Problems available for:

- Chapter 1: Basic concepts of thermodynamics
- Chapter 2: Manipulations of thermodynamic quanitites
- Chapter 3: Systems with variable composition
- Chapter 4: Practical handling of multicomponent systems
- Chapter 5: Thermodynamics of processes
- Chapter 6: Stability
- Chapter 7: Applications to molar Gibbs energy diagrams
- Chapter 8: Phase equilibria and potential phase diagrams
- Chapter 9: Molar phase diagrams
- Chapter 10: Projected and mixed phase diagrams
- Chapter 11: Directions of phase boundaries

There are no problems for chapter 12-22

- Chapter 12: Sharp and gradual phase transformations
- Chapter 13: Transformations at constant compostion
- Chapter 14: Partitionless transformations
- Chapter 15: Limit of stability and critical phenomena
- Chapter 16: Interfaces
- Chapter 17: Kinetics of transport processes
- Chapter 18: Methods of modelling
- Chapter 19: Modelling of disorder
- Chapter 20: Mathematical modelling of solution phases
- Chapter 21: Solution phases with sublattices
- Chapter 22: Physical solution models

Welcome to

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Problems to be solved on the Thermo-Calc data bank system

Based on the textbook by Mats Hillert:

Phase Equilibria, Phase Diagrams and Phase Transformations
2nd edition, Cambridge University Press, 2007

These Problems and their computerized solutions are open to anyone for reading and studying. However, in order to produce your own solution by following those presented in this document you at least need a free-of charge license to the Thermo-Calc DEMO package.

The present collection of problems was not designed to make a general instruction to the use of the Thermo-Calc package but will introduce the student to features essential for solving the special questions raised by the problems. Often these problems are not of the kinds of interest to the ordinary customers and Thermo-calc may not always be designed to give the most direct way of finding the answer to such questions. On the other hand, a more detailed path to a solution may be instructive for the student and may give her/him a deeper insight in how thermodynamics works.

The problems are designed as exercises to various sections in the textbook and are collected Chapter-wise. The student is advised first to study the **General instructions for using the Thermo-Calc System.** Later on it may also be useful to be familiar with the **Index of special features**.

1. General Instructions for Using the Thermo-Calc System

Introduction

Even though you may gain some experience in the use of the special free-of-charge version of the Thermo-Calc software and databank system, the main purpose of this instructions and in connection with the present set of Problems is to help you to understand those particular solutions. If trying to modify a problem, you may run into difficulties that require a deeper insight in the facilities offered by Thermo-Calc (T-C). Much more detailed instructions can be obtained by turning to the download area at www.thermocalc.com but they may require a substantial effort.

General structure of T-C

T-C is composed of modules. It operates with prompts and commands. When “:” appears at the end of a text, you are prompted to give a command. The command will be executed when you press “return”.

When you type your response to a prompt, it generally does not matter if you use upper or lower case characters. You may thus type fe for Fe and t for T.

Your response to a prompt may contain a main command and further information (arguments). Both the main command and arguments may be abbreviated as long as it can be distinguished from all other legal options.

A list of the optional commands can always be inspected by typing **?** or **help**. The content of the list depends on where in the program you are.

Often a default argument is given within / / just before “:”. You can accept the default by simply pressing “return”.

Often you are required to give several arguments to a command. You may type them on the same line if you know what will be required. Otherwise, simply press “return”, you will be prompted to type the arguments one by one.

The main command may consist of several words. They are connected by hyphens or underscores. They may be abbreviated by omitting a word completely or by abbreviating each word but keeping the hyphens or underscores. Arguments are separated by a blank space or by a comma and a blank space.

The prompt “SYS:” indicates that you have accessed the T-C system. You can go to any module with the command **goto <name of module>**.

The command **set-log <name of a file>** will allow you to save the commands used in the whole session into a file. You can run the created file as a macro by simply changing the file extension from “LOG” to “TCM” and then dragging-and-dropping the file to your T-C icon. If you want to modify your commands and arguments for similar calculations you may edit the macro file by using any simple editor (e.g. notepad, wordpad, emacs),

Units and symbols

T-C uses and requires SI units, e.g. pascal Pa (1 bar=1E5 Pa, 1 atm=1.01325E5 Pa), kelvin K (=^{o}C+273.15) and meter m for setting conditions and internal calculations. *Exception*: Mass (weight) must be expressed in gram, not kg. During post-processing of calculation results, non-SI units can be used for plotting some properties, for example temperature in Celsius or Fahrenheit.

The formula unit depends on the model used in the database. It could be $CaCO_3$ or $(Fe,Mn)_1(Va,C)_1$ or (H_2, O_2, H_2O) for a gas.

The symbol for mass is B but the symbol for mass (weight) fraction is W. Weight% or mole % is not used in calculations. They can be used in plots of results.

N is the symbol for the number of moles of components (usually atoms) in the system.
NP(phase) is the number of moles of a phase present in the system.
N(species) is the number of moles of the species in the system. Notice that this works only for species that have been defined as component.
N(phase,species) is the number of moles of the species in a phase.

If Z is an extensive property, whether for the whole system or for a phase, then
ZM is per mole of components (usually atoms)
ZW is per mass (in gram)
ZV is per volume (in m^3)
ZF is per mole of formula unit of a phase.

T-C uses the symbol A for Helmholtz energy instead of F.

Composition and constitution

The components of a system are usually the elements. This can be changed only by a special command.

The composition of the system is given by the mole fractions or mass fractions of components, e.g. x(C) or w(C). The composition of a phase is given by x(phase,C) or w(phase,C).

The constitution of a system or of a phase is defined as the distributions of the species among the phases and within each phase.

The constitution of a phase with sublattices, e.g. the fcc phase $(Fe,Mn)_1(Va,C)_1$, is given by the site fractions of the species, e.g. y(fcc,C#2) where C is a species in sublattice 2.

Species is any unit of matter used in the model of a phase stored in the database, e.g. H_2 in the gas phase.

Constituent is a species in a specified sublattice.

Save, print and plot options

When using the **step** or **map** commands in POLY the calculation results will automatically be saved on a file. The file will be stored in the default directory USERPROFILE, which is usually “C:\Documents and Settings\xxx”, where xxx is your login user name. The file name will be RESULT.POLY3. At the end of a **step/map** calculation the following line will thus appear:

```
*** Last buffer saved on file: USERPROFILE\RESULT.POLY3
```

However, it is possible (and recommended) to use the command SAVE just before the **step/map** command. This will enable you to use different file names for different calculations. The file may be uploaded using the command **read** in POLY.

A diagram that has been plotted in the POST-processor may also be printed on paper. The command in POST is **print_diagram**. It is available under Windows NT/2000/XP and Windows 95/98/ME environments.

The command **set_label_curve_option** may be used to identify the curves drawn in the post-processor by marking each curve with a digit and then list the meaning of these digits beside the plot. The options used in the Problems are:

E – lists stable phases along a line (color)
F – lists axis quantity (color)

Databases

There are several free databases accompanying this special version of Thermo-Calc. Some of them contain no data on molar volumes and others contain only rough values. High quality information on molar volumes may be found in a few databases.

All databases are not completely consistent with each other, depending on their special purposes.

One may append data from another database after having obtained data from a database.

The following list of databases available with the special free-of-charge version of T-C can always be obtained by typing **?** after **switch** when in the database module. It should be emphasized that the special version of T-C allows the use of information involving only three elements at a time. Once you have selected a database you may type the command **database_information** to get a description for the selected database.

```
 DALMGSI =  TCS Demo Al-Mg-Si Alloys TDB v1
 DFECRC  =  TCS Demo Fe-Cr-C Alloys TDB v1
 PURE4   =  SGTE Unary (Pure Elements) TDB v4
 PSUB    =  TCS Public Pure Substances TDB v1
 PBIN    =  TCS Public Binary Alloys TDB v1
 PKP     =  Kaufman Binary Alloys TDB v1
 PCHAT   =  Chatenay-Malabry Binary Alloys TDB v1
 PTERN   =  TCS Public Ternary Alloys TDB v1
 PG35    =  G35 Binary Semi-Conductors TDB v1
 PION    =  TCS Public Ionic Solutions TDB v2
 PAQ2    =  TCS Public Aqueous Solution TDB v2
 PGEO    =  Saxena Pure Minerals Database v1
 PFRIB   =  Fridberg Dilute Fe-Alloys MDB v1
```

2. Index of special features

3. Problems

All problems are available for download one by one from
http://www.thermocalc.com/PEPDPT/PEPDPT.html

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

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Chapter 1. Basic concepts of thermodynamics

1.1A. External state variables

a) Consider a system of pure carbon. Define the conditions in sufficient detail to allow the state of equilibrium to be computed, using a thermodynamic data bank. Choose the conditions any way you like, except that P=1 bar should be chosen. Then, evaluate the volume.

b) Use that volume when redefining the conditions and exclude another piece of information from the conditions. Then, evaluate the state of equilibrium, which should be the same as before. Check that by inspecting the value of the excluded property. It should be the same as before.

Hint

1) The conditions can be defined using the values of c+2=1+2=3 independent variables. So far we have discussed T, P and V but it is evident that another one is the amount of material, e.g. the number of moles of components (usually atoms), N. Since you are asked to evaluate V, it is evident that among those four variables you must give the values to all three of T, P and N to define the conditions. You may take 1000^{o}C, 1 bar and 1 mol. 1 bar is 100000 Pa.

2) There can never be more than c+1 independent *intensive* variables, in this case T and P, whereas V and N are *extensive* variables and at least one of them is required in order to have a complete definition of the conditions. It serves to define the size of the system. However, you could use more than one extensive variable. When including V in the new set of independent variables, you could exclude N but it may be more interesting instead to exclude one of the potentials, say T, and use two extensive variables, V and N, together with P.

Instructions for using T-C

1) Go first to the database module to fetch the thermodynamic information and then to the equilibrium module POLY. It is constructed to compute a state of equilibrium by minimizing the Gibbs energy and then to give information on the computed state. It is thus necessary first to make the program perform an equilibrium computation even if it is trivial when the set of conditions is sufficient to define the state without any minimization. The reason is that POLY does not accept the given conditions as a description of a state. They are just treated as conditions for the equilibrium to be computed.

2) Explanations are inserted in the following print-out of Prompts, commands and responses and are marked with *) and printed with a different font.

3) All commands that you should give are printed **bold** but usually in a much abbreviated form.

Prompts, commands and responses

```
SYS:
```

*) Thermo-Calc (T-C) is composed of several modules. You should first **go**to the **da**tabase module.

```
SYS: go
MODULE NAME: da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI:
```

*) You like to **sw**itch to another database. Press return after **sw** and you find the limited list of the databases available to you as a customer of the free-of-charge version of T-C. You should realize that it is really limited and there will be no ambition to use a wide variety of systems in the present set of problems. On the contrary, it may be of some pedagogical value that you get familiar to the systems you work with.

```
TDB_DALMGSI: sw
 Use one of these databases

 DALMGSI =  TCS Demo Al-Mg-Si Alloys TDB v1
 DFECRC  =  TCS Demo Fe-Cr-C Alloys TDB v1
 PURE4   =  SGTE Unary (Pure Elements) TDB v4
 PSUB    =  TCS Public Pure Substances TDB v1
 PBIN    =  TCS Public Binary Alloys TDB v1
 PKP     =  Kaufman Binary Alloys TDB v1
 PCHAT   =  Chatenay-Malabry Binary Alloys TDB v1
 PTERN   =  TCS Public Ternary Alloys TDB v1
 PG35    =  G35 Binary Semi-Conductors TDB v1
 PION    =  TCS Public Ionic Solutions TDB v2
 PAQ2    =  TCS Public Aqueous Solution TDB v2
 PGEO    =  Saxena Pure Minerals Database v1
 PFRIB   =  Fridberg Dilute Fe-Alloys MDB v1
 USER    =  User defined Database

DATABASE NAME /DALMGSI/: PTERN
 Current database: TCS Public Ternary Alloys TDB v1

 VA  DEFINED
TDB_TERN:
```

*) You should now define the system. It is usually convenient to **def**ine the system through the **el**ements. As stated just before the TDB_DALMGSI, you never need to define vacancies that some models use. Now your system should only contain carbon.

```
TDB_PTERN: def-el
ELEMENTS: C
 C  DEFINED
TDB_PTERN:
```

*) Before you are used to T-C you better **l**ist the **sys**tem to see what you have accomplished so far.

```
TDB_TERN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:  CONSTITUENT
 LIQUID:L    :C:
  > This is metallic liquid solution phase, with C species
 GRAPHITE    :C:
TDB_TERN:
```

*) You got two phases, liquid and graphite, but like to **rej**ect the **p**hase called **liq**uid. Then you are satisfied with the definition of the system and like to **get** the data.

```
TDB_TERN: rej
ELEMENTS, SPECIES, PHASES, CONSTITUENT OR SYSTEM: /PHASES/:  p
PHASES: liq
 LIQUID:L  REJECTED
TDB_TERN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           11
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_TERN:
```

*) Now you should **go**to the equilibration module called **POL**Y-3 (historically the 3rd version).

```
TDB_TERN: go
MODULE NAME: pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) In the database you defined what phases and elements the system should contain. In POLY you should give values of the state variables with which you like to define the conditions for the equilibrium. The command is **s**et-**c**onditions. You will then be prompted to define your choices. If you accept the default, you just press return. Notice that N is the size of the system expressed as the number of moles of components (here atoms). If you like to accept a default value, just press return.

```
POLY_3: s-c
State variable expression: P
Value /100000/:
POLY_3: s-c
State variable expression: T
Value /1000/:  1273
POLY_3: s-c
```

```
State variable expression: N
Value /0/:  1
POLY_3:
```

*) Just to be sure, you may **l**ist your the **c**onditions.

```
POLY_3:l-c
 P=1E5, T=1273, N=1
 DEGREES OF FREEDOM 0
POLY_3:
```

*) Degrees of freedom = 0 means that the equilibrium will be well defined. POLY can only compute equilibria with no degree of freedom. Evidently, you could now ask POLY to **c**ompute **e**quilibrium.

```
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in           0  s
POLY_3:
```

*) It seems that the computation was successful. Next you were asked to use the volume as a condition. In order to obtain the same equilibrium, you should require that V has the value of the state just computed. You don't need to inspect it in advance. The value of the current state will always be proposed to you as a default. You could type V or V=.

```
POLY_3: s-c V
POLY_3: Value /5.441691885E-06/:
```

*) Just press return.

```
POLY_3: Value /5.441691885E-06/:
POLY_3:
```

*) Just to be sure, you could again list the **c**onditions before asking POLY to compute equilibrium.

```
POLY_3: l-c
 P=1E5, T=1273, N=1, V=5.44169E-6
 DEGREES OF FREEDOM -1
POLY_3:
```

*) There is one condition too many which is expected because you have added one. You should remove another one. You are free to remove any one, even the size of the system because the size is now defined by the volume.

```
POLY_3: s-c N=none
POLY_3:
```

*) You should note that you will not remove the condition based on N by typing N=0. On the contrary, that will just change the previous condition to the new N value, being 0. Now you can again try to compute equilibrium.

```
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) You succeeded and like to show the **N** value in order to check that you obtained the same state of equilibrium.

```
POLY_3: sh N
 N=1.
POLY_3:
```

*) Fine! Try to use both N and V to define conditions. Enter V instead of P.

```
POLY_3: s-c P=none N=
POLY_3: Value /1/:1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
```

```
POLY_3: sh P
P=100002.13
```

*)This is close enough.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) You must give the value of at least one extensive state variable as condition. Here you saw that you could use more than one. In fact, you could give all the conditions with extensive state variables.

2) When giving commands it does not matter if you use upper or lower cases. Pressure could be typed with p and Fe with fe or even FE

3) The number of responses can be shortened when you learn to remember what prompts will automatically follow many main commands. You can type all those responses on the same line as the command. That will be demonstrated in the next Problem.

4) When you don't remember what would be a proper response to a prompt, you can get a list of all your options by typing **?** or **help**, followed by return.

1.1B. External state variables

Calculate and plot the function $V(P,T_1,N_1)$ for graphite between 1 bar and 1 kbar (i.e. 100000 to 1E8 Pa) at 1000°C and for 1 mol.

Hint

The method of computing and plotting a curve depends on your particular data bank system.

Instructions for using T-C

1) In order to plot a curve showing how some property of a system at equilibrium varies under changing conditions, you start by computing an initial equilibrium to be used as a starting point. Then you can let the computation be repeated at close intervals by varying one of the conditions. In the present case, let the P value vary between two limits.

2) The data should be fetched from a database as demonstrated in the previous Problem. If you have just solved that Problem, you may go back to the beginning of POLY and start from there using the command "reinitiate-module". Everything in POLY has been deleted but not data from the database.

3) Now you should begin typing responses on the same line as the command when possible.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
```

```
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI:
```

*) You need another database. You could type switch and return and get a list of databases available to you. You did that in the preceding Problem. If you remember that list, you can type it directly without consulting the list.

```
TDB_DALMGSI: sw ptern

 Current database: TCS Public Ternary Alloys TDB v1

 VA  DEFINED
TDB_PTERN:
```

*) Now you should define the system and could choose the option to give the elements. You may remember that you will be prompted to name the element. Then you could do that on the same line.

```
TDB_PTERN: def-el C
 C  DEFINED
TDB_PTERN:
```

*) You may note that words belonging to the same command should be connected with a hyphen "-" (or underscore "_") but words being the responses to new prompts or questions, however not seen, will not have a hyphen. This explains "def-el C". Now you could **l**ist the **sys**tem to see what it contains.

```
TDB_PTERN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:  CONSTITUENT
 LIQUID:L    :C:
  > This is metallic liquid solution phase, with C species
 GRAPHITE    :C:
TDB_PTERN:
```

*) There are two phases but you only want graphite. Thus, you **rej**ect the **p**hase **liq**uid.

```
TDB_PTERN: rej p liq
 LIQUID:L  REJECTED
TDB_PTERN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           11
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PTERN: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Next you should **s**et the **c**onditions for an initial equilibrium as an introduction to stepping through the range of P values. Remember that you can give several items on the same line.

```
POLY_3: s-c P=1E5 T=1273 N=1
POLY_3:
```

*) You should notice that P and 1E5 were responses to separate prompts and should normally be separated by a blank. However, when the second one is a value to the first one,

you should use "=". Just for safety, you can now list the conditions. You will find that the degree of freedom is zero and could thus continue with **c**omputing **e**quilibrium.

```
POLY_3: l-c
 P=1E5, T=1273, N=1
 DEGREES OF FREEDOM 0
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3:
```

*) You can now make a series of calculations for the range of P and for the values of T and N used in defining the conditions for the initial equilibrium. First you specify the axes in the diagram to be plotted by **s**etting the **a**xis **v**ariables. Often one can accept the default value of the increment. Then just press return or type the value.

