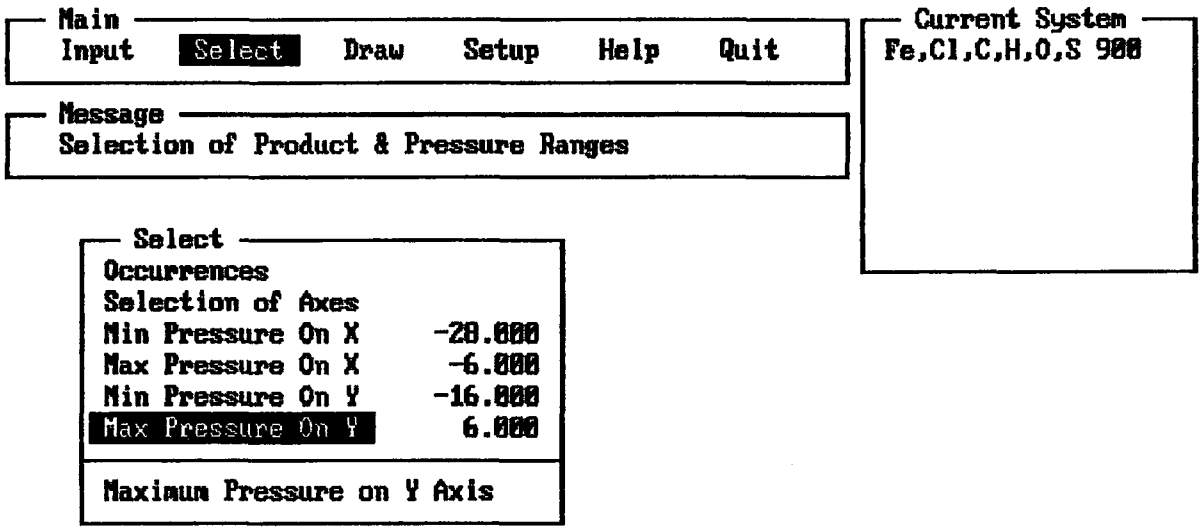


Figure 4.11 Determining Axes Ranges

function supported by this sub-menu is the "Drawing Style" function. This function enables the user to select diagram plotting quality from "Quick", "Normal" or "Detailed" modes. In "Quick" mode, predominance area diagram is plotted the fastest way with an acceptable print quality. In "Normal" mode SKOP plots the PAD with a higher printing quality than "Quick" mode, but as can be predicted, time required to complete a diagram is longer than the previous mode. With "Detailed" mode user can have the best printing quality, but this mode takes relatively longer period of time than other two modes.

As can be seen from Figure 4.12, second function of this sub-menu is the "Search Direction" function. With this option, user can determine the scan direction; "Along Y axis" or "Both axes". There is a third option present to help the user, that is "Auto" mode. In the "Auto" mode, SKOP program handles all necessary decisions for scan directions for different diagram types.

The last item of the "Draw" sub-menu is the "Draw" command. When this command is executed, program first abandons the text screen and initializes the graphics screen. At the next step, borders of the skeleton diagram for current graphics mode/monitor is drawn and control is transferred to computation algorithm which does plotting operation.

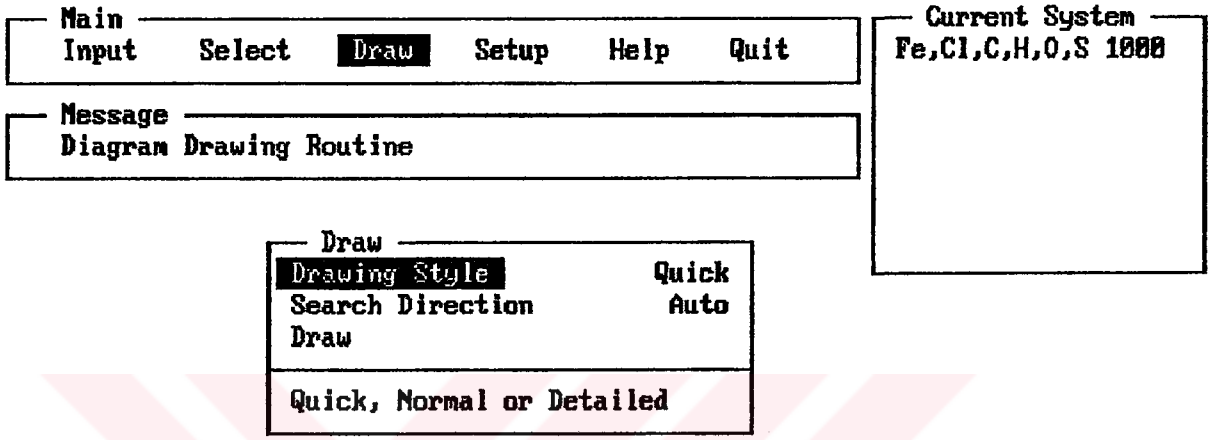


Figure 4.12 "Draw" Sub-Menu

The diagram as drawn for Fe-Cl-C-H-O-S (P_{H_2O} = 0.01 atm, P_{Cl_2} = 10^{-12} atm and $a_{C(s)}$ = 0.01) is shown in Figure 4.13.

4.6 Detailed Investigation of Diagrams

After plotting operation of the PAD is completed, a cursor (+) is placed at the left-bottom portion of the diagram. This cursor can be moved by the user to any location on screen with direction keys and it is used to examine diagrams in more detail.

Users can use three functions that are supported by SKOP for detailed diagram examination. These functions are : "Zoom In", "Zoom Out" and "Point Trace" functions.