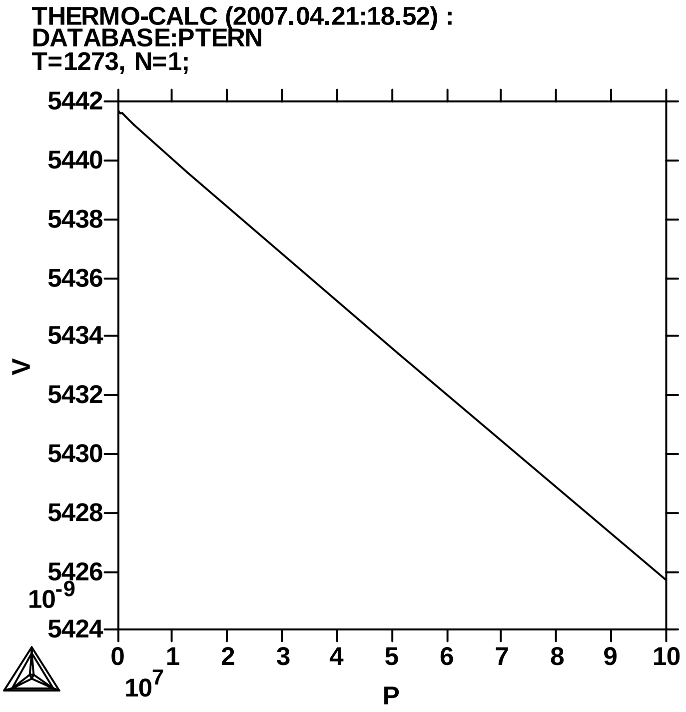
```
POLY_3: s-a-v
Axis number: /1/:  1
Condition /NONE/:  P
Min value /0/:  1e5
Max value /1/:  1e8
Increment /2497500/:  2*
POLY_3:
```

) 2 means logarithmic step. It is often used when the variable covers several orders of magnitude.

```
POLY_3: step
Option? /NORMAL/:  NORMAL
 looking for miscibility gaps..at:
 QSTEPP   100000000.000000
 QSTEPP   100000.000000000
 QSTEPP   50050000.0000000
 No new miscibility gap found!

 Phase Region from   0.100000E+09 for:
     GRAPHITE
 Calculated    13 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*)The computation is finished and you should go to the postprocessor module. It is actually a submodule to POLY and you don't need to type "goto".

```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a
AXIS (X, Y, or Z) :x
VARIABLE : P
POST: s-d-a y
VARIABLE : V
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            0  seconds
```

Comments

Here you have learned how to compute and plot a curve.

1.2. Internal state variables

Consider an Ag-Cu alloy with 10 mass% Cu at 600°C and 1 atm (101325 Pa). Compute the equilibrium and find the values of some internal variables. Then, use one of those values when redefining the conditions and instead exclude one of the external variables. Again calculate the equilibrium and check that the excluded variable got the same value as it had before.

Hint

You can certainly make your program present the calculated state of equilibrium. It will then give a long list containing the external variables but also some internal variables, e.g. the fractions of phases and their compositions if there is more than one phase. Choose any of these values when redefining the conditions for a new computation of the same of equilibrium.

Instructions for using T-C

1) There may be other properties of the equilibrium state that are not included in the list. As described later, you can ask specifically for a large number of such properties with the command "show <variable>", whether it is included in the list or not.

2) When defining a system with more than one component, one can either give the amount as the number of moles, N(i), or the mass in gram, B(i), of a component or the total amount, N or B, and the composition expressed by the mole fractions, x(i) etc., but omitting one because $\sum x(i) = 0$.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw
 Use one of these databases

 DALMGSI =  TCS Demo Al-Mg-Si Alloys TDB v1
 DFECRC  =  TCS Demo Fe-Cr-C Alloys TDB v1
 PURE4   =  SGTE Unary (Pure Elements) TDB v4
 PSUB    =  TCS Public Pure Substances TDB v1
 PBIN    =  TCS Public Binary Alloys TDB v1
 PKP     =  Kaufman Binary Alloys TDB v1
 PCHAT   =  Chatenay-Malabry Binary Alloys TDB v1
 PTERN   =  TCS Public Ternary Alloys TDB v1
 PG35    =  G35 Binary Semi-Conductors TDB v1
 PION    =  TCS Public Ionic Solutions TDB v2
 PAQ2    =  TCS Public Aqueous Solution TDB v2
 PGEO    =  Saxena Pure Minerals Database v1
 PFRIB   =  Fridberg Dilute Fe-Alloys MDB v1
 USER    =  User defined Database

DATABASE NAME /DALMGSI/:  pbin
 Current database: TCS Public Binary Alloys TDB v1

 VA                     /-  DEFINED
 IONIC_LIQ:Y            L12_FCC                 B2_BCC
 BCC_B2  REJECTED
TDB_PBIN: def-el Ag Cu
 AG                     CU  DEFINED
TDB_PBIN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L    :AG CU:
  > This is metallic liquid solution phase, with C-N species
 FCC_A1      :AG CU:VA:
 BCC_A2      :CU:VA:
 HCP_A3      :CU:VA:
 ALCU_EPSILON :CU:CU:
 ALCU_ETA    :CU:CU:
 CUZN_EPS    :CU:
TDB_PBIN:
```

*) As usual, the database contains more phases than you are interested in. This time accept all the phases on this level but make sure that unwanted phases don't interfere later on.

```
TDB_PBIN: get
```

```
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            3
 FUNCTIONS ....

 List of references for assessed data

   91Din 'A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, Vol.15,
       No.4, pp.317-425, (1991)'
   HAY-AGCU 'F.H. Hayes, H.L. Lukas, G. Effenberg, G. Petzow,
       Z. fur Metallkde, Vol 77 (1986), No 11, p 749-754; AG-CU-PB'
   NIG-ALCU 'Nigel Saunders, COST 507 round 1, (1993); Al-Cu'
   KOW-CUZN 'M Kowalski and P Spencer, J Phase Equil, p 432-438 (1993); CU-ZN'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PBIN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=873 P=101325 w(Cu)=0.1 N=1
```

*) You may **l**ist the **c**onditions. Then **c**ompute **e**quilibrium if degrees of freedom=0.

```
POLY_3: l-c
 T=873, P=1.01325E5, W(CU)=0.1, N=1
 DEGREES OF FREEDOM 0
POLY_3: c-e
 Using global minimization procedure
 Calculated          279  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Creating a new composition set FCC_A1#2
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) This time you like to inspect the computed equilibrium in detail by the command **l**ist-**e**quilibrium.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:  SCREEN
Options /VWCS/:
```

*) There are two options for each position. W means mass fraction but it could be exchanged for X, meaning mole fractions, which you may prefer. You could inspect all the options by printing ? and return.

```
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: PBIN

 Conditions:
 T=873, P=1.01325E5, W(CU)=0.1, N=1
 DEGREES OF FREEDOM 0

 Temperature  873.00 K ( 599.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  1.00837E+02
 Total Gibbs energy -4.56490E+04,  Enthalpy  1.68797E+04,  Volume  0.00000E+00

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 AG                       8.4132E-01 9.0000E-01 1.5374E-03 -4.7018E+04 SER
 CU                       1.5868E-01 1.0000E-01 5.0484E-03 -3.8388E+04 SER

 FCC_A1#1                    Status ENTERED     Driving force  0.0000E+00
```

```
 Number of moles 8.9013E-01, Mass 9.3780E+01
 Mass fractions: AG  9.65787E-01  CU  3.42131E-02

 FCC_A1#2                   Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0987E-01, Mass 7.0566E+00
 Mass fractions: CU  9.74283E-01  AG  2.57167E-02
 POLY_3:
```

*) First you see the conditions just as you would have seen them by the command list-conditions before computing equilibrium.

Then you see the main results of the computation, most of which is just a confirmation that the conditions were satisfied. The volume is given as 0 because this database does not include any data on volume.

Then you see the states of the two components, their amounts in mole as well as their mass fractions. Again, that confirms the conditions given. In addition, there is information on the activity and chemical potentials, both given relative to their references, which were here chosen as SER by default. You will later see how you could make different choices.

Then you see the states of the phases. There are two phases in the equilibrium. Both are fcc and are described with the same fundamental equation stored in the database because there is only one fcc phase in this database according to the response to the list-system command. Evidently, POLY was able to identify two fcc phases and decided to call them fcc#1 and fcc#2. Both are given as "entered" because you have not prevented them from taking part in the equilibrium. To the right you see that the driving force for more of them to form from the equilibrium is 0 because they are in equilibrium. The first number for a phase gives the fraction of that phase, measured in moles and then in mass fraction. The next line gives the composition of the phase and you can see that fcc#1 is Ag rich and fcc#2 is Cu rich. Unfortunately, on your screen the text "mass fractions" comes one line before the numbers. Here that text was moved to where it belongs.

You were next asked to use one of the internal variables as a condition. You could for instance use the composition of phase fcc#1, e.g. given as w(fcc#1,Cu). POLY knows the current numbers and you just have to type the symbol. However, you should also remove one of the old conditions and that *must be a realistic choice*. Here it would be reasonable to ask at what temperature the equilibrium fraction or composition of a phase should have the value given as a condition and you should thus remove the condition T=873. By computing equilibrium you should obtain the same equilibrium as before, a fact that you can easily check afterwards by showing the temperature.

```
POLY_3: sh w(fcc,Cu)
 W(FCC_A1#1,CU)=3.4213068E-2
POLY_3: s-c w(fcc,Cu)
Value /.0342130676/:
POLY_3: s-c T=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          279  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=873.
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) Internal variables can very well be used as conditions for equilibrium. However, you should be careful. The set of conditions should be logical.

2) Many details about the computed equilibrium can be shown by a single command, list-equilibrium. How the values of some quantities will be expressed is decided by what option is chosen. There are also options controlling what quantities will be shown.

1.3A. The first law of thermodynamics

1 kg of a steel (Fe+0.8 mass% C) is heated from a state of equilibrium at 500^{o}C to a new state of equilibrium at 800^{o}C. The pressure is kept at 1 atm. How much heat was needed for this operation?

Hint

Since there is no change of P, you should use the first law for the enthalpy, which yields $Q = \Delta H - \int VdP = \Delta H$ for constant P. You should thus compute the equilibria for the two sets of conditions, show the enthalpy and take the difference. It does not matter if you don't understand what reference state the values refer to because that does not affect the difference.

Instructions for using T-C

Remember that T-C expresses mass in gram.

Prompts, commands and responses

```
SYS: go da
THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pbin
 Current database: TCS Public Binary Alloys TDB v1

 VA                        /-  DEFINED
 IONIC_LIQ:Y               L12_FCC                 B2_BCC
 BCC_B2  REJECTED
TDB_PBIN: def-el Fe C
 FE                        C  DEFINED
TDB_PBIN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L     :C FE:
  > This is metallic liquid solution phase, with C-N species
 FCC_A1       :FE:C VA:
 BCC_A2       :FE:VA C:
 HCP_A3       :FE:C VA:
 CBCC_A12     :FE:C VA:
 CUB_A13      :FE:C VA:
 CEMENTITE    :FE:C:
 GRAPHITE     :C:
 DIAMOND_FCC_A4 :C:
  > This is the Diamond phase for Si-C
TDB_PBIN:
```

> *) There are many phases in the database. Try to keep them all. All may not be stable in the equilibrium you are going to compute and should automatically be excluded by POLY. On the other hand, graphite would be stable but by experience one knows that it may be slow to

form. In such a case one should in POLY take an action to stop it from taking part in the computation.

For each phase you can see the constituents in the various sublattices. Six of the phases have two sublattices and for five of them there are carbon and vacancies in the second sublattice. Those phases are interstitial solutions of C in Fe.

```
TDB_PBIN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           35
 FUNCTIONS ....

 List of references for assessed data

   90Din 'Alan Dinsdale, SGTE Data for Pure Elements, NPL Report
       DMA(A)195, Rev. August 1990'
   85Gus 'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267
       TRITA 0237 (1984); C-FE'
   89Din 'Alan Dinsdale, SGTE Data for Pure Elements, NPL Report
       DMA(A)195, September 1989'
   91Din 'A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, Vol.15,
       No.4, pp.317-425, (1991)'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PBIN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=773 P=101325 w(C)=.008 B=1000
POLY_3: c-e
 Using global minimization procedure
 Calculated          825  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You should check if graphite has taken part in the equilibrium by **l**isting the **st**atus of the **p**hases.

```
POLY_3: l-st p
 *** STATUS FOR ALL PHASES
 PHASE                  STATUS    DRIVING FORCE   MOLES
 GRAPHITE               ENTERED    0.00000000E+00  6.65765437E-01
 BCC_A2                 ENTERED    0.00000000E+00  1.77631060E+01
 FCC_A1                 ENTERED   -2.30208472E-01  0.00000000E+00
 CEMENTITE              ENTERED   -3.08111171E-01  0.00000000E+00
 HCP_A3                 ENTERED   -4.09496878E-01  0.00000000E+00
 DIAMOND_FCC_A4         ENTERED   -7.63728102E-01  0.00000000E+00
 CUB_A13                ENTERED   -8.97856313E-01  0.00000000E+00
 CBCC_A12               ENTERED   -1.04907383E+00  0.00000000E+00
 LIQUID                 ENTERED   -1.11457154E+00  0.00000000E+00
POLY_3:
```

*) Graphite has taken part in the equilibrium. You should **ch**ange the **st**atus of that **p**hase by suspending it.

```
POLY_3: ch-st p gra=sus
POLY_3: c-e
 Using global minimization procedure
```

```
 Calculated          824  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-st p
 *** STATUS FOR ALL PHASES
 PHASE                  STATUS    DRIVING FORCE   MOLES
 DIAMOND_FCC_A4         ENTERED    0.00000000E+00  6.65432313E-01
 BCC_A2                 ENTERED    0.00000000E+00  1.77634400E+01
 CEMENTITE              ENTERED   -1.17193213E-01  0.00000000E+00
 FCC_A1                 ENTERED   -2.19640425E-01  0.00000000E+00
 HCP_A3                 ENTERED   -4.09208720E-01  0.00000000E+00
 CUB_A13                ENTERED   -8.78849990E-01  0.00000000E+00
 LIQUID                 ENTERED   -9.96328024E-01  0.00000000E+00
 CBCC_A12               ENTERED   -1.02536049E+00  0.00000000E+00
 SUSPENDED PHASES:
 GRAPHITE
POLY_3:
```

*) This time diamond has formed. It should also be suspended. It had been easier to reject all phases from the beginning and then restore only those phases you like to study, bcc, fcc and cementite. But that requires that you are familiar with the system.

```
POLY_3: ch-st p dia=sus
POLY_3: c-e
 Using global minimization procedure
 Calculated          824  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-st p
 *** STATUS FOR ALL PHASES
 PHASE                  STATUS    DRIVING FORCE   MOLES
 CEMENTITE              ENTERED    0.00000000E+00  2.66068525E+00
 BCC_A2                 ENTERED    0.00000000E+00  1.57681870E+01
 FCC_A1                 ENTERED   -2.09112159E-01  0.00000000E+00
 HCP_A3                 ENTERED   -4.08888516E-01  0.00000000E+00
 CUB_A13                ENTERED   -8.58331365E-01  0.00000000E+00
 LIQUID                 ENTERED   -9.14933394E-01  0.00000000E+00
 CBCC_A12               ENTERED   -9.99646022E-01  0.00000000E+00
 SUSPENDED PHASES:
 GRAPHITE DIAMOND_FCC_A4
POLY_3: ent-sym var H773=H;
POLY_3: sh H773
 H773=284251.95
POLY_3:
```

*) Change to the higher temperature and evaluate the enthalpy for that equilibrium. You only need to set the new condition. The old value will automatically be deleted.

```
POLY_3: s-c T
Value /773/:  1073
POLY_3: c-e
 Using global minimization procedure
 Calculated          823  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: sh H
 H=585994.63
POLY_3: ent-sym var deltaH=H-H773;
POLY_3: sh deltaH
 DELTAH=301742.68
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) DeltaH is given in J for the system, i.e. for 1 kg (B=1000 gram).

2) A phase, that for some reason should not take part in the equilibrium, can either be rejected before data are fetched from the database or by suspending it in POLY.

3) One can store the current value of a variable by entering a symbol for it.

1.3B. The first law of thermodynamics

A mixture of 2 mol of H_2 and 0.1 mol of O_2 is kept in a very strong cylinder at 25°C. The cylinder has a moveable piston, working against an outside atmosphere of 1 atm. The mixture is ignited and reacts quickly to a state of equilibrium, containing mostly H_2O molecules, and without giving time for any exchange of heat. Calculate the new temperature. In order to simplify the computation you may reject all species except for H_2, O_2 and H_2O.

Hint

The internal energy is not directly affected by an internal reaction. It can be changed only by interactions with the surroundings as described by the first law, $dU=dQ-PdV$. In the present case $dQ=0$ but $dV>0$. It would thus be more convenient to consider the enthalpy, $dH=dU+d(PV)=dQ+VdP=0$ since $dQ=0$ and $dP=0$. One should thus evaluate H for the initial state (which is not at equilibrium) and then search for an equilibrium state that has the same H value.

Instructions for using T-C

1) As a default, T-C recognizes H and O as the components also in the gas but H_2, O_2 and H_2O as the species that define the constitution. The formula unit of a gas is defined for one mole of species.

2) If the H_2O species is first suspended in POLY, then there can be no reaction and the state will not change if the equilibrium is computed. The only effect on the computation is that the constitution has been evaluated directly from the composition, which was entered. It is then possible to show the initial properties, which POLY always evaluates from the correct constitution.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI:
```

*) **Sw**itch to the PSUB database, which is primarily for stoichiometric substances but also has data for a gas with H, N, O and S. It includes a large number of species between those elements.

```
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1
```

```
 VA  DEFINED
TDB_PSUB: def-el H O
 H                       O  DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:  CONSTITUENT
 GAS:G       :H H2 O O2 O3 H1O1 H1O2 H2O1 H2O2:
  > Gaseous Mixture, using the ideal gas model
 H2O_L       :H2O1:
 H2O2_L      :H2O2:
TDB_PSUB: rej p *
 GAS:G                   H2O_L                   H2O2_L
   REJECTED
TDB_PSUB: rest p gas
 GAS:G  RESTORED
TDB_PSUB:
```

*) The gas phase is the first phase you meet with a constitution controlled not only by elements and by crystallography, which may define sublattices that are fixed for each phase. The constitution of the gas depends on the presence of species, usually molecules, and for various reasons one may like or not like a species to be present in a computation. The aqueous solution is another example. In the present case it is thus necessary to reject all species and then restore H2 and O2 for the first part and then to restore H2O1 for the second part.

```
TDB_PSUB: rej sp *
 VA                      H                       O
 H1O1                    H1O2                    H2
 H2O1                    H2O2                    O2
 O3  REJECTED
TDB_PSUB: rest sp H2 O2
 H2                      O2  RESTORED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) When setting the conditions you should remember that you must define the values of state variables but for the composition you can only give values of the components. The database for the gas regards the atoms as the components, not the molecules, and a gas with 2 mol of H_2 and 0.1 mol of O_2 should thus be defined as 4 mol of H and 0.2 mole of O. However, POLY offers another possibility. You can **s**et the **i**nitial **a**mount of a species and POLY will immediately dissociate it and register the amounts of atoms. If you then give the

initial amount of another species that has an element in common with the first species, the new amount will be added to the previous amount.

```
POLY_3: s-c P=101325 T=298
POLY_3: s-i-a N(H2)=2
POLY_3: s-i-a N(O2)=.1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: sh H
 H=-9.091584
POLY_3:
```

*) It is interesting to note that the H value is very small. In fact it should have been exactly equal to zero if you had used the exact value of 298.15 K for 25^{o}C. The reason is that the database uses the elements in their stable states at 1 atm and 25^{o}C as references (called SER) and the enthalpy of mixing in the gas is zero according to the database that uses the ideal gas model. Now you should go back to the database and add the species H2O1. You can go back by simply typing **b**.

```
POLY_3: b
TDB_PSUB: def-sp H2O1
 H2O1  DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENTS/:  CONSTITUENTS
 GAS:G       :H2 O2 H2O1:
  > Gaseous Mixture, using the ideal gas model
 H2O_L       :H2O1:
TDB_PSUB:
```

*) With H2O1 you also introduced a new phase, water, and like to reject it.

```
TDB_PSUB: rej ph H2O_L
 H2O_L  REJECTED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

-OK-
TDB_PSUB:
```

*) You should notice the first line in the response, which says "REINITIATING GES5". That means that what you just did in POLY has been erased and when you again go to POLY you must give all the conditions again and the value of H has been forgotten. You would thus have to type it in by hand. In the present case that is no problem because it is practically 0 and should have been exactly equal to 0 if the correct value T=298.15 had been used. You can again type **b** to get back to POLY.

```
TDB_PSUB: b
 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 H=0
```

```
POLY_3: s-i-a N(H2)=2
POLY_3: s-i-a N(O2)=.1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in           0  s
  13 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=1094.1025
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) 1094 K is the end of the adiabatic reaction.

2) Sometimes one must make sure that the required phases are included and only those. That is particularly important when one is interested in a metastable equilibrium. For the gas phase the same is true for species. There it is important when one is interested in a restricted equilibrium.

3) If one goes back to the database to amend the data, then all information about the preceding session on POLY will be erased.

1.4 Freezing-in conditions

0.5 kg of a white cast iron with 3.5 mass % C (which contains no graphite due to insufficient rate of reaction during fast cooling) has been heat treated at 1100^{o}C to equilibrium (without graphite). Then it is cooled to 800^{o}C. Calculate the amount of “liberated” heat during the cooling under two experimental conditions. (A) The state at 1100^{o}C is completely frozen-in during the cooling. (B) A new state of full equilibrium has been established when 800^{o}C is reached due to slow cooling. Also (C) evaluate the heat evolution if the frozen-in state equilibrates isothermally at 800^{o}C if it were first retained during cooling to 800^{o}C.

Hint

1) Suppose the pressure is the same. Then $\Delta H = Q + \int VdP = Q$, where ΔH is the difference of H between the initial and final states.

2) After the equilibrium at 1100^{o}C has been computed, you should like to freeze-in the constitution and only change T. Thus, you should not compute equilibrium before evaluating H of the frozen-in state at 800^{o}C. The question is what facility your data bank system has for frozen-in states.

3) For (B) it does not matter how close to equilibrium the system was at various temperatures during the cooling because H is a state function.

Instructions for using T-C

After giving the conditions for the state of the system, find the equilibrium at 1100^{o}C and store H of the system as H1100. In order to evaluate H for the frozen-in alloy at 800^{o}C, consider each one of the phases separately at 800^{o}C but don't let them react with each other. Then, add the H values for the phases taking into account their actual amounts.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw ptern
 Current database: TCS Public Ternary Alloys TDB v1

 VA  DEFINED
TDB_PTERN: def-el Fe C
 FE                      C  DEFINED
TDB_PTERN:
```

*) You should **l**ist the content of the **sys**tem now defined in order to check that it does not contain a lot of unnecessary data.

```
TDB_PTERN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L    :C FE:
  > This is metallic liquid solution phase, with C species
 BCC_A2      :FE:C VA:
 FCC_A1      :FE:C VA:
 HCP_A3      :FE:VA C:
 CEMENTITE   :FE:C:
 M7C3        :FE:C:
 M23C6       :FE:FE:C:
 V3C2        :FE:C:
 GRAPHITE    :C:
TDB_PTERN:
```

*) You got many more phases than you are interested in. You could reject one phase after another or reject all **(*)** phases and then **rest**ore the **p**hases you want.

```
TDB_PTERN: rej p *
 LIQUID:L                BCC_A2                  FCC_A1
 HCP_A3                  CEMENTITE               M7C3
 M23C6                   V3C2                    GRAPHITE
   REJECTED
TDB_PTERN:
```

*) You can see that all the phases are now rejected. You like to **rest**ore the **p**hases **fcc** and **cem**entite, which are required for the equilibrium.

```
TDB_PTERN: rest p fcc cem
 FCC_A1                  CEMENTITE  RESTORED
TDB_PTERN:
```

*) The wanted phases are now shown. Accept the choice and **get** the data.

```
TDB_PTERN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           21
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R
```

```
 -OK-
TDB_PTERN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1373 B=500 w(C)=.035
POLY_3: l-c
 P=1.01325E5, T=1373, B=500, W(C)=3.5E-2
 DEGREES OF FREEDOM 0
POLY_3: c-e
 Using global minimization procedure
 Calculated          138  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You may like to store the resulting H value by **ent**ering a **sym**bol, which will contain the value of a **var**iable. The name could be **H1100** and it should contain the current value of **H**. You could just as well store other properties that you may like to use or inspect later on, e.g. Bp(fcc) being the mass (B) for the phase fcc or w(fcc,C) being the the mass fraction (w) of C in the fcc phase.

```
POLY_3: ent-sym var H1100=H;
POLY_3: ent-sym var Bpfcc=Bp(fcc);
POLY_3: ent-sym var Bpcem=Bp(cem);
POLY_3: ent-sym var wCfcc=w(fcc,C);
POLY_3: ent-sym var wCcem=w(cem,C);
POLY_3:
```

*) You like to know H of a non-equilibrium state with the same constitution but at 800^{o}C. In principle, that state could be obtained by cooling the alloy to 800^{o}C without the two phases interacting with each other. You should thus consider what happens to each one of the phases when cooled to 800^{o}C. Start with the fcc phase by **ch**anging the **st**atus of the **p**hase **cem**entite to **dor**mant. When giving the conditions you should give the size and composition of the system as the values for fcc at 1100^{o}C. Those values are available directly.

```
POLY_3: ch-st p cem=dor
POLY_3: s-c T=1073 B=Bpfcc w(C)=wCfcc
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Hfcc=H;
POLY_3:
```

*) It should be realized that this value of H is not for 1 mol but for the actual amount of fcc in the frozen-in alloy. Now, consider cementite.

```
POLY_3: ch-st p cem=ent 1
POLY_3: ch-st p fcc=dor
POLY_3: s-c B=Bpcem w(C)=wCcem
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
 Global minimization failed, error code        2011
 Fewer grid points than components
 . Using normal POLY minimization.
 Testing POLY result by global minimization procedure
 Using already calculated grid
   8 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) You can directly evaluate the sum of enthalpies for the two phases. The value for cementite is the current value available under the symbol H.

```
POLY_3: ent-sym var Hfr=H+Hfcc;
```

```
POLY_3:
```

*) Finally, compute the equilibrium at 800^{o}C.

```
POLY_3: ch-st p fcc=ent 1
POLY_3: s-c B=500 w(C)=.035
POLY_3: c-e
 Using global minimization procedure
 Calculated          138  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var H800=H;
POLY_3: ent-sym var HA=H1100-Hfr;
POLY_3: ent-sym var HB=H1100-H800;
POLY_3: ent-sym var HC=Hfr-H800;
POLY_3: sh HA HB HC
 HA=97398.071
 HB=107518.39
 HC=10120.32
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) Properties of frozen-in states can be obtained from POLY but only by considering the phases separately and adding the results.

2) The liberated heat for the piece of cast iron is 97 kJ under freezing-in conditions and otherwise 107 kJ.

1.5. Reversible and irreversible processes

Consider a cylinder that can be in contact with any of two heat reservoirs of 20 and 50^{o}C. There is a piston by which the volume can be changed. The cylinder contains pure N_2 gas and is initially at a pressure of 1 atm.

a) Using the first heat reservoir one compresses the gas slowly and isothermally at 20^{o}C to a pressure of 10 atm.
b) One continues by compressing adiabatically (i.e., with no heat exchange) until a temperature of 50^{o}C has been reached.
c) Using the second heat reservoir one releases the pressure to a value P_3 slowly and isothermally at 50^{o}C.
d) One continues releasing the pressure to 1 atm adiabatically. The pressure P_3 was chosen in such a way that the final temperature was 20^{o}C. It is thus possible to repeat this cycle any number of times.

Evaluate the heat and work received by the system for each one of the four steps. Then add up the net work, W, done *by the system* on the surroundings and calculate the ratio of that work and the heat drawn *from the warm reservoir,* Q_3. Assume that all the four processes are carried out in a reversible fashion.

Hint

Let conditions of the initial state be T_0,P_0 and after the first, second and third step T_0,P_1, T_2,P_2 and T_2,P_3, respectively. After the fourth step it is again T_0,P_0. P_2 and P_3 are not known but may be evaluated because the entropy is not changed by an adiabatic process. For the second step you thus have $S_2 = S_1$, i.e. $S(T_2, P_2) = S(T_0, P_1)$, which yields P_2. For the fourth step you have $S_3 = S_0$, i.e. $S(T_2, P_3) = S(T_0, P_0)$, which yields P3. Denote the heat and work received by the system during the first step by Q_1 and W_1 etc. The heats received during the isothermal steps, i.e. the first and third steps, are according to the definition of entropy for a reversible and isothermal process $Q_1 = \int T_0 dS = T_0(S_1 - S_0) = T_0(S(T_0, P_1) - S(T_0, P_0))$ and $Q_3 = \int T_2 dS = T_2(S_3 - S_2) = T_2(S(T_2, P_3) - S(T_2, P_2))$. The change of internal energy for the first step is equal to the work plus the heat, which yields $W_1 = U_1 - U_0 - Q_1 = U(T_0, P_1) - U(T_0, P_0) - Q_1$ and for the third step $W_3 = U_3 - U_2 - Q_3 = U(T_2, P_3) - U(T_2, P_2) - Q_3$. For the adiabatic steps $Q_2 = 0$ and $Q_4 = 0$ and $W_2 = U_2 - U_1 = U(T_2, P_2) - U(T_0, P_1)$ and $W_4 = U_0 - U_3 = U(T_0, P_0) - U(T_2, P_3)$. You can finally evaluate $W / Q_3 = -\Sigma W_i / Q_3$.

Instructions for using T-C

In POLY you can use the value of any state variable, e.g. S, as a condition for the equilibrium.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el N
 N  DEFINED
TDB_PSUB: rej p *
 GAS:G  REJECTED
TDB_PSUB: rest p gas
 GAS:G  RESTORED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol
```

```
 POLY version  3.32,  Aug 2001
```

*) You know the state after the first step, which has P_1 = 10 atm. In order to make the properties of that state available, you should compute it.

```
POLY_3: s-c T=293 P=1013250 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
POLY_3: ent-sym var S1=S;
POLY_3: ent-sym var U1=U;
```

*) You don't know P of the state after the second step but you know T=323. The new P can be obtained because S must be unchanged by the adiabatic compression. You should thus replace the condition on P by this condition on S. By just typing S, the current value of S will be used as a condition.

```
POLY_3: s-c T=323 P=none S=
Value /87.34372665/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
```

*) Save the new P value.

```
POLY_3: ent-sym var P2=P;
POLY_3: ent-sym var S2=S;
POLY_3: ent-sym var U2=U;
POLY_3: ent-sym var W2=U2-U1;
```

*) P after the third step is obtained in the same way by considering the fourth step, which is also adiabatic. You should thus start by computing the final state, which is equal to the initial state, and then compute the state after the third step using the S value from the final state.

```
POLY_3: s-c S=none T=293 P=101325
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
POLY_3: ent-sym var S0=S;
POLY_3: ent-sym var U0=U;
POLY_3: ent-sym var Q1=293*(S1-S0);
POLY_3: ent-sym var W1=U1-U0-Q1;
POLY_3: s-c T=323 P=none S=
Value /96.91616004/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var P3=P;
POLY_3: ent-sym var S3=S;
POLY_3: ent-sym var U3=U;
POLY_3: ent-sym var Q3=323*(S3-S2);
POLY_3: ent-sym var W3=U3-U2-Q3;
POLY_3: ent-sym var W4=U0-U3;
POLY_3: ent-sym var Ratio=-(W1+W2+W3+W4)/Q3;
```

*) You may inspect all the values by the command **eval**uate.

```
POLY_3: eval
Name(s):
 S1=85.924577
 U1=-1293.0812
 P2=1013250.
 S2=87.343727
```

```
 U2=-981.04929
 W2=312.03187
 S0=95.49701
 U0=-1293.0812
 Q1=-2804.723
 W1=2804.723
 P3=101325.
 S3=96.91616
 U3=-981.04929
 Q3=3091.896
 W3=-3091.896
 W4=-312.03187
 RATIO=9.2879257E-2
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The efficiency, i.e., the part of the heat, drawn from the warm reservoir, that is recovered as work was evaluated as is 0.09288.

2) This is actually the Carnot cycle and in Section 1.6 it will be shown that the maximum efficiency can be calculated from $(T_{high}-T_{low})/T_{high}=30/(50+273.15)=0.09284$. The difference is caused by approximating 273.15 by 273. The result does not at all depend on the gas being ideal but that simplified your calculations.

1.6. The second law of thermodynamics

When you in problem 1.3B calculated the final temperature when a gas mixture of 2 mole of H_2 and 0.1 mole of O_2 was reacting adiabatically after being ignited, you relied on an algorithm hidden inside the program. Check that the final state was really the state expected from the second law. To make a decisive test you may now use 2 mole of H_2 and 1 mole of O_2 but again under a constant pressure of 1 atm and with an initial temperature of 25^oC. The adiabatic temperature would then be very high and, although all of H_2 and O_2 could in principle form H_2O, some would be dissociated into H_2 and O_2 and one could easily introduce some deviation from the equilibrium constitution at one temperature by first computing the equilibrium at a different temperature.

Hint

1) Equilibria are usually computed by minimizing a function called Gibbs energy. However, it applies only under constant T and P and in the present case T varies during the reaction.

2) For a closed system the second law gives $dS=dQ/T+d_{ip}S$ and for adiabatic conditions $dS=d_{ip}S$. In Problem 1.5 you considered reversible, adiabatic processes, for which $d_{ip}S=0$ and the entropy does not change. The present process is adiabatic but not reversible because the formation of H_2O molecules occurs spontaneously. For each H_2O molecule formed, the temperature will rise and that should continue until $d_{ip}S/dN_{H2O}=0$, i.e., until S reaches a maximum where $dS/dN_{H2O}=0$. The problem is thus to examine if the amount of H_2O, formed when the final temperature is reached, gives a higher S value than any other amount of H_2O would do if evaluated at the temperature reached when that amount has formed. You should test a slightly higher amount and a slightly lower.

3) The SER reference is based on the enthalpy at 298 K and entropy at 0 K (= zero) for the pure elements in their stable states, e.g. H_2 and O_2, and at 25^{o}C and 1 bar. Furthermore, in ideal gases there is no heat of mixing. Thus H=0 for our initial gas mixture because no H_2O has yet formed. The final state under adiabatic conditions and constant pressure can thus be obtained from the condition H=0.

Instructions for using T-C

1) A convenient way to introduce a deviation from the state of equilibrium is to compute the equilibrium at a slightly different temperature. The problem is then to find the temperature where that constitution would give the prescribed H value. You could not use POLY because it cannot handle non-equilibrium states. Instead, go to the tabulation module, tabulate H for a range of temperatures and find the temperature where H has the initial value. At the same temperature you can read the S value and compare with the stored S value.

2) POLY can give the value of a property per mole of units of the components, X_m, and for the whole system, taking the size into account, X. The two quantities will be identical if the system is defined with N=1 because N is often the number of atoms. POLY can also give the properties for other measures of the size, e.g. per mass or volume. A further alternative is to get the properties per mole of the formula unit used in the model as it is stored in the database, X_f. That is sometimes useful when working with both POLY and the tabulation module because the tabulation module always gives properties per mole of formula unit. However, it must be remembered that the content in one formula unit may change if the composition changes, e.g. for an interstitial solution phase, or when a molecular reaction occurs inside the gas phase and results in a change in the number of molecules, i.e. species. Sometimes one would thus have to transform the value of a property from formula unit to atom. The present case gives an example.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el H O
 H                        O  DEFINED
TDB_PSUB: rej p *
 GAS:G                    H2O_L                    H2O2_L
   REJECTED
TDB_PSUB: rest p gas
 GAS:G  RESTORED
TDB_PSUB:
```

*) For the gas one must also decide what species to include.