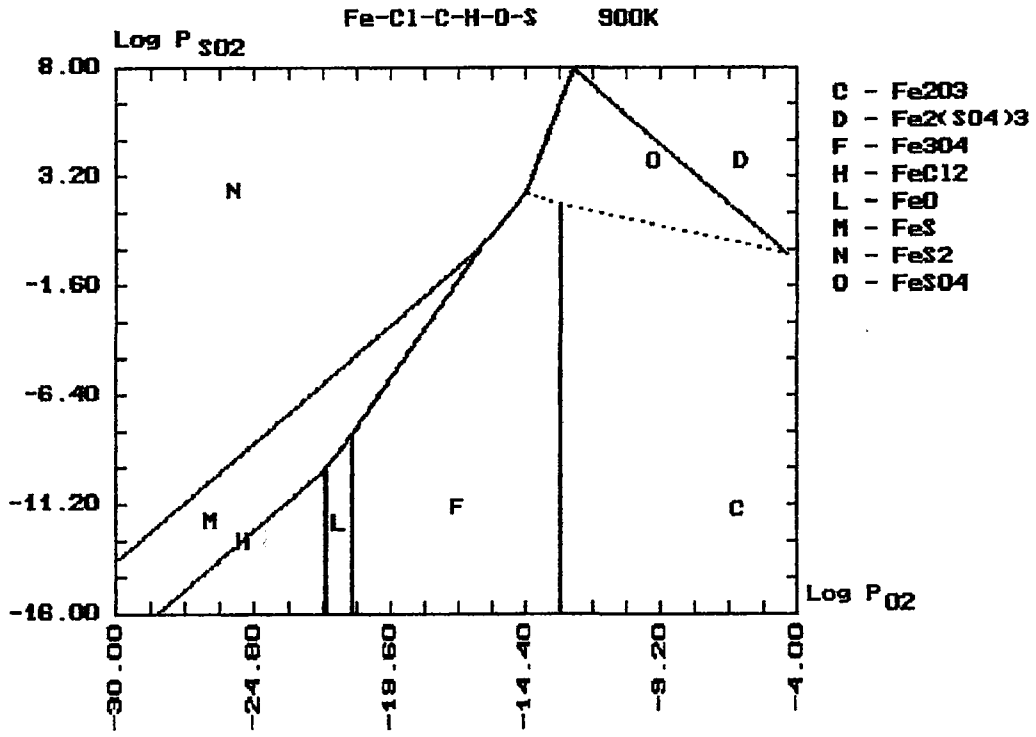


Figure 4.13 Fe-O-S-C-H-Cl System at 900°K (see text).

"Zoom In" function is used to experience close-up views of a desired zone, that is, a selected portion of diagram is re-drawn in enlarged form. To activate this function, user first moves the cursor near the selected area and starts to make a frame around the desired zone by pressing the <Z> key. When this key is pressed, a small rectangle appears at the cursor position. User can reduce or enlarge this rectangle with direction keys <←→↑↓>. When the frame is placed around the desired area precisely, user presses <Enter> key to start zooming operation, see Figure 4.14. Cu-O-S system at 1000°K is given as an example to illustrate "Zoom In" operation. As seen from this figure, relatively small region of Cu_2SO_4 in Figure 4.14 (a) is enlarged in Figure 4.14 (b), with "Zoom In" operation.

"Zoom Out" function is just the reverse of "Zoom In" function. Thus, it covers larger ranges on X and Y axes. Pressing <S> key invokes this function, amount of enlargement is done automatically by the program.