```
TDB_PSUB: rej sp *
 VA                       H                        O
 H1O1                     H1O2                     H2
 H2O1                     H2O2                     O2
 O3  REJECTED
TDB_PSUB: rest sp H2 O2 H2O1
 H2                       O2                       H2O1
   RESTORED
```

```
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Instead of the usual condition on T you should use the condition on H, which should have the value 0 if the initial temperature is 25°C and the gas only contains the stable species of the elements.

```
POLY_3: s-c P=101325 H=0
```

*) It may be tempting to use N(H2)=2 as a condition but that kind of condition can be used only if H_2 has been chosen as a component. As a default, the monatomic elements are used as components and N(H)=4 would be a proper condition if a different choice is not made. If the initial content is given through selected species, one can use a special command “set-initial amount”, applied to each one of the species. For each one POLY will dissociate the species in the defined components and add the new amount of each component (element) to whatever amount has already been entered. In the present, simple case one could thus give the commands s-i-a N(H2)=2 and s-i-a N(O2)=1.

```
POLY_3: s-i-a N(H2)=2
POLY_3: s-i-a N(O2)=1
POLY_3: c-e
 Normal POLY minimization, not global

 *** ERROR  1614 IN QTHISS
 *** CONDITIONS CAN NOT BE FULLFILLED
 Give the command INFO TROUBLE for help
```

*) The first way to try to overcome this difficulty is to try again.

```
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T y(gas,H2)
 T=3510.6826
 Y(GAS,H2)=0.28710262
```

*) Save the molar entropy of this state of equilibrium, to be compared with later on. Then you should introduce an equilibrium constitution from a slightly different temperature, e.g 3400 K.

```
POLY_3: ent-sym var Smeq=Sm;
POLY_3: s-c T=3400 H=none
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
```

```
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: sh y(gas,H2)
 Y(GAS,H2)=0.25240009
```

*) Go to TAB to evaluate the adiabatic temperature for a gas with this constitution.

```
POLY_3: go tab
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.2524000862/:
```

*) Here you can see that the H_2 content from the state of equilibrium is introduced.

```
H2O1 /.6213998707/:
Pressure /101325/:
Low temperature limit /298.15/:  3400
High temperature limit /2000/:  3800
Step in temperature /100/:  20
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 4.21                           19.51.49


 Phase : GAS                        Pressure :      101325.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 3400.00   5.11140E+01  -1.58737E+04   2.79248E+02  -9.65318E+05
 3420.00   5.11729E+01  -1.48509E+04   2.79548E+02  -9.70906E+05
 3440.00   5.12314E+01  -1.38268E+04   2.79847E+02  -9.76500E+05
 3460.00   5.12896E+01  -1.28016E+04   2.80144E+02  -9.82100E+05
 3480.00   5.13475E+01  -1.17753E+04   2.80440E+02  -9.87706E+05
 3500.00   5.14051E+01  -1.07477E+04   2.80734E+02  -9.93317E+05
 3520.00   5.14624E+01  -9.71905E+03   2.81027E+02  -9.98935E+05
 3540.00   5.15193E+01  -8.68923E+03   2.81319E+02  -1.00456E+06
 3560.00   5.15760E+01  -7.65828E+03   2.81609E+02  -1.01019E+06
 3580.00   5.16323E+01  -6.62620E+03   2.81898E+02  -1.01582E+06
 3600.00   5.16883E+01  -5.59299E+03   2.82186E+02  -1.02146E+06
 3620.00   5.17441E+01  -4.55866E+03   2.82473E+02  -1.02711E+06
 3640.00   5.17995E+01  -3.52323E+03   2.82758E+02  -1.03276E+06
 3660.00   5.18546E+01  -2.48669E+03   2.83042E+02  -1.03842E+06
 3680.00   5.19095E+01  -1.44904E+03   2.83325E+02  -1.04408E+06
 3700.00   5.19640E+01  -4.10309E+02   2.83606E+02  -1.04975E+06
 3720.00   5.20173E+01   6.29503E+02   2.83887E+02  -1.05543E+06
 3740.00   5.20703E+01   1.67038E+03   2.84166E+02  -1.06111E+06
 3760.00   5.21231E+01   2.71231E+03   2.84443E+02  -1.06680E+06
 3780.00   5.21756E+01   3.75530E+03   2.84720E+02  -1.07249E+06
 3800.00   5.22279E+01   4.79934E+03   2.84996E+02  -1.07818E+06
```

*) You are looking for T where H=0. It is closer to 3700 than 3720 K. Try again.

```
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.2524000862/:
H2O1 /.6213998707/:
Pressure /101325/:
Low temperature limit /3400/:  3700
High temperature limit /3800/:  3710
Step in temperature /20/:  1
Output file /SCREEN/:
```

```
                O U T P U T  F R O M  T H E R M O - C A L C
                2007. 4.21                         19.51.49


 Phase : GAS                         Pressure :      101325.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 3700.00   5.19640E+01  -4.10309E+02   2.83606E+02  -1.04975E+06
 3701.00   5.19666E+01  -3.58344E+02   2.83620E+02  -1.05004E+06
 3702.00   5.19693E+01  -3.06376E+02   2.83634E+02  -1.05032E+06
 3703.00   5.19720E+01  -2.54406E+02   2.83648E+02  -1.05060E+06
 3704.00   5.19746E+01  -2.02432E+02   2.83662E+02  -1.05089E+06
 3705.00   5.19773E+01  -1.50456E+02   2.83676E+02  -1.05117E+06
 3706.00   5.19800E+01  -9.84776E+01   2.83690E+02  -1.05146E+06
 3707.00   5.19826E+01  -4.64963E+01   2.83704E+02  -1.05174E+06
 3708.00   5.19853E+01   5.48767E+00   2.83719E+02  -1.05202E+06
 3709.00   5.19880E+01   5.74743E+01   2.83733E+02  -1.05231E+06
 3710.00   5.19906E+01   1.09464E+02   2.83747E+02  -1.05259E+06
```

*) Now you can see that T should be closer to 3708 than 3707 K

```
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.2524000862/:
H2O1 /.6213998707/:
Pressure /101325/:
Low temperature limit /3700/:  3707
High temperature limit /3750/:  3708
Step in temperature /1/:  .1
Output file /SCREEN/:

                O U T P U T  F R O M  T H E R M O - C A L C
                2007. 4.21                         19.51.49


 Phase : GAS                         Pressure :      101325.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 3707.00   5.19826E+01  -4.64963E+01   2.83704E+02  -1.05174E+06
 3707.10   5.19829E+01  -4.12980E+01   2.83706E+02  -1.05177E+06
 3707.20   5.19832E+01  -3.60997E+01   2.83707E+02  -1.05180E+06
 3707.30   5.19834E+01  -3.09014E+01   2.83709E+02  -1.05182E+06
 3707.40   5.19837E+01  -2.57030E+01   2.83710E+02  -1.05185E+06
 3707.50   5.19840E+01  -2.05047E+01   2.83712E+02  -1.05188E+06
 3707.60   5.19842E+01  -1.53062E+01   2.83713E+02  -1.05191E+06
 3707.70   5.19845E+01  -1.01078E+01   2.83714E+02  -1.05194E+06
 3707.80   5.19848E+01  -4.90934E+00   2.83716E+02  -1.05197E+06
 3707.90   5.19850E+01   2.89153E-01   2.83717E+02  -1.05199E+06
 3708.00   5.19853E+01   5.48767E+00   2.83719E+02  -1.05202E+06
```

*) The temperature should be close to 3707.9 K and the entropy at that temperature is about 283.716. However, this is for 1 formula unit. Go to POLY and evaluate the entropy for 1 mole of atoms. First you must evaluate the **n**umber of **a**toms **per f**ormula unit, Naperf. Soon you will see that it is an advantage that it was entered as a function.

```
TAB: b
POLY_3: ent-sym fun Naperf=2*y(gas,H2)+2*y(gas,O2)+3*y(gas,H2O1);
POLY_3: ent-sym var Sm1=2.83717E+02/Naperf;
```

*) Now, examine the effect of the equilibrium constitution from a slightly higher temperature.

```
POLY_3: s-c T=3600
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: sh y(gas,H2)
 Y(GAS,H2)=0.31480022
POLY_3: go tab
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.3148002234/:
H2O1 /.527799665/:
Pressure /101325/:
Low temperature limit /3707/:  3200
High temperature limit /3708/:  3500
Step in temperature /.1/:  20
Output file /SCREEN/:

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 4.21                           19.51.50



 Phase : GAS                        Pressure :      101325.00
 Specie: *

 ******************************************************************************
    T      Cp            H            S            G
   (K)    (Joule/K)     (Joule)      (Joule/K)     (Joule)
 ******************************************************************************
 3200.00   4.86922E+01  -7.12688E+03   2.71444E+02  -8.75749E+05
 3220.00   4.87512E+01  -6.15244E+03   2.71748E+02  -8.81181E+05
 3240.00   4.88099E+01  -5.17683E+03   2.72050E+02  -8.86619E+05
 3260.00   4.88683E+01  -4.20005E+03   2.72350E+02  -8.92063E+05
 3280.00   4.89263E+01  -3.22210E+03   2.72650E+02  -8.97513E+05
 3300.00   4.89840E+01  -2.24300E+03   2.72947E+02  -9.02969E+05
 3320.00   4.90415E+01  -1.26274E+03   2.73243E+02  -9.08430E+05
 3340.00   4.90986E+01  -2.81341E+02   2.73538E+02  -9.13898E+05
 3360.00   4.91554E+01   7.01199E+02   2.73831E+02  -9.19372E+05
 3380.00   4.92119E+01   1.68487E+03   2.74123E+02  -9.24852E+05
 3400.00   4.92681E+01   2.66967E+03   2.74414E+02  -9.30337E+05
 3420.00   4.93241E+01   3.65560E+03   2.74703E+02  -9.35828E+05
 3440.00   4.93797E+01   4.64263E+03   2.74991E+02  -9.41325E+05
 3460.00   4.94350E+01   5.63078E+03   2.75277E+02  -9.46828E+05
 3480.00   4.94901E+01   6.62003E+03   2.75562E+02  -9.52336E+05
 3500.00   4.95448E+01   7.61038E+03   2.75846E+02  -9.57850E+05
```

*) You can see that H=0 for a temperature closer to 3340 than 3360 K.

```
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.3148002234/:
```

```
H2O1 /.527799665/:
Pressure /101325/:
Low temperature limit /3200/:  3345
High temperature limit /3500/:  3350
Step in temperature /20/:  .5
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 4.21                          19.51.50



 Phase : GAS                        Pressure :      101325.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 3345.00   4.91128E+01  -3.58130E+01   2.73611E+02  -9.15266E+05
 3345.50   4.91142E+01  -1.12562E+01   2.73619E+02  -9.15403E+05
 3346.00   4.91157E+01   1.33013E+01   2.73626E+02  -9.15540E+05
 3346.50   4.91171E+01   3.78594E+01   2.73633E+02  -9.15677E+05
 3347.00   4.91185E+01   6.24183E+01   2.73641E+02  -9.15813E+05
 3347.50   4.91199E+01   8.69779E+01   2.73648E+02  -9.15950E+05
 3348.00   4.91213E+01   1.11538E+02   2.73655E+02  -9.16087E+05
 3348.50   4.91228E+01   1.36099E+02   2.73663E+02  -9.16224E+05
 3349.00   4.91242E+01   1.60661E+02   2.73670E+02  -9.16361E+05
 3349.50   4.91256E+01   1.85223E+02   2.73677E+02  -9.16498E+05
```

*) You may estimate the temperature for H=0 to 3345.7 K and there the entropy is 273.622. When now evaluating the molar entropy it is not necessary again to write the expression for Naperf because being a function it will always be evaluated for the current equilibrium.

```
TAB: b
POLY_3: ent-sym var Sm2=2.73622E+02/Naperf;
POLY_3: eval
Name(s):
 SMEQ=108.27891
 NAPERF=2.5277997
 SM1=108.2311
 SM2=108.24513
POLY_3:
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) Both Sm1 and Sm2 are lower than Smeq, supporting the accuracy of the optimisation procedure hidden inside POLY even for a case where T is not constant.

2) There may be numerical difficulties to find the equilibrium constitution if a condition requires that a state variable should be zero. Sometimes you get an error message after the compute-equilibrium command.

3) Numerical difficulties in POLY may be overcome by using better start values for the constitution. POLY can provide you with such values as default values in response to the command set-start-constitution. The quickest way is to try again. It works sometimes.

4) The amount of species can be used as conditions using the command "set-initial-amount". A mistake (e.g. an incorrect value of N(H2O1) can be corrected either by setting the contents of all the components equal to zero, e.g. N(H)=0 and N(O)=0 or by entering the negative of the incorrect value (e.g. “s-i-a N(H2O1)=-2”), and then entering the correct value.

5) You should remember that TAB gives values per mole of formula units.

6) The present problem concerned non-equilibrium states and so did Problem 1.4. In that case it was possible to apply POLY because the deviation from equilibrium could be represented by the fraction of each phase and the internal conditions of each phase were not a sign of non-equilibrium for that phase alone. POLY could thus be applied to each phase separately. In the present case the non-equilibrium concerned the internal constitution of a single phase and POLY could not be applied because it requires that the state of equilibrium be computed before it can yield any thermodynamic information.

1.7. Condition of internal equilibrium

Most programs for the computation of equilibria work by minimizing a function G, called Gibbs energy, under constant T and P. So far you have only learned that equilibrium is found where $d_{ip}S$ has a maximum. Use that criterion in order to check that the state obtained from an available program is actually a state where $d_{ip}S$ has a maximum. Make the test with an Al alloy with 50 mass% Si at 500^{o}C and 1 atm.

Hint

The constitution of the alloy is varied when the program searches for the minimum of G. You should use the program to evaluate the equilibrium and examine how the equilibrium constitution is described. Then you can vary the constitution around the equilibrium constitution and check that $d_{ip}S$ has a maximum there. You know that $d_{ip}S=dS-dQ/T$. From the first law you know $dU=dQ-PdV$ and thus $d_{ip}S=dS-dQ/T=dS-(dU+PdV)/T$. For constant P you get $d_{ip}S=d[S-(U+PV)/T]$. You should thus define a function FUNC=S-(U+PV)/T and test if the equilibrium state obtained from the program actually is a maximum of FUNC when the constitution is varied around the equilibrium constitution. Since you are going to compare situations at the same temperature, 500^{o}C, you could just as well multiply by T and define the function as FUNC=ST-U-PV.

Instructions for using T-C

You are going to consider situations of non-equilibrium and sometimes one has to use the tabulation module for such cases. However, in the present case, as in Problem 1.4, it is possible to use POLY by considering one phase at a time.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pbin
 Current database: TCS Public Binary Alloys TDB v1
```

```
 VA                      /-  DEFINED
 IONIC_LIQ:Y             L12_FCC                 B2_BCC
 BCC_B2  REJECTED
TDB_PBIN: def-el Al Si
 AL                      SI  DEFINED
TDB_PBIN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:  CONSTITUENT
 LIQUID:L    :SI AL:
  > This is metallic liquid solution phase, with C-N species
 FCC_A1      :AL:VA:
 BCC_A2      :AL:VA:
 HCP_A3      :AL:VA:
 DIAMOND_FCC_A4 :SI:
  > This is the Diamond phase for Si-C
 ALCU_THETA  :AL:AL:
 AL3NI2      :AL:AL:VA:
 TIAL        :AL:AL:
 TI3AL       :AL:AL:
TDB_PBIN: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  DIAMOND_FCC_A4          ALCU_THETA
 AL3NI2                  TIAL                    TI3AL
   REJECTED
TDB_PBIN: rest p liq diam
 *** DIAM INPUT IGNORED
 LIQUID:L  RESTORED
TDB_PBIN:
```

*) It is evident that "diam" was not accepted for the Si phase. From the list you can see its full name. Try a longer abbreviation.

```
TDB_PBIN: rest p diam_fcc
 DIAMOND_FCC_A4  RESTORED
TDB_PBIN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions             2
 FUNCTIONS ....

 List of references for assessed data

   90Din 'Alan Dinsdale, SGTE Data for Pure Elements, NPL Report
       DMA(A)195, Rev. August 1990'
   91Din 'A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, Vol.15,
       No.4, pp.317-425, (1991)'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PBIN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=773 P=101325 N=1 x(Si)=.5
POLY_3: c-e
 Using global minimization procedure
 Calculated          138  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
```

```
POLY_3:
```

*) The ordinary thermodynamic quantities for the state of equilibrium are now available but the expression derived in the Hint must be calculated from those available. That is done by entering a symbol for a variable or function with the value of the expression. The value of such a variable will never change unless it is entered again. A function will be evaluated from the current equilibrium every time it is called upon. It cannot be entered again unless it is first deleted.

```
POLY_3: ent-sym fun FUNC=S*T-U-P*V;
POLY_3: ent-sym var FUNCeq=FUNC;
POLY_3: sh FUNCeq
 FUNCEQ=23650.72
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) The option C will give you the composition of phases. Option N will in addition give you the constitution of phases, i.e., the amounts of species for a gas and site-fraction for phases with sublattices.

```
Options /VWCS/:  XN
 Output from POLY-3, equilibrium =     1, label A0  , database: PBIN

 Conditions:
 T=773, P=1.01325E5, N=1, X(SI)=0.5
 DEGREES OF FREEDOM 0

 Temperature  773.00 K ( 499.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  2.75340E+01
 Total Gibbs energy -2.36507E+04,  Enthalpy  1.78647E+04,  Volume  0.00000E+00

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 AL                       5.0000E-01 5.0000E-01 1.5148E-02 -2.6929E+04 SER
 SI                       5.0000E-01 5.0000E-01 4.2013E-02 -2.0372E+04 SER

 LIQUID                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 5.0711E-01, Mass 1.3691E+01         Mole fractions:
 AL  9.85988E-01  SI  1.40122E-02
 Constitution:
 AL  9.85988E-01  SI  1.40122E-02

 DIAMOND_FCC_A4              Status ENTERED     Driving force  0.0000E+00
 Number of moles 4.9289E-01, Mass 1.3843E+01         Mole fractions:
 SI  1.00000E+00  AL  0.00000E+00
 Constitution:
 SI  1.00000E+00
POLY_3:
```

*) The state of equilibrium consists of two phases, liq and Si with the diamond structure. There are several internal variables in this list. However, only one can be chosen as independent. It is not necessary to decide which one if the deviation from equilibrium is simply defined by using the state of equilibrium from different temperatures, e.g. 770 and 776 K.

```
POLY_3: s-c T=770
POLY_3: c-e
 Using global minimization procedure
 Calculated          138  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You will soon need the constitution of this state. Store it as variables.

```
POLY_3: ent-sym var Npliq=Np(liq);
```

```
POLY_3: ent-sym var Npdia=Np(dia);
POLY_3: ent-sym var xSiliq=x(liq,Si);
POLY_3: ent-sym var xSidia=x(dia,Si);
POLY_3:
```

*) At 773 K you should now evaluate the function for the constitution obtained by a computation at 770 K. That can be done with the tabulation module but also with POLY. In both cases one must consider each phase separately and taking into account its amount. This time you can use POLY as in Problem 1.4. See the last Comment to Problem 1.6 for which it was not possible to use POLY. Start by suspending the Si phase and give the liquid the composition characteristic of 770 K.

```
POLY_3: ch-st p dia=sus
POLY_3: s-c T=773 N=Npliq x(Si)=xSiliq
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var FUNCliq=FUNC;
POLY_3:
```

*) Do the same for the Si phase.

```
POLY_3: ch-st p dia=ent 1
POLY_3: ch-st p liq=sus
POLY_3: s-c N=Npdia x(Si)=xSidia
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
 Global minimization failed, error code         2011
 Fewer grid points than components
 . Using normal POLY minimization.
 Testing POLY result by global minimization procedure
 Using already calculated grid
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var FUNClow=FUNC+FUNCliq;
POLY_3:
```

*) Now, go to a constitution characteristic of a higher temperature.

```
POLY_3: s-c T=776 N=1 x(Si)=.5
POLY_3: ch-st p liq=ent 1
POLY_3: c-e
 Using global minimization procedure
 Calculated          138  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Npliq=Np(liq);
POLY_3: ent-sym var Npdia=Np(dia);
POLY_3: ent-sym var xSiliq=x(liq,Si);
POLY_3: ent-sym var xSidia=x(dia,Si);
POLY_3: ch-st p dia=sus
POLY_3: s-c T=773 N=Npliq x(Si)=xSiliq
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var FUNCliq=FUNC;
POLY_3: ch-st p dia=ent 1
POLY_3: ch-st p liq=sus
POLY_3: s-c N=Npdia x(Si)=xSidia
POLY_3: c-e
 Using global minimization procedure
```

```
 Calculated            1  grid points in            0  s
 Global minimization failed, error code        2011
 Fewer grid points than components
 . Using normal POLY minimization.
 Testing POLY result by global minimization procedure
 Using already calculated grid
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var FUNChi=FUNC+FUNCliq;
POLY_3: sh FUNClow FUNCeq FUNChi
 FUNCLOW=23650.698
 FUNCEQ=23650.72
 FUNCHI=23650.698
POLY_3: exit
 CPU time           0  seconds
```

Comments

You find that FUNC is higher for the state of equilibrium than for the non-equilibrium states at the same temperature, which actually means that $d_{ip}S=0$ for that constitution if T, P and the composition are constant. In fact, this function is identical to Gibbs energy, G.

1.8. Driving force

Consider an Fe alloy with 30 mol% Cr at 650°C and 1 atm. It is in a state of homogeneous bcc and is supersaturated with respect to the sigma phase of an approximate 50/50 composition. Evaluate the driving force for the precipitation of sigma, using the basic definition $D = T \cdot d_{ip}S / d\xi$.

Hint

From Problem 1.7 you know that $d_{ip}S=d[S-(U+PV)/T]$. You may thus evaluate the function S-(U+PV)/T for the initial state and for a state with a minute amount, ΔN, of sigma, measured per mole. Take the difference, multiply by T and divide by ΔN because the amount of sigma expressed in mole can be used to represent the progress of the process, ξ.

Instructions for using T-C

The initial homogeneous bcc state is not a state of equilibrium but may be treated as such if sigma is dormant or suspended. The same goes for the bcc matrix after some sigma has precipitated but then one may have to consider that the amount of bcc is less than in the first case. Similarly, the properties of the minute amount of sigma can be treated by POLY if bcc is made dormant.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI:
```

*) This time you should **sw**itch to the database **tern** that has a good description of a few ternary systems, among them Fe-Cr-C.

```
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1
```

```
 VA  DEFINED
TDB_DALMGSI: def-el Fe Cr
 FE                      CR  DEFINED
TDB_DALMGSI:
```

*) You may expect that the database will contain more phases than those you are interested in. You may thus **rej**ect all(*) **p**hases and then **rest**ore the **p**hases **bcc** and **sigma** and finally **get** data.

```
TDB_DALMGSI: rej p *
 LIQUID:L                BCC_A2                  FCC_A1
 HCP_A3                  SIGMA  REJECTED
TDB_DALMGSI: rest p bcc sigma
 BCC_A2                  SIGMA  RESTORED
TDB_DALMGSI: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           25
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PTERN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=923 P=101325 N(Fe)=0.7 N(Cr)=0.3
POLY_3:
```

*) Sigma should not be present in the initial state. You should thus **ch**ange the **st**atus of that **p**hase to **dor**mant before computing the equilibrium, which will be a restricted equilibrium.

```
POLY_3: ch-st p sigma=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Now you like to define the special function discussed in the hint. However, it may be advantageous to multiply by T because $D = T \cdot d_{ip}S \ / d\xi$. You should thus **ent**er a **sym**bol for a **fun**ction you may call **FUNC** and store the present value of ST-U-PV in it.

```
POLY_3: ent-sym fun FUNC=S*T-U-P*V;
POLY_3:
```

*) This function will later be available to you when considering other restricted equilibria. In order to retain the present value you should store it in a variable that may be called FUinit. The value of FUNC for other states you may later store as other variables.

```
POLY_3: ent-sym var FUini=FUNC;
POLY_3:
```

*) It may be interesting to **l**ist the **st**atus of the **p**hases.

```
POLY_3:l-st p
*** STATUS FOR ALL PHASES
 PHASE   STATUS    DRIVING FORCE moles
BCC_A2   ENTERED    0.00000000E+00    1.0000000E+00
```

```
SIGMA         DORMANT   1.58194990E-02
POLY_3:
```

*) For the dormant phase, sigma, POLY gives a quantity called driving force. It may be interesting to save it for later comparisons. POLY recognizes it by the symbol DGm(phase name).

```
POLY_3: ent-sym var Drforc=DGm(sigma);
POLY_3:
```

*) Next, allow 0.001 mole of sigma to precipitate and consider two subsystems. The first one should be the bcc phase and sigma is already dormant but you also need to know the composition of bcc remaining after some sigma has precipitated. You don't know the composition of sigma exactly but it is well known that in the Fe-Cr system it is close to equiatomic. Accepting that composition you know that 0.001 mole of sigma contains N(Fe)=0.0005=N(Cr). Thus, you know the content of bcc, N(Fe)=0.6995 and N(Cr)=0.2995.

```
POLY_3: s-c N(Fe)=.6995 N(Cr)=.2995
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) The value of FUNC in this state may be stored in a variable FUbcc.

```
POLY_3: ent-sym var FUbcc=FUNC;
POLY_3:
```

*) Finally you turn to the sigma phase by entering it and making bcc dormant.

```
POLY_3: ch-st p sigma=ent 0
POLY_3: ch-st p bcc=dor
POLY_3: s-c N(Fe)=.0005 N(Cr)=.0005
POLY_3: c-e
 Using global minimization procedure
 Calculated         137  grid points in             0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) The value of FUNC in this state you may store in a variable FUsig.

```
POLY_3: ent-sym var FUsig=FUNC;
```

*) You may like to inspect the results so far. Just print **eval**uate-functions.

```
POLY_3: eval
Name(s):
 FUNC=37.04877
 FUINIT=37744.672
 DRFORC=0.015819499
 FUBCC=37707.715
 FUSIG=37.04877
POLY_3:
```

*) The three values of FUNC are shown. You like to know how much it has changed by the precipitation of the small quantity of sigma. The change will be Δ FUNC=FUbcc+FUsig-FUinit. It was caused by the change in the amount of sigma, $\Delta\xi$ =0.001 moles of atoms in sigma. The driving force for the precipitation of sigma can thus be approximated by the ratio.

```
POLY_3: ent-sym var Dappr=(FUbcc+FUsig-FUinit)/0.001;
```

*) Now you may compare with the quantity called driving force. Multiply it by RT.

```
POLY_3: ent-sym fun Dtrue=Drforc*8.3145*T;
POLY_3: sh Dappr Dtrue
 DAPPR=91.992213
 DTRUE=121.40347

POLY_3: exit
 CPU time           0  seconds
```

Comments

1) Of course, POLY has an efficient method of evaluating the driving force for formation of a phase that does not take part in an equilibrium but for some reason it is presented as a dimensionless quantity by dividing it with RT.

2) POLY's method will yield the most favourable composition for the new phase, i.e. the composition that has the highest driving force. In the present problem you were asked to derive the value for a sigma phase with a 50/50 composition. If both values, Dtrue and Dappr, were trusted, then the conclusion would be that 50/50, which was used in the present calculations, is not the most favourable composition.

1.9. The combined first and second law

Evaluate the quantity $(\partial S/\partial N)_{U,V}$ from a tabulation module that can list H and S for a series of temperatures. Choose Al_2O_3 at 1 atm.

Hint

1) The combined law can be written as $dS = (1/T)dU + (P/T)dV - (G_m/T)dN + (D/T)d\xi$ and $(\partial S/\partial N)_{U,V} = -G_m/T$. Thermodynamic tables usually give values under a given P and for a series of T and, as a consequence, they usually list values of H and S. It would have been nice to have a table of U and S but if that is not available one could usually approximate U with H for condensed materials. Use that approximation here.

2) Primarily one should expect both S and H to increase if the size, N, is increased because they are both extensive quantities. In order to vary S but keep H constant it seems necessary to allow T to decrease to a level where the tabulated value, which may be given for 1 mole of formula units, has decreased by a factor equal to the one by which N has increased. Denoting the two temperatures by 1 and 2, we get $H=N_1H_1=N_2H_2$ where $N_1=1$. On the other hand, for the entropy we have $\Delta S=N_1S_1-N_2S_2=N_1(S_1-S_2N_2/N_1)=N_1(H_2S_1-H_1S_2)/H_2$. However, $\Delta N=N_2-N_1=N_1(N_2/N_1-1)=N_1(H_1/H_2-1)=N_1(H_1-H_2)/H_2$. We find $\Delta S/\Delta N=(H_2S_1-H_1S_2)/(H_1-H_2)$. From the table one should thus examine the H and S values for two neighbouring temperatures and evaluate $(\partial S/\partial N)_{U,V} \cong \Delta S/\Delta N = (H_2S_1 - H_1S_2)/(H_1 - H_2)$. That should be a reasonably correct value in the middle of the range of T. Make the test at 1000 and 1100 K.

3) Sometimes a table also gives the values of G but all values given in a table of properties are molar quantities. G should thus be identical to G_m as given under (1), provided that N is expressed in the same kind of mole, in the present case mole of formula units. You may thus check your result by comparing with G_m/T at the two temperatures.

Instructions for using T-C

Indeed, the tabulation module in T-C also lists G.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pgeo
 Current database: Saxena Pure Minerals Database v1

 O                       VA  DEFINED
 STEAM                   OXYGEN                  HYDROGEN
   REJECTED
 CARBON_MONOXIDE         CARBON_DIOXIDE          METHANE
   REJECTED
TDB_PGEO:
```

*) This is a database for mineral oxides and the element O is automatically defined.

```
TDB_PGEO: def-el Al O
 AL  DEFINED
TDB_PGEO: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:  CONSTITUENT
 GAS:G       :O2:
  > Gaseous Mixture with C-H-O species, using ideal gas model
 CORUNDUM    :AL2O3:
TDB_PGEO: rej p gas
 GAS:G  REJECTED
TDB_PGEO: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            1
 FUNCTIONS ....
 -OK-
TDB_PGEO: go tab
TAB:
```

*) Print **?** and press return to see what options TAB offers. You like to **tab**ulate a **sub**stance.

```
TAB: tab-sub
Substance (phase): CORUND
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
Pressure /100000/:
Low temperature limit /298.15/:  1000
High temperature limit /2000/:  1500
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 4.21                           20.49.58



 Phase : CORUNDUM                   Pressure :      100000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)       (Joule/K)      (Joule)
 ******************************************************************************
 1000.00   1.23205E+02  -1.59839E+06   1.79265E+02  -1.77765E+06
```

```
 1100.00   1.24863E+02  -1.58598E+06   1.91087E+02  -1.79618E+06
 1200.00   1.26312E+02  -1.57342E+06   2.02015E+02  -1.81584E+06
 1300.00   1.27609E+02  -1.56072E+06   2.12177E+02  -1.83656E+06
 1400.00   1.28793E+02  -1.54790E+06   2.21678E+02  -1.85825E+06
 1500.00   1.29892E+02  -1.53497E+06   2.30602E+02  -1.88087E+06

TAB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You like to evaluate $(H_2S_1\text{-}H_1S_2)/(H_1\text{-}H_2)$ and could start with the denominator. You could take numbers from the rows for 1000 and 1100 K in the Table.

```
POLY_3: ent-sym var deltaH=-1.59839E+06-(-1.58598E+06);
POLY_3: ent-sym var deriv=(-1.58598E+06*1.79265E+02-(-
1.59839E+06*1.91087E+02))/deltaH;
POLY_3: ent-sym var G00T1000=-1.77765E+06/1000;
POLY_3: ent-sym var G00T1100=-1.79618E+06/1100;
POLY_3: eval
Name(s):
 DELTAH=-12410
 DERIV=-1701.9215
 G00T1000=-1777.65
 G00T1100=-1632.8909
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) DERIV is very close to the average of G00 for 1000 and 1100 K. Accepting the approximation of U as H, you have thus confirmed that $(\partial S/\partial N)_{U,V} = -G_m/T$.

2) In the problems for Chapter 3 you will learn that this kind of partial derivative can be evaluated directly from POLY.

3) In this case you did not need to worry about being consistent with the unit, mole or formula, because all the values came from the tabulation module.

1.10. General conditions of equilibrium

At the melting point of a pure element the liquid and solid phases are in equilibrium with each other and each potential should thus have the same value in both phases. It should be possible to evaluate the melting point by comparing tables of properties of the two phases. Do that for molybdenum.

Hint

The combined law expressed in terms of dU shows that G_m is a potential and is conjugate to N, the amount of matter. There would thus be a driving force for the transfer of matter between the two phases if G_m did not have the same value in both phases. One of them would grow at the expense of the other. You should thus examine at what temperature the two phases have the same G_m value.

Instructions for using T-C

1) The tabulation module in T-C lists a function G and for pure elements its value is given per mole of atoms because the formula unit is there one atom. It is then identical to G_m. You should thus make the tabulation module produce tables for both phases in a temperature range and locate the temperature where the G_m values are most similar. Then you can repeat the procedure with a more and more narrow range of T.

2) As an alternative, you may apply the tabulation module to a reaction liquid → solid and check where G for the reaction is zero.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PURE
 Current database: SGTE Unary (Pure Elements) TDB v4

 VA                      /-  DEFINED
TDB_PURE4: def-el Mo
 MO  DEFINED
TDB_PURE4: rej p *
 BCC_A2                  FCC_A1                   HCP_A3
 LIQUID:L  REJECTED
TDB_PURE4: rest p bcc liq
 BCC_A2                  LIQUID:L  RESTORED
TDB_PURE4: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.4), developed by
      SGTE (Scientific Group Thermodata Europe), 1991-2003, and provided by
      TCSAB (Aug. 2003). '

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PURE4: go tab
TAB: tab-sub bcc
SPECIFY SUBLATTICE (0 FOR ALL) /0/:
Pressure /100000/:
Low temperature limit /298.15/:  2500
High temperature limit /2000/:  3500
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 4.22                          14. 5.24
```

```
 Phase : BCC_A2                     Pressure :      100000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 2500.00   4.40733E+01   7.03846E+04   9.08040E+01  -1.56625E+05
 2600.00   4.60960E+01   7.48916E+04   9.25714E+01  -1.65794E+05
 2700.00   4.82956E+01   7.96097E+04   9.43518E+01  -1.75140E+05
 2800.00   5.06817E+01   8.45570E+04   9.61507E+01  -1.84665E+05
 2900.00   5.30122E+01   8.97519E+04   9.79735E+01  -1.94371E+05
 3000.00   5.00294E+01   9.48948E+04   9.97173E+01  -2.04257E+05
 3100.00   4.79631E+01   9.97882E+04   1.01322E+02  -2.14310E+05
 3200.00   4.65146E+01   1.04508E+05   1.02821E+02  -2.24518E+05
 3300.00   4.54879E+01   1.09105E+05   1.04235E+02  -2.34871E+05
 3400.00   4.47524E+01   1.13615E+05   1.05582E+02  -2.45363E+05
 3500.00   4.42204E+01   1.18062E+05   1.06871E+02  -2.55986E+05

TAB: tab-sub liq
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
Pressure /100000/:
Low temperature limit /2500/:  2500
High temperature limit /3500/:  3500
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 4.22                          14. 5.24


 Phase : LIQUID                     Pressure :      100000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 2500.00   3.97203E+01   1.10661E+05   1.04773E+02  -1.51272E+05
 2600.00   4.05881E+01   1.14677E+05   1.06348E+02  -1.61829E+05
 2700.00   4.13880E+01   1.18777E+05   1.07895E+02  -1.72541E+05
 2800.00   4.20897E+01   1.22951E+05   1.09414E+02  -1.83407E+05
 2900.00   4.26383E+01   1.27190E+05   1.10901E+02  -1.94423E+05
 3000.00   4.26383E+01   1.31454E+05   1.12346E+02  -2.05585E+05
 3100.00   4.26383E+01   1.35718E+05   1.13745E+02  -2.16890E+05
 3200.00   4.26383E+01   1.39981E+05   1.15098E+02  -2.28333E+05
 3300.00   4.26383E+01   1.44245E+05   1.16410E+02  -2.39909E+05
 3400.00   4.26383E+01   1.48509E+05   1.17683E+02  -2.51614E+05
 3500.00   4.26383E+01   1.52773E+05   1.18919E+02  -2.63444E+05

TAB:
```

*) If you can read both tables on your screen, you could see that the G values are very similar for 2900 K and the melting point should be very close to 2900 K. If you cannot read the previous table on your screen, then you should print this one and go back and repeat the first tabulation. However, you could actually have asked for the difference between the two tables directly by another option to TAB that concerns reactions.

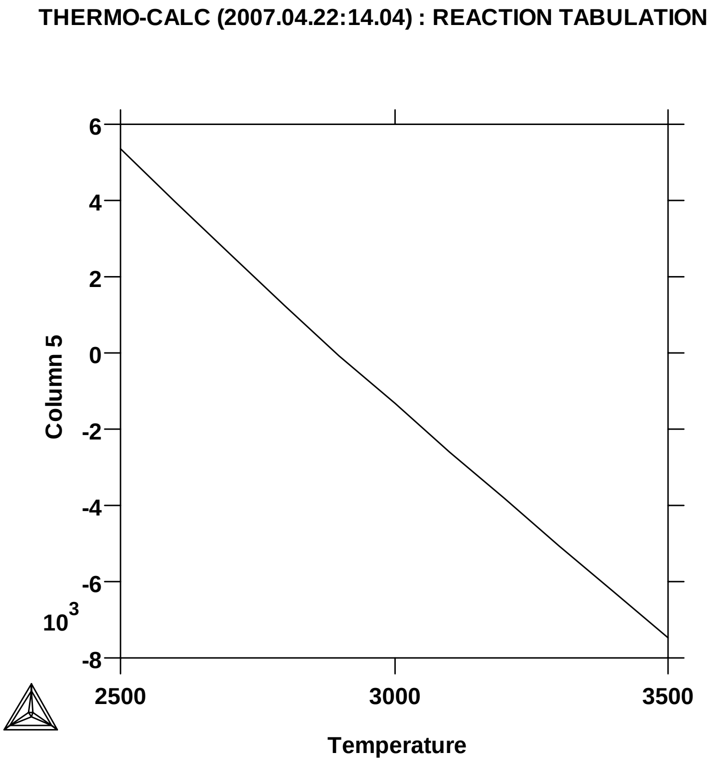
```
TAB: tab-rea MO<bcc>=MO<liq>;
 Use one of these databases
```

```
 DALMGSI =  TCS Demo Al-Mg-Si Alloys TDB v1
 DFECRC  =  TCS Demo Fe-Cr-C Alloys TDB v1
 PURE4   =  SGTE Unary (Pure Elements) TDB v4
 PSUB    =  TCS Public Pure Substances TDB v1
 PBIN    =  TCS Public Binary Alloys TDB v1
 PKP     =  Kaufman Binary Alloys TDB v1
 PCHAT   =  Chatenay-Malabry Binary Alloys TDB v1
 PTERN   =  TCS Public Ternary Alloys TDB v1
 PG35    =  G35 Binary Semi-Conductors TDB v1
 PION    =  TCS Public Ionic Solutions TDB v2
 PAQ2    =  TCS Public Aqueous Solution TDB v2
 PGEO    =  Saxena Pure Minerals Database v1
 PFRIB   =  Fridberg Dilute Fe-Alloys MDB v1
 USER    =  User defined Database

DATABASE NAME /PURE4/:
```

*) With this option you are again asked what database to use. You could thus have gone directly here and never gone to the database module. Now you accept the defaults by pressing return.

```
DATABASE NAME /PURE4/:
 VA                        /-  DEFINED
 REINITIATING GES5 .....
 MO  DEFINED
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.4), developed by
      SGTE (Scientific Group Thermodata Europe), 1991-2003, and provided by
      TCSAB (Aug. 2003). '

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
Pressure /100000/:
Low temperature limit /2500/:  2500
High temperature limit /3500/:  3500
Step in temperature /100/:

Output file /SCREEN/:  file
Grapical output? /Y/:
Plot column? /2/:  5

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 4.22                         14. 5.25


 Reaction:  MO<C>=MO<L>
 MO<BCC_A2>
 MO<LIQUID>

 ******************************************************************************
    T      Delta-Cp      Delta-H       Delta-S       Delta-G
```

```
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 *******************************************************************************
 2500.00  -4.35298E+00   4.02767E+04   1.39694E+01   5.35317E+03
 2600.00  -5.50791E+00   3.97856E+04   1.37769E+01   3.96554E+03
 2700.00  -6.90763E+00   3.91670E+04   1.35436E+01   2.59915E+03
 2800.00  -8.59201E+00   3.83945E+04   1.32629E+01   1.25839E+03
 2900.00  -1.03739E+01   3.74381E+04   1.29274E+01  -5.14896E+01
 3000.00  -7.39112E+00   3.65591E+04   1.26292E+01  -1.32839E+03
 3100.00  -5.32483E+00   3.59295E+04   1.24225E+01  -2.58036E+03
 3200.00  -3.87635E+00   3.54736E+04   1.22777E+01  -3.81495E+03
 3300.00  -2.84960E+00   3.51402E+04   1.21750E+01  -5.03729E+03
 3400.00  -2.11414E+00   3.48940E+04   1.21015E+01  -6.25092E+03
 3500.00  -1.58213E+00   3.47106E+04   1.20483E+01  -7.45826E+03


  POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: exit
TAB: CPU time           0  seconds
```



Comments

1) With this option you get a diagram. From the last Table you can confirm that the melting point is very close to 2900 K and the diagram shows the same result.