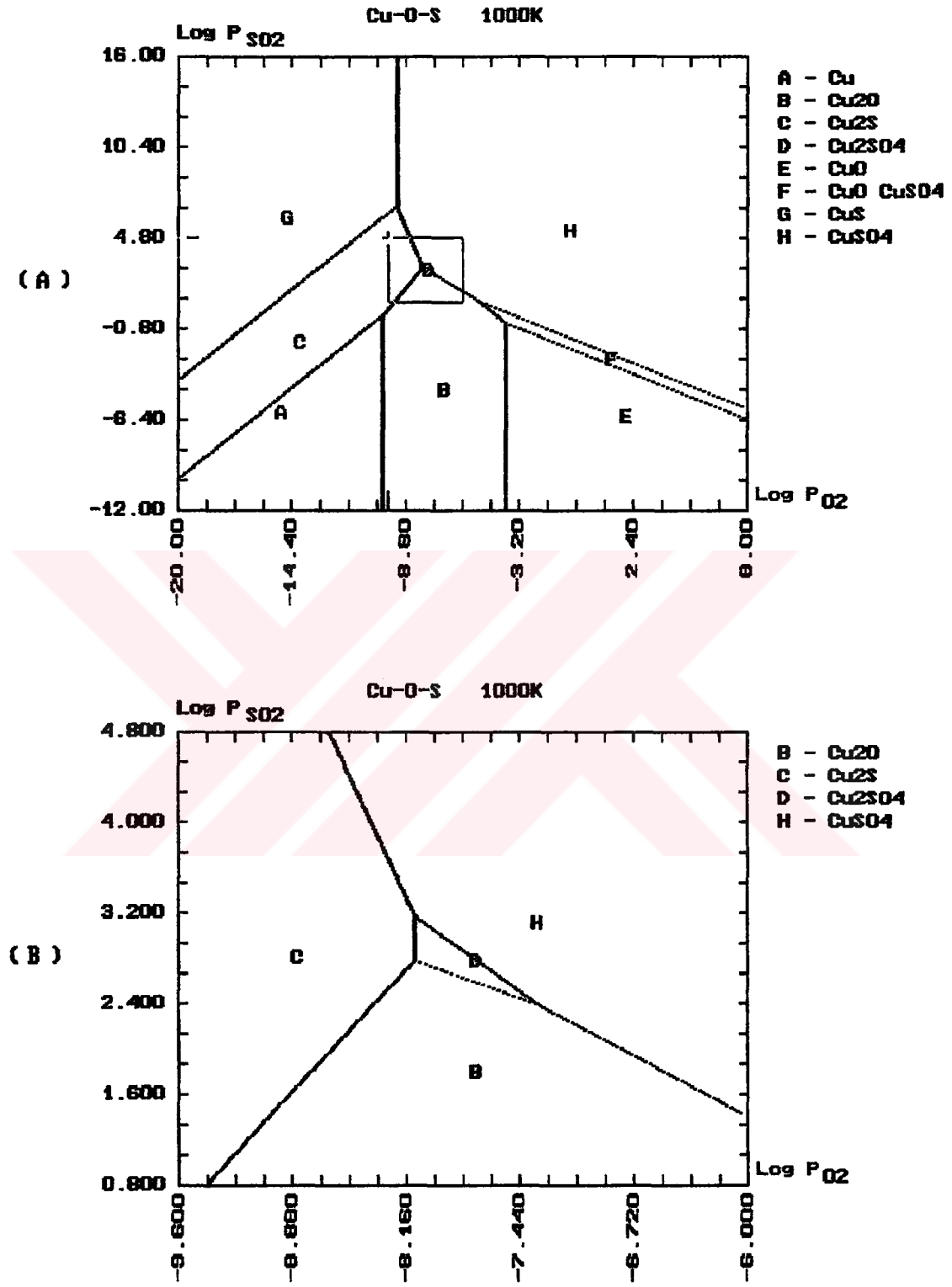


Figure 4.14 (a) Determining the Area That Will be Zoomed.
(b) Zoomed View.

Last function, "Point Trace", helps the user to determine X and Y coordinates of any point on the diagram. Pressing <T> key activates trace function. After this function is invoked, current coordinates of the cursor are written on the top-right position near the diagram. This function also serves user with a second feature, that is, if cursor is on any of the invariant points or univariant lines then the procedure warns the user by typing "ON" sign near the coordinate data. Execution of "Point Trace" function continues until it is deactivated by <T> key.

User can annul "Zoom In" and "Point Trace" functions with <Esc> key.

4.7 Setup and Quit

"Setup" menu contains a monitor selection command that can be used to run the SKOP program in color mode. Program uses different colors for different graphics cards.

To quit from the program, user selects the "Quit" command. Pressing <Esc> key twice at the main menu also lets the user exit the program. Exit operation lets user to return to the DOS environment.

4.8 Using Help Utility

"Help to User" utility of the SKOP v.2 program can be activated by the user at any menu by pressing <F1> key. When this key is pressed, program opens a window that informs the user about current menu/command. User can also find general help about the SKOP program in "Help" sub-menu.

4.9 Example Applications of SKOP

Necessary data to define and plot example predominance area diagrams of different systems are given below together with related diagrams.

Fig No	Components	Temp (K)	Add Inter	Disc. Deco	Axes X	Axes Y	X Min	X Max	Y Min	Y Max
13	Fe-O-S-C-H-Cl	900	no	yes	P_{O_2}	P_{SO_2}	-30	-4	-16	8
	(P_{H_2O} = 0.01 atm, P_{Cl_2}= 10^{-12} atm, $a_{C(s)}$= 0.01)									
15	Cu-O-S	1000	no	yes	P_{O_2}	P_{SO_2}	-12	0	-4	8
16	Fe-O-S	1000	no	yes	P_{O_2}	P_{SO_2}	-25	5	-20	15
17	Cu-O-S	1000	no	yes	P_{O_2}	P_{SO_2}	-12	0	-4	8
	(a_{Cu} = 0.5, a_{CuS} = 0.7)									
18	Fe-O-S	900	no	yes	P_{O_2}	P_{S_2}	-30	-2	-18	10