2) You could have obtained a more accurate value by interpolation or by simply running the tabulation from 2890 to 2900 K.

3) Here you have learned how to list the properties of a reaction.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

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Chapter 2. Manipulation of thermodynamic quantities

2.1. Evaluation of one characteristic function from another

1) Test if your system can yield the value of a state variable that in principle could be used as a characteristic state function.

2) Test if it can accept values of a set of variables that are the natural set for another characteristic state function.

3) Try to use the value of a site fraction as condition.

Hint

An advanced data bank systems may be composed of modules, one of which stores thermodynamic properties of individual phases as fundamental equations representing some characteristic state function, usually the Gibbs energy, G, as function of its natural set of variables, e.g. T, P and N for G of a pure substance. However, since G is an extensive state function it can be expressed with the molar Gibbs energy, $G = N \cdot G_m$, and it is sufficient to store $G_m(T,P)$ for a pure substance. Multiplying with N is a trivial matter. For a phase with more components, G may be stored as a function of T, P, N_1, N_2 etc. and, in principle, one could then evaluate G for a set of values of these variables, the natural set for G. However, one still prefers to store the information on G as a function of the molar Gibbs energy. For a simple case one would use a function $G_m(T,P,x_1,x_2,...)$ and it is a trivial matter to evaluate N and all the x_i from the set of N_i values. For a phase with sublattices one prefers $G_m(T,P,y_1',y_2'... y_1'',y_2''...)$ where y_i are the site fractions, i.e., mole fractions defined for each sublattice. In a simple case one can also evaluate the site fractions from the set of N_i values. In more complicated cases there is one or more degrees of freedom and there is not only one set of y_i values that satisfies the set of N_i values. The equilibrium set of y_i values is then found by minimizing the Gibbs energy. In the same way, when there is more than one phase and each has no degree of freedom, there is a degree of freedom for the material to be distributed between the phases. The equilibrium composition and amount of each phase are then again found by minimizing the Gibbs energy.

To the customer all this is like a black box and s/he simply trusts that it contains information stored as a fundamental equation based on the Gibbs energy. S/he will thus give the values of T, P, N_1, N_2, etc. when setting the conditions or s/he will use T, P, N and x_1, x_2 etc. Your data bank system will probably accept the mass, B_i, instead of N_i and the mass fraction, w_i, instead of x_i.

The above conditions are all based on the natural set of variables for G and it is an interesting question whether your data bank system can also accept other sets of variables as conditions. Could it even behave as if it were based on another characteristic state function?

Start with a unary system of your choice and set conditions for the state to be studied. Evaluate S after computing equilibrium. Then, enter the S value as a condition and remove one of the initial conditions. First, remove the initial T value, which makes a conjugate pair with S. Compute equilibrium and evaluate T. Then, enter the T value and, instead, remove the initial P value, which is part of another conjugate pair. Compute equilibrium and evaluate P. Again you should obtain its initial value if the equilibrium module can accept a set of conditions that does not contain one variable from each pair of conjugate variables.

Instructions for using T-C

Choose carbon from the DFECRC database and reject all phases but graphite. Later, go back to the database module, add Fe and reject all phases but bcc and fcc.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el C
 C  DEFINED
TDB_DFECRC: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L    :C:
  > This is metallic liquid solution phase, with C species
 GRAPHITE    :C:
TDB_DFECRC: rej p liq
 LIQUID:L  REJECTED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          11
 FUNCTIONS ....
```

```
 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Set conditions for the natural set of variables for G.

```
POLY_3: s-c P=101325 T=1100 N=1
POLY_3: sh S
 S=0
POLY_3:
```

*) You can get no reliable information without first computing equilibrium.

```
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in           0  s
POLY_3: sh S
 S=26.528829
POLY_3:
```

*) For H the natural set of variables is S, P, N. Use this set by entering the S value.

```
POLY_3: s-c S
Value /26.5288292/:
POLY_3: c-e

 *** ERROR  2003 IN QMJBSV
 *** Degrees of freedom not zero
POLY_3:
```

*) You must delete an old condition when you have introduced a new one. Inspect the conditions and decide which one to delete.

```
POLY_3: l-c
 P=1.01325E5, T=1100, N=1, S=26.5288
 DEGREES OF FREEDOM -1
POLY_3: s-c T=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=1100.
POLY_3:
```

*) Fine! It is thus possible to use S, P and N as conditions. It is as if POLY were using a fundamental equation based on H as the characteristic state function. Now try to delete P instead.

```
POLY_3: s-c P=none T=
Value /1100/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in           0  s
   7 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh P
 P=101347.89
```

```
POLY_3:
```

*) This is not quite exact but good enough considering numerical difficulties. This time the variables were T, S and N. It is thus demonstrated that POLY does not even require conditions for one variable from each pair of conjugate variables.

Now you should turn to the bcc and fcc phases in the Fe-C system in order to test if one could exchange w(C) for one of the site fractions.

```
POLY_3: b
TDB_DFECRC: def-el Fe
 FE  DEFINED
TDB_DFECRC: rej p *
 FCC_A1                  BCC_A2                  HCP_A3
 CEMENTITE               M7C3                    M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p bcc fcc
 BCC_A2                  FCC_A1  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           37
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: b

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=1100 P=101325 N=1 w(C)=.002
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) This time you may like to inspect the constitution of the phases, not just their compositions.

```
Options /VWCS/:  N
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1100, P=1.01325E5, N=1, W(C)=2E-3
 DEGREES OF FREEDOM 0

 Temperature 1100.00 K ( 826.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.54423E+01
 Total Gibbs energy -4.90638E+04,  Enthalpy  3.17008E+04,  Volume  7.24065E-06
```

```
 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        9.2319E-03 2.0000E-03 3.5177E-02 -3.0615E+04 SER
 FE                       9.9077E-01 9.9800E-01 4.5925E-03 -4.9236E+04 SER

 BCC_A2                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.4953E-01, Mass 8.3481E+00         Mass fractions:
 FE  9.99907E-01  C   9.33735E-05
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  3.0000E+00
 VA  9.99855E-01  C   1.44732E-04

 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.5047E-01, Mass 4.7094E+01         Mass fractions:
 FE  9.97662E-01  C   2.33798E-03
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  1.0000E+00
 VA  9.89104E-01  C   1.08963E-02
POLY_3:
```

*) Using the N option, the whole constitution is now presented, i.e., the fractions of the phases and the site fractions on their sublattices. Much more information is available but you have to ask for it by the command **sh**ow. Try some.

```
POLY_3: sh S Sm(bcc) Sm(fcc)
 S=73.422333
 SM(BCC_A2)=71.973154
 SM(FCC_A1)=73.677135
POLY_3:
```

*) Try to use the site fraction of C in fcc as a condition and delete another, related condition.

```
POLY_3: s-c w(C)=none y(fcc,C#2)=
Value /.01089625966/:
POLY_3: c-e
 Normal POLY minimization, not global
 Convergence problems, increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS

 *** ERROR  1611 IN QEQUIL
 *** TOO MANY ITERATIONS
 Give the command INFO TROUBLE for help
POLY_3:
```

*) Maybe your set of conditions was not logical although you tried to replace a condition with a related one. Inspect the set.

```
POLY_3: l-c
 T=1100, P=1.01325E5, N=1, Y(FCC_A1,C#2)=1.08963E-2
 DEGREES OF FREEDOM 0
POLY_3:
```

*) Now you may realize that the equilibrium constitution of fcc is directly related to the temperature of the equilibrium. You could not prescribe values of both at the same time. Delete the T condition and instead take back the alloy composition.

```
POLY_3: s-c w(C)=.002 T=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in           0  s
   8 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
```

```
 T=1980.7016
POLY_3:
```

*) This is an unexpected result. You should inspect this equilibrium in detail.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWNS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, N=1, W(C)=2E-3, Y(FCC_A1,C#2)=1.08963E-2
 DEGREES OF FREEDOM 0

 Temperature 1980.70 K (1707.55 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.54423E+01
 Total Gibbs energy -1.24190E+05,  Enthalpy  6.66737E+04,  Volume  7.74613E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        9.2319E-03 2.0000E-03 1.4534E-03 -1.0760E+05 SER
 FE                       9.9077E-01 9.9800E-01 5.2589E-04 -1.2434E+05 SER

 BCC_A2                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.5442E+01         Mass fractions:
 FE  9.98000E-01  C   2.00000E-03
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  3.0000E+00
 VA  9.96894E-01  C   3.10598E-03
```

*) This equilibrium does not seem to concern the bcc/fcc equilibrium you were interested in. It is a one-phase state of bcc. It is evident that the condition on w(C) at the same time as y(fcc,C#2) does not really add anything. If you are really interested in knowing the temperature where y(fcc,C#2) has a certain value when bcc is in equilibrium with fcc, then you should fix the two phases and remove the condition on w(C) and another one, which should be N=1 unless you like to let P differ from 1 atm.

```
POLY_3: ch-st p bcc fcc=fix 1
POLY_3: s-c N=none w(C)=none
POLY_3: l-c
 P=1.01325E5, Y(FCC_A1,C#2)=1.08963E-2
 FIXED PHASES
 BCC_A2=1  FCC_A1=1
 DEGREES OF FREEDOM 0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in            0  s
   9 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=1793.0299
POLY_3:
```

*) This is a correct value, which could be confirmed by **l**isting the **e**quilibrium, but it may be unexpected. Actually, the bcc/fcc equilibrium at low temperatures disappears above 1184 K but it returns at much higher temperatures. In order to find the point you are interested in, you could **s**et a lower temperature as a **s**tart **v**alue. Instead of the value T=1980.7 K, which was automatically taken as a start value from the current state of equilibrium.

```
POLY_3: s-s-v T
Value: /1793.029875/:  1000
POLY_3: c-e
 Normal POLY minimization, not global
```

```
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in           0  s
  18 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=1100.
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) From the stored fundamental equation one can compute an equilibrium after defining the conditions using its natural set of variables. All characteristic state functions can then be evaluated from the state of equilibrium but also many other properties.

2) It is also possible to define the conditions using the natural set of variables for another characteristic state function. In fact, the conditions can be defined in various ways with a considerable flexibility. It is not even necessary to use one state variable from each pair of conjugate variables when defining the conditions but any set of conditions may not be appropriate.

3) The requirement that a phase must take part in the equilibrium plays the role of a condition.

4) It should be mentioned that there is actually a second solution to the final set of conditions for the Fe-C system. By **s**etting the **s**tart **v**alue T=1900 you should get the value T=1793.0299. That is another correct solution. The bcc/fcc equilibrium disappears over 911^{o}C but it returns at very much higher temperatures.

5) By properly adjusting a start value you can help POLY to find the equilibrium you are interested in.

2.2. Internal variables at equilibrium

At equilibrium D=0 and the driving force, D, can be evaluated in different ways that all should give the same result. For instance, $D = -(\partial G / \partial \xi)_{T,P} = -(\partial F / \partial \xi)_{T,V}$ where ξ is an internal variable. Demonstrate this by a numerical calculation on an Fe-C alloy with 1 mol% C at 1 bar and 1050 K.

Hint

1) First you must choose a system with an internal variable. For systems with more than one phase, the fraction of a phase is such a variable. For one-phase systems with a variable degree of order, one can choose some site fraction as the internal variable. For a gas, there may be a variable constitution due to reactions between molecules. For the present demonstration it may be convenient to choose a binary system with two phases, which can both dissolve the two components.

2) With a binary bcc+fcc alloy you may establish two slightly different constitutions by computing equilibrium at two temperatures, 1 K apart. Define this difference as $\Delta\xi = Nfcc2 - Nfcc1$ where Nfcc is the amount of the fcc phase. Examine their properties at a quite different temperature where they are far from equilibrium. In order not to change their constitutions at that

temperature you must evaluate the bcc and fcc phases separately and for extensive properties you can then add the contributions from the phases.

3) For the first constitution you evaluate V_1, G_1 and F_1. For the second one you evaluate G_2 and approximate the driving force according to G as DFG=-(G_2-G_1)/(Nfcc2-Nfcc1) for the values of T and P used as conditions. To get the corresponding quantity for the Helmholtz energy, F, you must compare two states of the same T and V, not P. When you first evaluate V_2 for the second constitution you find that it differs from V_1 because of the difference in constitution, mainly in the amounts of the phases. You must find a new pressure that makes the volume of the second constitution equal to V_1. Just try a different P and evaluate its effect on V_2. Then you may find the proper P by extrapolation.

Instructions for using T-C

Remember that the Helmholtz energy has the symbol A instead of F in T-C. Choose an Fe-C alloy with 1 mol% C at 1 atm. Establish the equilibrium constitution at 999 and 1000 K and study the properties at 1050 K.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE                M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc
 FCC_A1                   BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           37
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R
```

```
 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) For case 1, equilibrate the alloy at 1000 K.

```
POLY_3: s-c P=1E5 T=1000 N=1 x(C)=.01
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution      0 s, total time     0  s
POLY_3:
```

*) Store information on the constitution.

```
POLY_3: ent-sym var Nbcc1=NP(bcc);
POLY_3: ent-sym var Nfcc1=NP(fcc);
POLY_3: ent-sym var xCbcc1=x(bcc,C);
POLY_3: ent-sym var xCfcc1=x(fcc,C);
POLY_3:
```

*) Increase T to 1050 K and consider each phase as its own system. Start with the fcc constituent by excluding bcc.

```
POLY_3: ch-st p bcc=dor
POLY_3: s-c T=1050 x(C)=xCfcc1 N=Nfcc1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution      0 s, total time     0  s
POLY_3:
```

*) It is now possible to evaluate various properties of the fcc phase with the composition from 1000 K. Remember that T-C uses A as the symbol for Helmholtz energy, which we denote by F.

```
POLY_3: ent-sym var Vfcc1=V;
POLY_3: ent-sym var Gfcc1=G;
POLY_3: ent-sym var Ffcc1=A;
POLY_3:
```

*) Next, study a system composed of the bcc constituent.

```
POLY_3: ch-st p fcc=dor
POLY_3: ch-st p bcc=ent 1
POLY_3: s-c x(C)=xCbcc1 N=Nbcc1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution      0 s, total time     0  s
POLY_3:
```

*) When you now evaluate the properties of bcc you can also evaluate the values for the whole alloy in case 1.

```
POLY_3: ent-sym var Vbcc1=V;
POLY_3: ent-sym var V1=Vfcc1+Vbcc1;
POLY_3: ent-sym var G1=Gfcc1+G;
POLY_3: ent-sym var F1=Ffcc1+A;
POLY_3:
```

*) This will be the initial state and you should evaluate the changes of G and F when the constitution is changed to the one characteristic of 999 K, i.e. case 2. Compute that state by entering fcc. Bcc is already entered.

```
POLY_3: ch-st p fcc=ent 1
```

```
POLY_3: s-c T=999 x(C)=.01 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Store the new constitution and evaluate the difference in amount of fcc.

```
POLY_3: ent-sym var Nbcc2=NP(bcc);
POLY_3: ent-sym var Nfcc2=NP(fcc);
POLY_3: ent-sym var deltaN=Nfcc2-Nfcc1;
POLY_3: ent-sym var xCbcc2=x(bcc,C);
POLY_3: ent-sym var xCfcc2=x(fcc,C);
POLY_3:
```

*) Take each one of the phases to 1050 K. Start with the fcc constituent by making bcc dormant.

```
POLY_3: ch-st p bcc=dor
POLY_3: s-c T=1050 x(C)=xCfcc2 N=Nfcc2
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Vfcc2=V;
POLY_3: ent-sym var Gfcc2=G;
```

*) And now the bcc constituent.

```
POLY_3: ch-st p fcc=dor
POLY_3: ch-st p bcc=ent 1
POLY_3: s-c x(C)=xCbcc2 N=Nbcc2
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Vbcc2=V;
POLY_3: ent-sym var V2=Vfcc2+Vbcc2;
POLY_3: ent-sym var G2=Gfcc2+G;
POLY_3:
```

*) You may now evaluate the driving force according to G and compare the volumes.

```
POLY_3: ent-sym var DFG=(G1-G2)/deltaN;
POLY_3: sh deltaN Vbcc1 Vbcc2 Vfcc1 Vfcc2 V1 V2
 DELTAN=-2.6550306E-3
 Vbcc1=5.3286538E-6
 Vbcc2=5.3480902E-6
 Vfcc1=1.9439908E-6
 Vfcc2=1.9248294E-6
 V1=7.2726447E-6
 V2=7.2729196E-6
POLY_3:
```

*) The volume has increased from V1 to V2 mainly because the amount of fcc, the denser phase, has decreased by deltaN = -0.0026550306. In order to find the change of the Helmholtz energy you need the pressure that would make the volume for case 2 equal to V_1. As a first attempt you may increase the pressure by 50 atm. Start with the bcc constituent that is already entered.

```
POLY_3: s-c P=51E5
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
```

```
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Vbcc3=V;
POLY_3:
```

*) Continue with the fcc constituent.

```
POLY_3: ch-st p bcc=dor
POLY_3: ch-st p fcc=ent 1
POLY_3: s-c x(C)=xCfcc2 N=Nfcc2
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Vfcc3=V;
POLY_3: ent-sym var V3=Vbcc3+Vfcc3;
POLY_3: sh V1 V3
 V1=7.2726447E-6
 V3=7.2726966E-6
POLY_3:
```

*) You were quite fortunate. Most of the difference has disappeared. However, you should still make an adjustment by extrapolation.

```
POLY_3: ent-sym var P4=1E5+50E5*(V2-V1)/(V2-V3);
POLY_3: sh P4
 P4=6264323.6
POLY_3:
```

*) Try to use this P value. Since you hope that P4 will be good enough, you might evaluate F at the same time that you examine if the volume is kept constant at P4. Remember that fcc is already the entered constituent.

```
POLY_3: s-c P=P4
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Ffcc4=A;
POLY_3: ent-sym var Vfcc4=V;
POLY_3:
```

*) Continue with the bcc constituent.

```
POLY_3: ch-st p fcc=dor
POLY_3: ch-st p bcc=ent 1
POLY_3: s-c x(C)=xCbcc2 N=Nbcc2
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Vbcc4=V;
POLY_3: ent-sym var V4=Vfcc4+Vbcc4;
POLY_3: sh V1 V4
 V1=7.2726447E-6
 V4=7.2726447E-6
POLY_3:
```

*) V has thus been kept constant and the value of P4 can be accepted. Complete the evaluation of the Helmholtz energy.

```
POLY_3: ent-sym var F4=Ffcc4+A;
POLY_3: ent-sym var DFF=(F1-F4)/deltaN;
POLY_3: sh DFG DFF
 DFG=151.90466
 DFF=152.22376
POLY_3:
```

*) The two methods of evaluating the driving force have not given the same result. The theoretical relation has not been confirmed. The explanation is that Helmholtz energy is suited only for homogeneous systems. If the new pressure is adjusted to keep the volume of the whole system constant, it does not mean that the volume of each phase is kept constant. Inspect the changes of their individual volumes.

```
POLY_3: sh Vbcc1 Vbcc4 Vfcc1 Vfcc4
 Vbcc1=5.3286538E-6
 Vbcc4=5.3478908E-6
 Vfcc1=1.9439909E-6
 Vfcc4=1.9247539E-6
POLY_3:
```

*) It is evident that the volumes of the phases have not been kept constant and it was not justified to try to evaluate the change in the Helmholtz energy by comparing the states. That would require that one applies different pressures to the two phases, which is not physically possible in reality. In fact, the fcc phase has decreased its amount by dN=-2.6550306E-6 and thus its volume. Of course, there is no physical justification to try to compensate for that effect by decreasing the pressure. It would even have to be strongly negative in order to expand the fcc phase back to Vfcc1. Helmholtz energy can thus be used for homogeneous systems only.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The positive value of DFG means that there is a driving force for the growth of the fcc phase at 1050 K if the system has first been equilibrated at 1000 K.