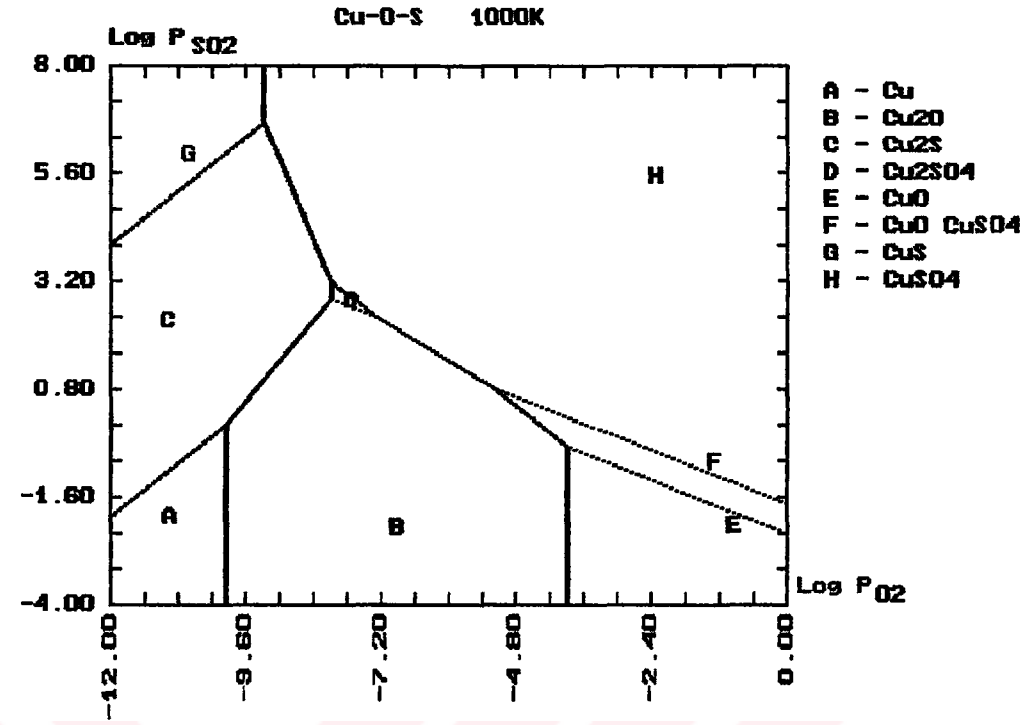


Figure 4.15 Cu-O-S System at 1000°K.

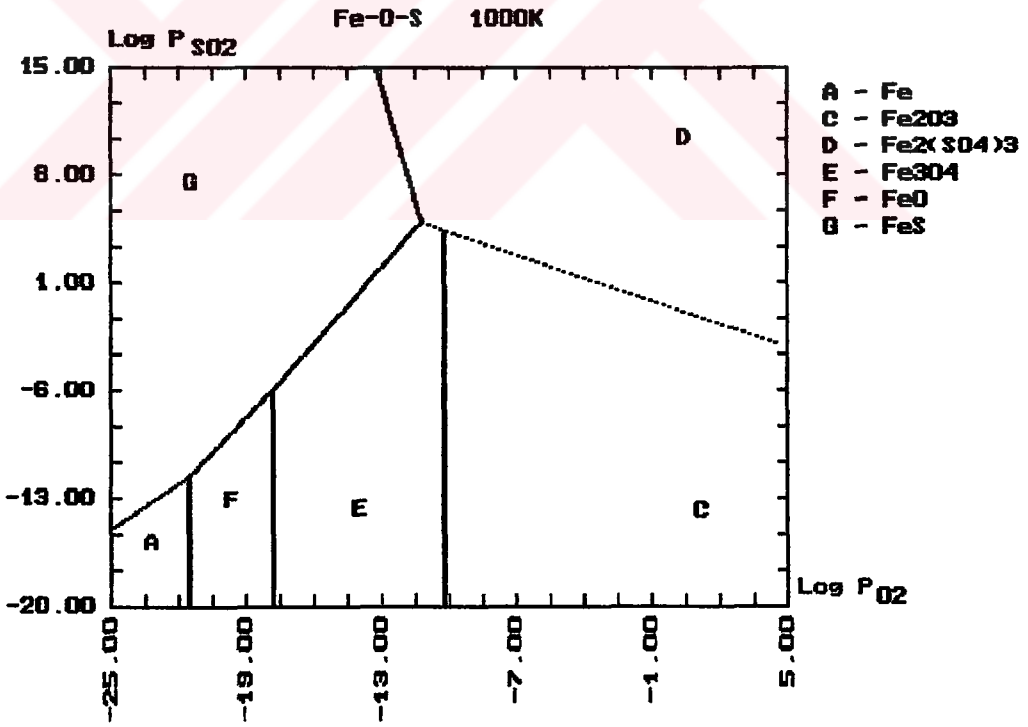


Figure 4.16 Fe-O-S System at 1000°K.

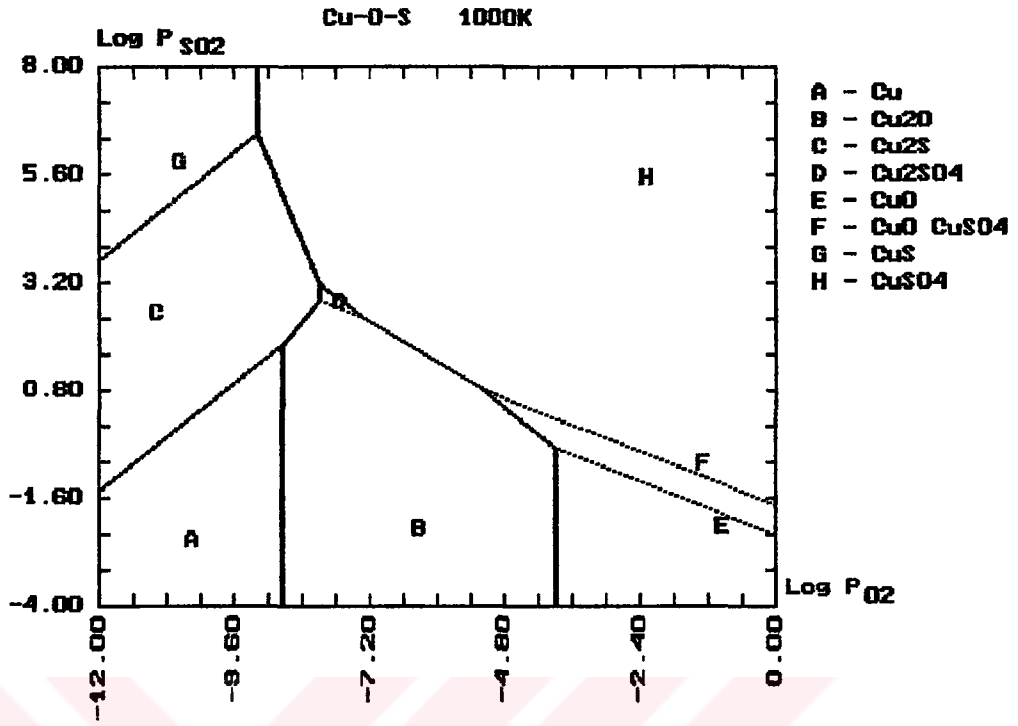


Figure 4.17 Cu-O-S System at 1000°K (a_{Cu}=0.5, a_{CuS}=0.7).

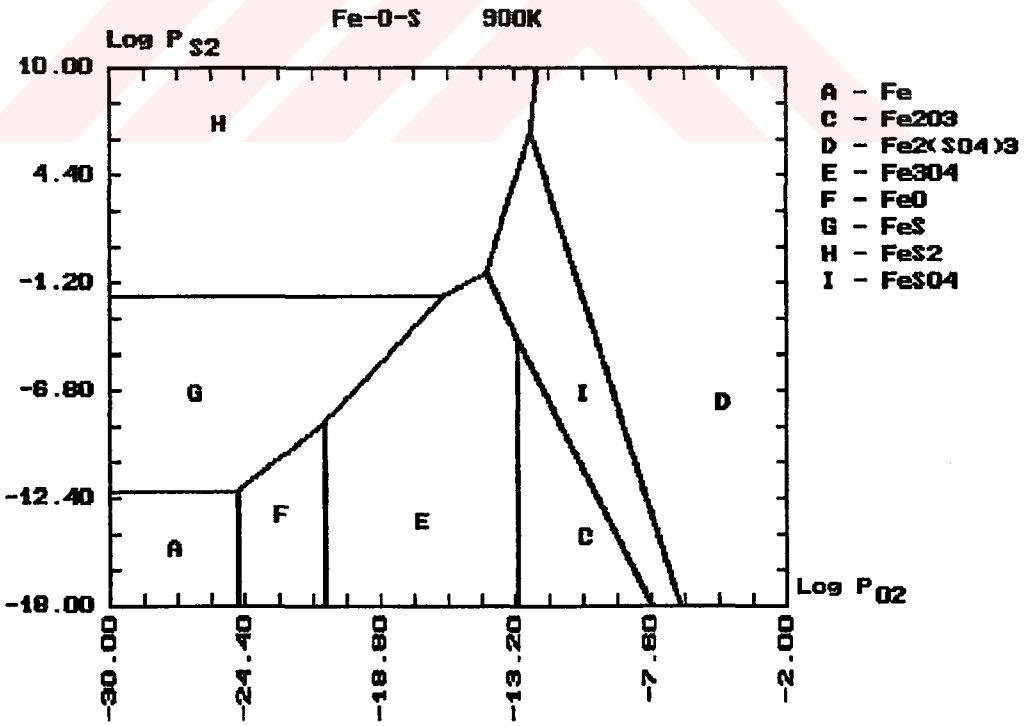


Figure 4.18 Fe-O-S System at 900°K.

4.10 Two-metal and Higher Order Predominance Area Diagrams

The examples and discussions given until now were involving PAD computations with one base element. In the literature, two-metal (Al+Si, Fe+Cu, etc.) and higher order predominance area diagrams are not well documented. Diagrams which are published have often been tediously generated and they are limited to single multi-metal compounds. In addition, there appears to be no general simple methodology to calculate the multi-metal diagram and explain the rules of construction.

Putting two single-metal predominance area diagrams on top of each other only works for simple systems having no intermediate (two-metal) species. To plot true two-metal predominance area diagrams, an improved version of "Constrained Chemical Potential Method" [15, 17] employed for single-metal systems, is used. Theory of construction of both single-metal and double-metal PAD is completely identical to each other except handling of intermediate phases ($Al_2O_3 \cdot SiO_2$, Cu_5FeS_4, etc.). For the computation, two groups of phases; species that contain the first metal and species that contain the second metal are manipulated separately. For example, suppose that the PAD diagram of the Al, Si, C, O system be computed. For the construction, Al bearing species (Al, Al_2O, Al_2O_2, Al_2O_3, Al_4C_3, AlO, AlO_2) are manipulated separately from the Si bearing species (Si, SiC, SiO, SiO_2) as if there are two single-metal PAD present. Intermediate phases are introduced into calculation with a different procedure; part of the intermediate species ($Al_2O_3 \cdot SiO_2$, etc) are processed together with Al bearing species and the rest with the Si bearing species. Separation is directed by user request. Thus, user gives the limits of the metallic fraction R where R= Si/ (Al+Si) . If metallic fraction of intermediate phase is within the limits given by the user then that phase is processed with Si bearing species, else it is manipulated with the other group. Predominance area diagrams of the given example system is shown in Figure 4.19. Figure 4.19 (a) represents two one metal predominance area diagrams that are put on top of each other and Figure 4.19 (b) represents real two-metal predominance area diagram for Al-Si-C-O system.