2) Of course, T-C was not constructed to produce this kind of test of a theoretical relation. It is encouraging that it is nevertheless possible to make this kind of test, although a little awkward.

3) This exercise has demonstrated that the Helmholtz energy is not suited for systems with more than one phase.

2.4A. Experimental conditions

Evaluate C_V and C_P for pure Cr at 500^{o}C and 1 atm.

Hint

The heat capacities can be obtained from the second derivatives of F and G with respect to T but can also be obtained from first derivatives, e.g. $C_P = -TG_{TT} = (\partial H/\partial T)_P = T(\partial S/\partial T)_P$ and $C_V = (\partial U/\partial T)_V = T(\partial S/\partial T)_V$.

Instructions for using T-C

1) POLY can give first-order partial derivatives of state functions directly by using the period sign "." as an operator but one must be careful and consider what variable is kept constant.

2) This kind of operation works only if the set of independent variables is composed of the variable in the denominator and those in the subscript. You should thus use them when defining

the conditions for the state of equilibrium. That is how a state variable becomes independent in POLY.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw
 Use one of these databases

 DALMGSI =  TCS Demo Al-Mg-Si Alloys TDB v1
 DFECRC  =  TCS Demo Fe-Cr-C Alloys TDB v1
 PURE4   =  SGTE Unary (Pure Elements) TDB v4
 PSUB    =  TCS Public Pure Substances TDB v1
 PBIN    =  TCS Public Binary Alloys TDB v1
 PKP     =  Kaufman Binary Alloys TDB v1
 PCHAT   =  Chatenay-Malabry Binary Alloys TDB v1
 PTERN   =  TCS Public Ternary Alloys TDB v1
 PG35    =  G35 Binary Semi-Conductors TDB v1
 PION    =  TCS Public Ionic Solutions TDB v2
 PAQ2    =  TCS Public Aqueous Solution TDB v2
 PGEO    =  Saxena Pure Minerals Database v1
 PFRIB   =  Fridberg Dilute Fe-Alloys MDB v1
 USER    =  User defined Database

DATABASE NAME /DALMGSI/:  PTERN
 Current database: TCS Public Ternary Alloys TDB v1

 VA  DEFINED
TDB_PTERN: def-el Cr
 CR  DEFINED
TDB_PTERN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L    :CR:
  > This is metallic liquid solution phase, with C species
 BCC_A2      :CR:VA:
 FCC_A1      :CR:VA:
TDB_PTERN: rej p *
 LIQUID:L                BCC_A2                  FCC_A1
   REJECTED
TDB_PTERN: rest p bcc
 BCC_A2  RESTORED
TDB_PTERN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           11
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R
```

```
 -OK-
TDB_PTERN: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) For C_P the set of independent variables is T, P and N although N is usually omitted when writing the partial derivative of a pure element.

```
POLY_3: s-c P=101325 T=773 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var CP=H.T;
POLY_3:
```

*) For C_V the set of independent variables is T, V and N.

```
POLY_3: s-c P=none V=
Value /7.323224298E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var CV=U.T;
POLY_3: eval
Name(s):
 CP=28.810421
 CV=27.74913
POLY_3: exit
 CPU time            0  seconds
```

Comments

A partial derivative of a state function with respect to one variable while one or several other variables are kept constant can be evaluated only if all those variables make a set of independent variables. In POLY it is necessary to use that set when defining the conditions for the state of equilibrium and that is when the constant values are fixed.

2.4B. Experimental conditions

One mole of N_2 gas at 400^{o}C and 1 atm is compressed adiabatically and reversibly to 100 kbar. Evaluate the new temperature.

Hint

$\Delta S=Q/T+\Delta_{ip}S=0+0=0$. The final state should thus have the same entropy as the initial state. You should evaluate S for the initial state and then find the temperature where S has the same value at the higher P.

Instructions for using T-C

In order to evaluate S of the initial state from POLY, you must first compute its equilibrium. Then you should remove the condition on T and instead introduce the S value.

Prompts and commands

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el N
 N  DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 GAS:G       :N N2 N3:
  > Gaseous Mixture, using the ideal gas model
TDB_PSUB:
```

*) For pure N this database only had the gas phase. However, there are several species and for a realistic calculation one should include them. For the present exercise you may reject them.

```
TDB_PSUB: rej sp *
 VA                      N                        N2
 N3  REJECTED
TDB_PSUB: rest sp N2
 N2  RESTORED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Set the initial conditions. Remember that the size of the system must be defined in some way. N=1 is the simplest.

```
POLY_3: s-c P=101325 T=673 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3:
```

*) Set S as a condition instead of T. The value of S should be the same as for the equilibrium you have just computed. You should also set a new P value as condition. For a pure element a new value may be processed immediately and change the state. In the present case it may thus change the current value of S and in order to use the old S value as condition it must be fetched before the new P value is introduced.

```
POLY_3: s-c T=none S=
```

```
Value /107.77277/:
POLY_3: s-c P=1E10
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=9575.2555
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The resulting temperature is extremely high and one may doubt that one could extrapolate the information in the database so far. Of course, from a practical point of view it may be quite impossible to carry out this kind of experiment.

2) Remember the difference between irreversibly adiabatic (e.g. Problem 1.3B and 1.6) and reversibly adiabatic. A process is reversible if there is no internal reaction, $d\xi = 0$, as in the present case, or a very slow internal reaction that keeps pace with the change caused by a change of external conditions that results in D being extremely small.

2.4C. Experimental conditions

One mole of diamond at 400^{o}C and 1 atm is compressed adiabatically and reversibly to 100 kbar. Evaluate the work.

Hint

ΔS=Q/T+Δ_{ip}S=0+0=0. The final state should thus have the same entropy as the initial state. The work is equal to the change of U since there is no exchange of heat.

Instructions for using T-C

When changing a condition from one variable as independent to a second one, e.g. from T to S, you can use the value of the second one from the current state of equilibrium by just typing its symbol and the current value will be offered as default. However, if one likes to change the value of a third condition that should be made afterwards. For a system with only one element, it would otherwise affect the value offered as default to the second variable.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pgeo
 Current database: Saxena Pure Minerals Database v1

 O                        VA  DEFINED
 STEAM                    OXYGEN                   HYDROGEN
```

```
   REJECTED
 CARBON_MONOXIDE         CARBON_DIOXIDE          METHANE
   REJECTED
TDB_PGEO:
```

*) Since O is automatically defined as an element in this database, you should reject it for the present application.

```
TDB_PGEO: rej-el O
 O  REJECTED
TDB_PGEO: def-el C
 C  DEFINED
TDB_PGEO: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 DIAMOND     :C1:
 GRAPHITE    :C1:
TDB_PGEO: rej p gra
 GRAPHITE  REJECTED
TDB_PGEO: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            1
 FUNCTIONS ....
 -OK-
TDB_PGEO: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=673 P=101325 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3:
```

*) To keep track of what happens later, it may be wise to show some properties of this equilibrium.

```
POLY_3: sh S U
 S=12.08605011
 U=6670.2495
POLY_3: ent-sym var U0=U;
POLY_3: s-c T=none S=
Value /12.08605011/:
POLY_3:
```

*) Now you can change P.

```
POLY_3: s-c P=1E10
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T U
 T=686.92129
 U=7029.4067
POLY_3: ent-sym var W1=U-U0;
POLY_3: sh W1
 W1=359.15716
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The work of compression will be 360 J/mol, which is not very much, the reason being that diamond has a very low compressibility.

2) For a unary system the state will be changed in POLY as soon as a new P value is introduced as a condition.

2.6A. Use of various derivatives

Evaluate α and κ_T for an Fe alloy with 0.5 mass% C at 850 and 750^{o}C under 1 atm.

Hint

1) Expressed with first-order derivatives we find $\alpha = (\partial V / \partial T)_P / V$ and $\kappa_T = -(\partial V / \partial P)_T / V$.

2) At 850^{o}C the alloy is inside the fcc one-phase field. At 750^{o}C it is inside the bcc+fcc two-phase field. There you may evaluate the properties for the whole as well as for each phase.

Instructions for using T-C

1) You can make the evaluation for the whole system at T=1023 without considering that it is a two-phase state of equilibrium.

2) These cases have the same independent variables, P and T, in addition to the usual N.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                     C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L               FCC_A1                  BCC_A2
 HCP_A3                 CEMENTITE               M7C3
 M23C6                  GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc
 FCC_A1                 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           37
 FUNCTIONS ....
```

```
 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1123 N=1 w(C)=.005
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Now, use the operator “.” for evaluating partial derivatives.

```
POLY_3: ent-sym var alpha1=V.T/V;
POLY_3: ent-sym var kappa1=-V.P/V;
POLY_3:
```

*) All the symbols will be evaluated at the end. The discussion is postponed until then. Now, go to the lower temperature.

```
POLY_3: s-c T=1023
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) For a reason soon to become evident, it will be interesting to inspect the constitution of this state of equilibrium.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1023, N=1, W(C)=5E-3
 DEGREES OF FREEDOM 0

 Temperature 1023.00 K ( 749.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.48462E+01
 Total Gibbs energy -4.31762E+04,  Enthalpy  2.92590E+04,  Volume  7.17030E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        2.2832E-02 5.0000E-03 1.7010E-01 -1.5067E+04 SER
 FE                       9.7717E-01 9.9500E-01 5.7801E-03 -4.3833E+04 SER

 BCC_A2                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.7391E-01, Mass 9.7063E+00         Mass fractions:
 FE  9.99833E-01  C   1.67230E-04
```

```
 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.2609E-01, Mass 4.5140E+01         Mass fractions:
 FE  9.93961E-01  C   6.03918E-03
POLY_3:
```

*) This is a two-phase state, which is important for the interpretation of the result.

```
POLY_3: ent-sym var alpha2=V.T/V;
POLY_3:
```

*) You will soon see that this quantity is negative, which is unusual for the thermal expansivity. You should thus examine the values for the individual phases.

```
POLY_3: ent-sym var alp2fcc=Vm(fcc).T/Vm(fcc);
POLY_3: ent-sym var alp2bcc=Vm(bcc).T/Vm(bcc);
POLY_3: ent-sym var kappa2=-V.P/V;
POLY_3: ent-sym var kap2fcc=-Vm(fcc).P/Vm(fcc);
POLY_3: ent-sym var kap2bcc=-Vm(bcc).P/Vm(bcc);
POLY_3: eval
Name(s):
 ALPHA1=7.5819633E-5
 KAPPA1=6.3682434E-12
 ALPHA2=-5.828903E-5
 ALP2FCC=1.7330685E-4
 ALP2BCC=5.1466861E-5
 KAPPA2=1.0846535E-11
 KAP2FCC=2.9966318E-12
 KAP2BCC=5.936857E-12
POLY_3: exit
 CPU time            0  seconds
```

Comments

The numbers show that both bcc and fcc have positive alpha values but the two-phase mixture has a negative value (ALPHA2). The explanation is that the amount of bcc decreases at higher temperatures and bcc has the largest molar volume. At 850^{o}C the alloy fell inside the fcc one-phase field.

2.6B. Various derivatives

Test numerically the relation $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ on two Cr alloys with 5 or 10 mass% Fe, both kept at 800^o C and 1 atm.

Hint

Both partial derivatives are based on the same two independent variables, T and V, but the experimental conditions are given through T and P. You should thus compute equilibrium and then introduce the computed V value as a condition for a new computation of equilibrium. Both partial derivatives can then be evaluated from the new description of the equilibrium based on the correct set of independent variables.

Instructions for using T-C

Use the special operator "." for the evaluation of partial derivatives.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Cr Fe
 CR                       FE  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                  BCC_A2
 HCP_A3                   SIGMA  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           22
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1073 w(Fe)=.05 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Change to the wanted set of independent variables.

```
POLY_3: s-c P=none V=
Value /7.395233554E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Now you could define the wanted quantities. If you do it as functions you could repeat the evaluation for the next alloy much quicker.

```
POLY_3: ent-sym fun LHS=U.V;
```

```
POLY_3: ent-sym fun RHS=T*P.T-P;
POLY_3: eval
Name(s):

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 LHS=7.6662711E9
 RHS=7.6662711E9
POLY_3:
```

*) The two value are equal and the relation was confirmed. Set conditions for the other alloy and repeat the evaluation. Remember to restore the pressure for the first computation of equilibrium.

```
POLY_3: s-c w(Fe)=.1
POLY_3: s-c V=none P=101325
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Change to the wanted set of independent variables.

```
POLY_3: s-c P=none V=
Value /7.3921799E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Since you used functions you can evaluate the wanted quantities directly.

```
POLY_3: eval
Name(s):

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 LHS=7.7502092E9
 RHS=7.7502092E9
POLY_3:
```

*) Again the relation was confirmed. This time the value was somewhat different because the alloy content was different.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

When evaluating a partial derivative you must be careful and use the correct set of independent variables, which is done when using them as conditions.

2.7. Comparison between C_V and C_P

Evaluate C_V and C_P for Cr at 500 K and 1 bar.

Hint

C_P is usually measured at 1 atm and can be evaluated from a database as $(\partial H / \partial T)_{P,N}$. For clarity it may be denoted $C_P(T,P_0)$ where P_0 represents 1 atm. For C_V the situation is not quite so clear. Experimentally, one prefers to work under constant pressure and C_V is usually obtained by calculation from other properties, mainly but not only from C_P. C_V may be evaluated from a database as $(\partial U / \partial T)_{V,N}$ and it is evident that one must allow P to change in order to keep V constant when making the small variation of T. However, one could still be interested in the values of C_V when starting from 1 atm at different temperatures. For each temperature one should then first compute the equilibrium at 1 atm as condition. Then one could instead introduce the current volume as condition and compute equilibrium, which should result in the same state of equilibrium. Then one could evaluate $(\partial U / \partial T)_{V,N}$. That quantity could be described as $C_V(T,P_0)$. The alternative would be to keep V constant at its value from room temperature for all temperatures and that would require that P increases with temperature in order to balance the natural thermal expansion. That quantity could be described as $C_V(T,V_0)$. Since all the experimental information usually used when C_V is evaluated from C_P has been obtained from 1 atm, the C_V values usually reported would most probably be $C_V(T,P_0)$.

Instructions for using T-C

$C_P(T,P_0)$ and $C_V(T,P_0)$ can be evaluated by applying the "." operator on the same state of equilibrium at 500^{o}C and 1 atm but the set of independent variables must be different. $C_P(T,P_0)$ is found directly and $C_V(T,P_0)$ after changing the condition on P to the equivalent condition on V. In order to find $C_V(T,V_0)$ you must first find V at room temperature and 1 atm, i.e. V_0. Then you compute the equilibrium at 500^{o}C and V_0 and directly evaluate $(\partial U / \partial T)_{V,N}$.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PTERN
 Current database: TCS Public Ternary Alloys TDB v1

 VA  DEFINED
TDB_PTERN: def-el Cr
 CR  DEFINED
TDB_PTERN: rej p *
 LIQUID:L                BCC_A2                  FCC_A1
   REJECTED
TDB_PTERN: rest p bcc
 BCC_A2  RESTORED
TDB_PTERN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
```

```
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           11
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PTERN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=773 P=101325 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var CP=H.T;
POLY_3: s-c P=none V=
Value /7.323224298E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var CVP0=U.T;
POLY_3:
```

*) Go back to the equilibrium at 298 K and 1 atm in order to evaluate V_0 and introduce it as condition. Then find the state of equilibrium at 773 K for $V=V_0$.

```
POLY_3: s-c P=101325 V=none T=298
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: s-c P=none V=
Value /7.230407803E-06/:
POLY_3: s-c T=773
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
  21 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Now you can evaluate $C_V(T,V_0)$.

```
POLY_3: ent-sym var CVV0=U.T;
POLY_3: eval
Name(s):
 CP=28.810421
 CVP0=27.74913
 CVV0=27.41756
POLY_3: exit
 CPU time            0  seconds
```

Comments

It is an interesting question how the heat capacities published in tables are defined. Experimentally, it is easiest to measure $C_P(T,P_0)$ and then to derive C_V at each temperature using Eq. 2.34, which can be written as $C_V = C_P - TV\alpha^2/\kappa_T$. All the quantities C_P, α and κ_T have probably been measured at ordinary pressure. Primarily, one will thus obtain $C_V(T,P_0)$ and publish those values.

2.8. Changing independent variables

Show numerically that $C_V\kappa_T = C_P\kappa_S$ for Cr at 1500 K and 1 atm.

Hint

Remember that $C_V = (\partial U/\partial T)_V$, $C_P = (\partial H/\partial T)_P$, $V\kappa_T = -(\partial V/\partial P)_T$ and $V\kappa_S = -(\partial V/\partial P)_S$. You have to be careful with the sets of independent variables that are not the same for all the partial derivatives.

Instructions for using T-C

Again you can use the special operator for partial derivatives.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Cr
 CR  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L               FCC_A1                  BCC_A2
 HCP_A3  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          11
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
```

```
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) As always, you must start setting the conditions with the set of variables for which you know the values.

```
POLY_3: s-c P=101325 T=1500 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3:
```

*) There are two partial derivatives using this set of variables.

```
POLY_3: ent-sym var VKT=-V.P;
POLY_3: ent-sym var CP=H.T;
POLY_3:
```

*) Change the set of variables for the next partial derivative.

```
POLY_3: s-c P=none V=
Value /7.527872324E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var CV=U.T;
POLY_3:
```

*) Again, change the set of variables for the fourth partial derivative.

```
POLY_3: s-c V=none P=101325
POLY_3: s-c T=none S=
Value /70.56209834/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var VKS=-V.P;
POLY_3:
```

*) Time to test the relation.

```
POLY_3: ent-sym var LHS=CV*VKT;
POLY_3: ent-sym var RHS=CP*VKS;
POLY_3: sh LHS RHS
 LHS=1.4375568E-15
 RHS=1.4375568E-15
POLY_3: CPU time            0  seconds
```

Comments

As expected, you have found that LHS = RHS.