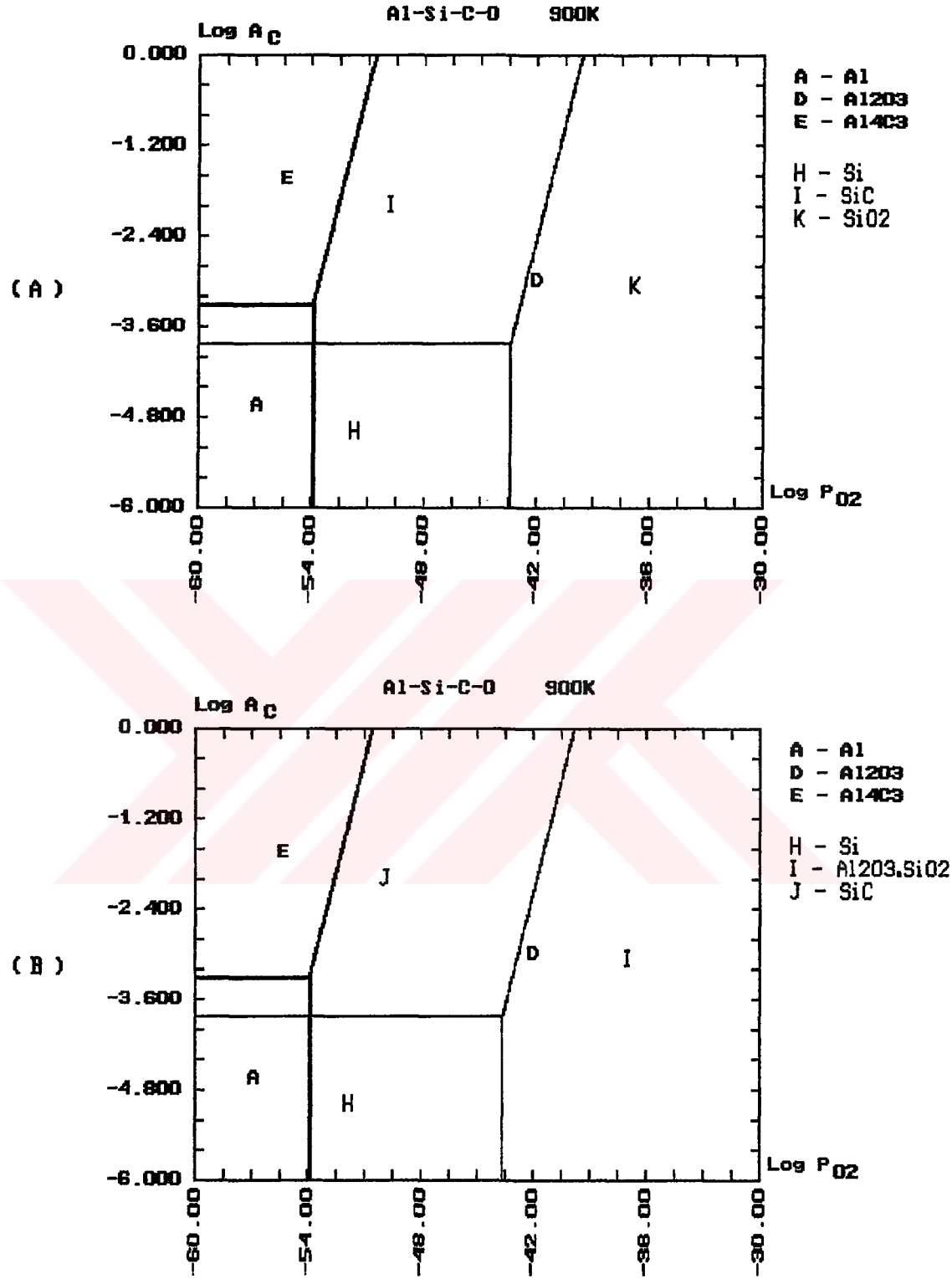


Figure 4.19 (a) Al-C-O + Si-C-O Systems at 900°K.
(b) Al-Si-C-O System at 900°K (0<R<0.333).

CHAPTER V

CONCLUSIONS

An interactive computer program, SKOP v.2, was developed to construct Predominance Area diagrams on IBM PC and compatibles. Program uses elementary thermodynamic data for computations.

Since program is designed in the way to take minimum amount of input from the user, entering elements that builds up the system, constant temperature and diagram axes is sufficient to construct any diagram. Multicomponent systems, composed of maximum 6 elements, and systems that bear two-metals can be handled by the program. Support for non-stoichiometric and decomposing phases are also present. SKOP does all necessary thermochemical calculations using its upgradable thermochemical database. There is no need for user to interfere this database. Since program lets user to select diagram axes freely, a high variety of diagrams can be computed. For the plotting part, "Constrained Chemical Potential" method is applied.

SKOP program serves advanced features to users like detailed diagram examination with zooming and point tracing. Program is driven by pull-down menu system and contains a "help to user" utility. To demonstrate the performance of SKOP, predominance area diagrams for Cu-O-S, Fe-O-S, Fe-O-S-C-H-Cl and Al-Si-C-O systems were calculated.

SKOP program can be used in the analysis and interpretation of metallurgical processes, it can also be a design tool for selecting materials in hot corrosion studies. Since SKOP is designed to be a "user friendly" program, it can be an educational tool for computer aided education.

5.1 Suggestions for Future Work

Although SKOP program supports multicomponent and two-metal bearing systems, component number is limited (maximum 6 element). One can increase this number to higher values to investigate the metal behavior in more complex atmospheres. Development of computer programs that handle higher order systems (bearing more than 2 metals) can also be suggested for future work.

In the case of relatively simple environments, two dimensional predominance area diagrams are sufficient, but in more complex situations, where the corrosive atmosphere contains several reactants, the construction of three dimensional models may be necessary. Different approaches are present to construct these types of diagrams [29], this approaches can be further developed.

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APPENDICES

APPENDIX A

EXTRACT ALGORITHM

Since species present in the database of the SKOP program are represented with their chemical symbols, a procedure to decode these symbols and select necessary species from the database is required. For this purpose, an algorithm called EXTRACT is designed. Algorithm scans entire database, tests every species present in the database and selects species which contain any combination of given elements.

Testing species starts with checking presence of sign " $\cdot$ " in the species name (e.g $Al_2O_3 \cdot SiO_2$), if this sign is present, then the name of the species is divided into two parts. First part contains the chemical symbols before the " $\cdot$ " sign and second part contains the rest of it. Each part of the species name then manipulated separately. At the second step, presence of system components (e.g Al,O and Si) in the species name (e.g Al_2O_3) is checked. Elements that are found in the species are extracted from the name of the species and necessary computations, to find occurrence of elements in the species, are done. Procedure continues until the extraction of all the components is completed. At the end of extraction operation, if species is in correct form, then it is selected, else algorithm proceeds with next species of the database. Brief outline of the algorithm is given below in Figure A.1.

Procedure can identify and handle most of the chemical symbols like $Fe_2(SO_4)_3$, $Fe_{0.947}O$ and $Al_2O_3 \cdot SiO_2$

```
        Procedure Check:
        Begin
              Find Positions of '.' , '(' , ')' , '-' in specie name
              Find length of specie name
        Return

        Procedure Extract:
        Begin
              Repeat
                    Find position of element n in specie name
                    Analyze the form
                    If form OK
                    Then extract element from name
                    Else  next element
              Until all elements are finished
        Return

        Main Part:
        begin
Step 1  Repeat
              Check (specie name)
Step 2        If '-' present in the name
              Then
                    Divide  specie name  into parts
                    Repeat
Step 3                    Extract (parts)
                    Until all parts are finished
              Else
Step 4              Extract (specie name)
              If current specie is in correct form then store it
Step 5  Until all species are finished
        End.
```

Figure A.1 Brief Outline of Extract Algorithm

APPENDIX B

C_p FITTING AND DATABASE ORGANIZATION

The formulation of mathematical models of many physical systems is a basic first step in the process of evaluating their behavior. Unfortunately, such formulations may become too complex or may not even be possible. Consequently, empirical functional relationships are often developed to describe system behavior using experimental data.

In fitting data with an approximating function, there are two basic approaches. The first approach involves passing an assumed function (preferably a polynomial) through every data point. However this approach suffer from three significant limitations. These are

1. Unexpectedly large deviations from a smooth curve (wiggle).
2. An *n*th-order polynomial for n+1 data points is too complex for large n values.
3. Experimental data are subjected to errors and to pass a polynomial through every point is inappropriate.

The first two of these limitations can be eliminated by using different methods (cubic splines). Unfortunately, there is little can be done to address the third of these deficiencies. Alternatively, one may resort to the second approach. This involves assuming a function which best describes the shape of the curve representing the given data set, and having it pass as close as possible, but not necessarily through every data point.

B.1 Least Squares Method

This method attempts to fit a simple function through a set of data points without the wiggle problem associated with high-order polynomials. The procedure involves approximating a function such that the sum of squares of the differences between the approximating function and the actual functional values given by the data is a minimum.

For a given set of N data points, one can fit an approximating function of the form G(x) having the following form

$$G(x) = a_1 \cdot g_1(x) + a_2 \cdot g_2(x) + \ldots + a_m \cdot g_m(x) \qquad (B.1)$$

where $m \leq N$ and $g_1(x),\ldots,g_m(x)$ are assumed functions of the independent variable x. The problem is then to evaluate regression coefficients $a_1,\ldots,a_m$. The method of least squares suggests that these coefficients can be calculated by minimizing a deviation function F defined as

$$F = \sum_{i=1}^{N} [\, f(x_i) - G(x_i) \,]^2 \qquad (B.2)$$

where $f(x_i)$ are data points.

Function given by equation (B.2) can be minimized by taking the first derivative of F with respect to coefficients and then equating to zero

$$\begin{aligned} \frac{\delta F}{\delta a_1} &= 0 \\ \frac{\delta F}{\delta a_2} &= 0 \\ \frac{\delta F}{\delta a_m} &= 0 \end{aligned} \qquad (B.3)$$

The set of m×m linear algebraic equations given by equation (B.3) can be solved for the unknowns $a_1,...,a_m$. These coefficients are then substituted into equation (B.1) to give the desired approximating function [34].

B.2 C_p Fitting With Least Squares

The molar heat capacities of pure substances can be described with sufficient accuracy over a relatively wide temperature range by means of the following polynomial

$$C_p = A + B \cdot T + C \cdot T^{-2} + D \cdot T^2 + E \cdot T^3 + F \cdot T^{-3} \qquad (B.4)$$

Where

A,B,C,D,E,F = constants
T = temperature (°K)

For many gases it is not necessary to employ all the terms of the polynomial, particularly if the temperature range is not very wide. For crystalline phases the temperature dependence of C_p is not adequately described by a rigorous mathematical approximation [27]. Using a four term expression, shown below, gives satisfactory results for most applications :

$$C_p = A + B \cdot T + C / T^2 + D \cdot T^2 \qquad (B.5)$$

For the SKOP v.2 program, above expression is used to fit the C_p data. If we define deviation function for equation (B.5) as given below

$$F = \sum_{i=1}^{N} [f_i - (A + B \cdot T + C / T^2 + D \cdot T^2)]^2 \qquad (B.6)$$

where

N = number of data points

f_i = data point at location i

Differentiating with respect to coefficients and equating results to zero gives

$$\frac{\delta F}{\delta A} = 2 \cdot \sum_{i=1}^{N} [\, f_i - (A + B \cdot T + C \,/\, T^2 + D \cdot T^2 \,)] \,(-1) = 0 \qquad \text{(B.7.a)}$$

$$\frac{\delta F}{\delta B} = 2 \cdot \sum_{i=1}^{N} [\, f_i - (A + B \cdot T + C \,/\, T^2 + D \cdot T^2 \,)] \,(-T) = 0 \qquad \text{(B.7.b)}$$

$$\frac{\delta F}{\delta C} = 2 \cdot \sum_{i=1}^{N} [\, f_i - (A + B \cdot T + C \,/\, T^2 + D \cdot T^2 \,)] \,(-T^{-2}) = 0 \qquad \text{(B.7.c)}$$

$$\frac{\delta F}{\delta D} = 2 \cdot \sum_{i=1}^{N} [\, f_i - (A + B \cdot T + C \,/\, T^2 + D \cdot T^2 \,)] \,(-T^2) = 0 \qquad \text{(B.7.d)}$$

simplifying and rearranging yields

$$\sum_{i=1}^{N} f_i = A \cdot N + B \cdot \sum_{i=1}^{N} T + C \cdot \sum_{i=1}^{N} \frac{1}{T^2} + D \cdot \sum_{i=1}^{N} T^2 \qquad \text{(B.8.a)}$$

$$\sum_{i=1}^{N} f_i T = A \cdot \sum_{i=1}^{N} T + B \cdot \sum_{i=1}^{N} T^2 + C \cdot \sum_{i=1}^{N} \frac{1}{T} + D \cdot T^3 \qquad \text{(B.8.b)}$$

$$\sum_{i=1}^{N} \frac{f_i}{T^2} = A \cdot \sum_{i=1}^{N} \frac{1}{T^2} + B \cdot \sum_{i=1}^{N} \frac{1}{T} + C \cdot \sum_{i=1}^{N} \frac{1}{T^4} + D \cdot N \qquad \text{(B.8.c)}$$

$$\sum_{i=1}^{N} f_i T^2 = A \cdot \sum_{i=1}^{N} T^2 + B \cdot \sum_{i=1}^{N} T^3 + C \cdot N + D \cdot \sum_{i=1}^{N} T^4 \qquad \text{(B.8.d)}$$

non-linear system of equations given above can be represented in matrix form

$$\begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} \begin{bmatrix} N & L_1 & L_6 & L_2 \\ L_1 & L_2 & L_5 & L_3 \\ L_6 & L_5 & L_6 & N \\ L_2 & L_3 & N & L_4 \end{bmatrix} = \begin{bmatrix} K_1 \\ K_2 \\ K_3 \\ K_4 \end{bmatrix} \tag{B.9}$$

where

$$K_1 = \sum_1^N C_p\,,\quad K_2 = \sum_1^N C_p \cdot T\,,\quad K_3 = \sum_1^N \frac{C_p}{T^2}\,,\quad K_4 = \sum_1^N C_p \cdot T^2$$

$$L_1 = \sum_1^N T\,,\quad L_2 = \sum_1^N T^2\,,\quad L_3 = \sum_1^N T^3\,,\quad L_4 = \sum_1^N T^4\,,$$

$$L_5 = \sum_1^N \frac{1}{T}\,,\ L_6 = \sum_1^N \frac{1}{T^2}\,,\ L_7 = \sum_1^N \frac{1}{T^4}$$

Above matrix can be solved to give unknown coefficients, A,B,C and D. These coefficients, then substituted into C_p equation (B.5) to find the approximating function.

To get a better analytical fit, more than one approximating functions are used for some of the C_p data. This method is applied to species when one approximating function becomes inadequate to represent the experimental data.

B.3 Database Organization

Database format of the SKOP v.2 program is shown in Figure B.1. Each species in the database is represented with a block. A database block can be divided into 3 parts. The first part (first row) contains, database number, name, state at 298 °K, standard entropy at 298 °K, melting, boiling and decomposition points, and allotropic transformation temperatures of a species. The second part (starts from third row), contains temperature limits and coefficients (A,B,C,D) of the C_p function, and enthalpy additions at corresponding transformation temperatures. The last part of the block (starts at the end of 2nd part), contains information and necessary messages about

```
----
 No        Name        Ste S°298 Mp Bp Dp Nt T1  T2  T3  T4  T5
----┌-------------------┌--┌------┌--┌--┌--┌--┌--┌--┌--┌--┌---
 T1  T2      A          B          C          D        H at T1
----┌---┌-----------┌----------┌----------┌----------┌----------
----┌---┌-----------┌----------┌----------┌----------┌----------
        :

* Information about species *
* Messages and warnings *
----
```

Figure B.1 Format of the Database.

related species. In the third part, the "S" sign, alone or together with two numbers, states that the current phase is a reference phase. The sign "M", together with a text represent a message and/or a warning about related species. Data blocks for each different specie are separated with "----" sign. Example block for Cu element is given in Figure B.2. Database of the SKOP v.2 program can be further developed using sources of thermodynamic and thermochemical data compilations [27, 35, 36, 37].

```
 23 Cu                    s 7.926386 1358 2843   -   0

 298  700      5.9418  0.0004759980  -25159.5158  4.67471E-7      0
 700 1100      8.3928 -0.0037269508  -260477.4250 2.44816E-6      0
1100 1358     57.3547 -0.0620722197  -10537983.93 2.20445E-5      0
1358 2843      7.8499             0             0             0   3140
S
----
```

Figure B.2 Example Database Block for Cu Element.

APPENDIX C

DISKETTE CONTAINING SKOP v.2 PROGRAM