2.9. Maxwell relation

Prove numerically that $(\partial S/\partial V)_T = (\partial P/\partial T)_V$. Use an Fe alloy with 10 mass% Cr at 900 and 700^{o}C under 1 atm.

Hint

1) These partial derivatives use the same three independent variables, including N that is omitted.

2) This alloy is bcc at those temperatures.

Instructions for using T-C

This is a simple case for the special "." operator.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Cr Fe
 CR                       FE  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                  BCC_A2
 HCP_A3                   SIGMA  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           22
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1173 N=1 w(Fe)=.1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Only one variable must be changed.

```
POLY_3: s-c P=none V=
Value /7.421121642E-06/:
```

```
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Use functions because you will soon repeat the evaluation.

```
POLY_3: ent-sym fun SV=S.V;
POLY_3: ent-sym fun PT=P.T;
POLY_3: eval
Name(s):

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 SV=7583868.5
 PT=7583868.5
POLY_3:
```

*) The values are the same and Maxwell's relation was confirmed. Do it for the other temperature also.

When changing to the new temperature, you must take back the known pressure and compute equilibrium. Then change again to the wanted set of variables.

```
POLY_3: s-c V=none P=101325 T=973
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in            0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: s-c P=none V=
Value /7.364757305E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Because you used functions, you can now evaluate them for the new temperature directly.

```
POLY_3: eval
Name(s):

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 SV=6862135.8
 PT=6862135.8
POLY_3: exit
 CPU time            0  seconds
```

Comments

For both temperatures you have confirmed Maxwell's relation.

Chapter 3. Systems with variable composition

3.1. Chemical potential

Evaluate a chemical potential of a component in a state of equilibrium in a binary system with two phases, one of which is stoichiometric. Also, evaluate it for each one of the phases.

Hint

1) You may choose the Fe-C system with the Fe-rich fcc and the carbide called cementite, Fe_3C, at 1200 K and 1 atm.

2) You may define the conditions for a two-phase system in different ways. One way is to give the composition of the system but it will not fall into the two-phase field unless the composition is chosen within a certain range. It would be safer to give no condition regarding the composition but require that the two phases must be present. When the two-phase equilibrium has been computed, the composition of each phase will be known. In order to identify the equilibrium you may record its chemical potential of C.

3) In order to study fcc you should remove cementite. Then you will find that you must add another condition and it should define the composition of fcc in some way. Test that you get the same result as before if you give the system the same composition that fcc had before.

4) Then take back cementite, remove fcc and give the system the composition of cementite, $x_C=0.25$. Compute equilibrium and test if you get the same chemical potential of C as before. Comment the result. Remember that the chemical potential of a component j is defined by varying its content, N_j.

Instructions for using T-C

1) When you have defined the system, you can inspect the defined system and check that cementite is actually described as a stoichiometric phase.

2) After computing the equilibrium you can directly show μ_C with the symbol mu(C).

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE                M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc cem
 FCC_A1                   CEMENTITE  RESTORED
TDB_DFECRC:
```

*) Now you should check that cementite is actually described as a stoichiometric phase by **l**isting the **sys**tem.

```
TDB_DFECRC: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENTS/:  CONSTITUENTS
 FCC_A1      :FE:C VA:
 CEMENTITE   :FE:C:
TDB_DFECRC:
```

*) For fcc you can see that Fe has its own sublattice and C mixes with vacancies on another one, which will thus be an interstitial sublattice. For cementite you can see that Fe and C are alone on their respective sublattice. It is thus described as a stoichiometric phase with a fixed composition. You are thus ready to **get** the data.

```
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          21
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) In order to force both phases to take part in the equilibrium you can **ch**ange the **st**atus of these **p**hases from the default, "entered", that means that a phase will be considered in the computation of equilibrium and *may* take part in the equilibrium. If a phase is **fix**ed, it has to take part in the equilibrium and you must even declare the amount if it (even 0 if appropriate).

```
POLY_3: ch-st p fcc
Status: /ENTERED/:  fix
Number of moles /0/:  1
POLY_3: ch-st p cem
Status: /ENTERED/:  fix
Number of moles /0/:  1
POLY_3:
```

*) Now it is time to **s**et the other **c**onditions for the equilibrium.

```
POLY_3: s-c T=1200 P=101325
POLY_3: l-c
 T=1200, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  FCC_A1=1
 DEGREES OF FREEDOM 0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          138  grid points in            0  s
   9 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) It is often wise to examine the result of a computation, especially if one is not used to the system. You could **l**ist the **e**quilibrium just computed.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) The results can be presented in different ways and quantities. You can examine the options by printing **?** . The letter C stands for composition. If you like to see the whole constitution, you could select **N**. The function of the other three letters will not change.

```
Options /VWCS/:  N
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1200, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  FCC_A1=1
 DEGREES OF FREEDOM 0

 Temperature 1200.00 K ( 926.85 C),  Pressure  1.013250E+05
 Number of moles of components  5.65987E+00,  Mass  2.43325E+02
 Total Gibbs energy -2.33857E+05,  Enthalpy  2.22950E+05,  Volume  3.49459E-05

 Component                 Moles      W-Fraction Activity   Potential   Ref.stat
 C                         1.6599E+00 8.1935E-02 3.3108E+02  5.7893E+04 SER
 FE                        4.0000E+00 9.1807E-01 2.5674E-04 -8.2488E+04 SER

 CEMENTITE                    Status FIXED       Driving force  0.0000E+00
 Number of moles 4.0000E+00, Mass 1.7955E+02          Mass fractions:
 FE  9.33106E-01  C   6.68943E-02
 Constitution:
 Sublattice  1,  Number of sites  3.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  1.0000E+00
 C   1.00000E+00

 FCC_A1                       Status FIXED       Driving force  0.0000E+00
```

```
 Number of moles 1.6599E+00, Mass 6.3773E+01         Mass fractions:
 FE  8.75720E-01  C   1.24280E-01
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  1.0000E+00
 C   6.59869E-01  VA  3.40131E-01
POLY_3:
```

*) On the last line you can see that the second sublattice, which is the interstitial sublattice, is filled to 66% by C. That is not to be expected for interstitial solutions, which are usually rather dilute. Something may have gone wrong in the iteration procedure. Try to **s**et-**a**ll-**s**tart values in a different way.

```
POLY_3: s-a-s
Automatic start values for phase constituents? /N/: f
```

*) Do not accept the default **N** that here means no. **f** (**f**orced) is a better alternative and gives POLY a new change to find suitable start values.

```
 Forcing automatic start values
 Automatic start values will be set
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Using already calculated grid
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWNS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1200, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  FCC_A1=1
 DEGREES OF FREEDOM 0

 Temperature 1200.00 K ( 926.85 C),  Pressure  1.013250E+05
 Number of moles of components  5.06159E+00,  Mass  2.36139E+02
 Total Gibbs energy -2.48038E+05,  Enthalpy  1.72832E+05,  Volume  3.19827E-05

 Component                 Moles      W-Fraction Activity   Potential   Ref.stat
 C                         1.0616E+00 5.3997E-02 1.7519E-01 -1.7380E+04 SER
 FE                        4.0000E+00 9.4600E-01 3.1742E-03 -5.7397E+04 SER

 CEMENTITE                    Status FIXED       Driving force  0.0000E+00
 Number of moles 4.0000E+00, Mass 1.7955E+02         Mass fractions:
 FE  9.33106E-01  C   6.68943E-02
 Constitution:
 Sublattice  1,  Number of sites  3.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  1.0000E+00
 C   1.00000E+00

 FCC_A1                       Status FIXED       Driving force  0.0000E+00
 Number of moles 1.0616E+00, Mass 5.6587E+01         Mass fractions:
 FE  9.86926E-01  C   1.30739E-02
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  1.0000E+00
 VA  9.38406E-01  C   6.15944E-02
POLY_3:
```

*) The last line says that now there is only 6% C in the interstitial sublattice 2. You may continue by **sh**owing the chemical potential of C, **mu(C)**.

```
POLY_3: sh mu(C)
 MU(C)=-17379.691
POLY_3:
```

*) Next you like to consider only fcc by **ch**anging the **st**atus of the **p**hase **cem**entite to either dormant or **sus**pended. Then try to **c**ompute **e**quilibrium.

```
POLY_3: ch-st p cem=sus
POLY_3: c-e

 *** ERROR  2003 IN QMJBSV
 *** Degrees of freedom not zero
POLY_3:
```

*) You should **l**ist the **c**onditions in order to find what went wrong.

```
POLY_3: l-c
 T=1200, P=1.01325E5
 FIXED PHASES
 FCC_A1=1
 DEGREES OF FREEDOM 1
POLY_3:
```

*) It is evident that a fixed phase is regarded as a condition. When cementite from being fixed was suspended you should have added another condition, preferably the composition of fcc that it had in the two-phase equilibrium already computed. It is still stored in the current state of equilibrium. You can recall it without first inspecting its value.

```
POLY_3: s-c x(fcc,C)
Value /0.05802069348/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Since you have given the equilibrium composition of fcc, according to the first computation, you should get the same potential as before. Make the test.

```
POLY_3: sh mu(C)
 MU(C)=-17379.691
POLY_3:
```

*) Yes, it is exactly the same. Now you should turn to the cementite phase and **sus**pend the **p**hase **fcc**.

```
POLY_3: ch-st p fcc=sus
POLY_3: ch-st p cem=fix 1
POLY_3: s-c x(fcc,C)=none
POLY_3: s-c x(C)=.25
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh mu(C)
 MU(C)=12317.792
POLY_3:
```

*) Now you got a different value although you gave the equilibrium composition of the cementite. The reason is that a stoichiometric phase by itself cannot define a chemical potential. No value of mu(C) can thus be incorrect. It may be interesting to test if cementite with the same composition really can accept a completely different value of mu(C). In order to keep the correct number of conditions you should then remove the condition regarding composition, of course hoping to get it back as a result of the computation of equilibrium.

```
POLY_3: s-c mu(C)=2
POLY_3: s-c x(c)=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Using already calculated grid
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh x(C)
 X(C)=2.5E-1
POLY_3:
```

*) Yes, the correct composition came back which is not surprising since cementite, being stoichiometric, must have this composition. Nevertheless, this result demonstrated that POLY was able to carry out a proper computation using any value of mu(C).

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) Sometimes POLY will not find the correct phase equilibrium. It usually leads to some inconsistency later on or may be discovered by inspecting the computed equilibrium.

2) When POLY has obtained the wrong equilibrium, one can improve the performance by giving reasonable start values for the computation. There are three commands for doing this, set-start-value, set-all-start-values and set-start-constitution.

3) When a phase has a miscibility gap, it may be wise to give it a start composition on the side you are interested in.

4) Since $\mu_j = (\partial U / \partial N_j)_{S,V}$, one cannot give a particular value to the chemical potential of a component in a single stoichiometric phase where N_j cannot be varied. However, it can be done for the two-phase equilibrium if the stoichiometric phase is in equilibrium with another phase.

3.2. Molar and integral quantities

Gibbs defined size as mass, not as number of moles. Choose a simple binary solution of a given composition and at given T and P. Evaluate $\Sigma\mu_i N_i$ in both ways and check that the result is the same.

Hint

1) Denoting mass by B, you can evaluate Gibbs' chemical potential of j as U.B$_j$ but only if you have used S, V, B$_1$ and B$_2$ when defining the conditions because $\mu_1 = (\partial U / \partial B_1)_{S,V,B_2}$ according to Gibbs, rather than $\mu_1 = (\partial U / \partial N_1)_{S,V,N_2}$.

2) You may choose an alloy of 200 gram Fe and 20 gram Cr in the bcc state at 800 K and 1 bar.

Instructions for using T-C

After computing the equilibrium, you can inspect the values of S and V. They can be used as conditions for a new computation of the same equilibrium.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Cr Fe
 CR                       FE  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   SIGMA  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           22
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You must first find the values of S and V under the given conditions and then use S and V as conditions. You can find S and V after computing the equilibrium.

```
POLY_3: s-c P=101325 T=800 B(Fe)=200 B(Cr)=20
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0
POLY_3:
```

*) Evaluate and store $\Sigma\mu_i N_i$ for later comparison with result according to Gibbs.

```
POLY_3: ent-sym var Nsum=N(Fe)*mu(Fe)+N(Cr)*mu(Cr);
POLY_3:
```

*) It may be interesting also to store the ordinary chemical potentials.

```
POLY_3: ent-sym var muFe=mu(Fe);
POLY_3: ent-sym var muCr=mu(Cr);
POLY_3:
```

*) Change to the new set of independent variables.

```
POLY_3: s-c T=none S=
Value /236.846264/:
POLY_3: s-c P=none V=
Value /2.873929319E-05/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Now you can evaluate Gibbs' chemical potentials and also his value of $\Sigma\mu_i N_i$.

```
POLY_3: ent-sym var GmuFe=U.B(Fe);
POLY_3: ent-sym var GmuCr=U.B(Cr);
POLY_3: ent-sym var Gsum=B(Fe)*GmuFe+B(Cr)*GmuCr;
POLY_3: eval
Name(s):
 NSUM=-120578.6
 MUFE=-30463.361
 MUCR=-29853.017
 GMUFE=-516.63641
 GMUCR=-862.56571
 GSUM=-120578.6
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) NSUM and GSUM, i.e, $(\partial U/\partial N_1)_{S,V,N_2}$ and $(\partial U/\partial B_1)_{S,V,B_2}$, are indeed equal, a consequence of the fact that they are both based on the same logic and are expressed in the same unit, J.

2) On the other hand, the chemical potentials are different because they are expressed in different units, J/mol and J/kg.

3.3. Characteristic state functions

There is a characteristic state function which can be defined as $\Omega = U - TS - \Sigma\mu_i N_i = -PV$ and its natural state variables are *T*, *V* and μ_i because $d\Omega = d(-PV) = -SdT - PdV - \Sigma N_i d\mu_i$ under reversible conditions. It is called "Grand Potential" and is much used in modelling, one advantage being that it is well suited for conditions under constant volume in simple models, which implies that the distances between atoms should stay constant. On the other hand, the Gibbs energy, $G = \Sigma\mu_i N_i$, is well suited for describing experimental results and applications because it is most easy to keep its natural variables, *P* and *T*, constant in experiments. Suppose the grand potential as function of its natural variables, *T*, *V* and μ_i, is available. Evaluate Gibbs energy for a simple binary solution of a given composition.

Hint

1) For the user of a thermodynamic data bank system it may not be evident what characteristic state function is used for storing the thermodynamic information. What matters is the choice of variables in the definition of the conditions because they will thus become independent

variables. One may thus mimic the grand potential by giving the values of *T*, *V* and μ_i as conditions.

2) You may use the same system as in the preceding problem, i.e. an alloy of 200 gram Fe and 20 gram Cr in the bcc state at 800 K and 1 bar.

3) Accepting the preceding system and conditions it is necessary first to evaluate the values of *V* and μ_i to be used for mimicking the grand potential. As usual, it is necessary first to compute equilibrium for the conditions given primarily.

4) The grand potential yields $N(Fe) = -(\partial\Omega / \partial mu(Fe))_{T,V,mu(Cr)} = V(\partial P / \partial mu(Fe))_{T,V,mu(Cr)}$ since $\Omega = -PV$ and *V* is constant for this partial derivative.

Instructions for using T-C

Use the "." operator.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Cr Fe
 CR                        FE  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                  FCC_A1                    BCC_A2
 HCP_A3                    SIGMA  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           22
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol
```

```
 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You must first compute the equilibrium under the given conditions in order to find the values of *V* and μ_i to be used in the grand potential.

```
POLY_3: s-c P=101325 T=800 B(Fe)=200 B(Cr)=20
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Store some values for later comparison.

```
POLY_3: sh mu(Fe) mu(Cr) N(Fe) N(Cr) G
 MU(FE)=-30463.361
 MU(CR)=-29853.017
 N(FE)=3.581213
 N(CR)=0.38464497
 G=-120578.6
POLY_3:
```

*) Delete the whole set of independent variables and introduce the one characteristic of the grand potential.

```
POLY_3: s-c *=none
POLY_3: s-c T=
Value /800/:
POLY_3: s-c V=
Value /2.873929319E-05/:
POLY_3: s-c mu(Fe)=
Value /-30463.36077/:
POLY_3: s-c mu(Cr)=
Value /-29853.01676/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Now you have a state of equilibrium described in the way of a grand potential. Evaluate N(Fe) and N(Cr) according to the Hint.

```
POLY_3: ent-sym var NFe=V*P.mu(Fe);
POLY_3: ent-sym var NCr=V*P.mu(Cr);
POLY_3: ent-sym var sum=NFe*mu(Fe)+NCr*mu(Cr);
POLY_3: eval
Name(s):
 NFE=3.581213
 NCR=0.38464497
 SUM=-120578.6
POLY_3: sh N(Fe) N(Cr) G
 N(FE)=3.581213
 N(CR)=0.38464497
 G=-120578.6
POLY_3: exit
 CPU time            0  seconds
```

Comments

There is full agreement between the quantities evaluated from the Gibbs energy and those obtained from the grand potential.

3.4. Additivity of extensive quantities. Free energy and exergy.

Consider 1 m^3 of pure H_2 at 600^oC and 1 atm being burned to H_2O with air containing 20 mol% O_2 and 1.5 mol% H_2O of 18^oC and the resulting gas being cooled to 18^oC. Evaluate the free energy that could theoretically be extracted from that system if the air can be regarded as an infinite reservoir of O_2 and recipient of H_2O, i.e., the exergy. Assume that one can neglect the minute amount of H_2 that is not oxidized.

Hint

One way to solve this problem is to define an initial system with the final content of matter, i.e., including the oxygen required for oxidizing the H_2 gas. Initially, there are thus two subsystems, the H_2 gas and the proper amount of oxygen in the surrounding reservoir, and one should add the Gibbs energy of them. The value of the H_2 gas must be evaluated from U(873 K,101325 Pa) – 291*S(873 K,101325 Pa) + 101325*V(873 K,101325 Pa). The value of the oxygen is obtained directly from μ_{O_2} of the atmosphere. The Gibbs energy of the final state is obtained from the H_2O gas at μ_{H_2O} of the atmosphere.

In reality one would not be able to make use of all that exergy because the local conditions in the surroundings will change by the loss of O_2 and the receipt of H_2O. The most critical information would be the local H_2O pressure. This is evident if one realizes that the decrease in Gibbs energy would be infinite if there were no moisture in the atmosphere initially and one would wait until the H_2O would spread infinitely far away. Of course, there would be no practical method to utilize that part of the process. A method to obtain a value of the practically available Gibbs energy decrease could be to calculate the amount of air that is needed for oxidizing the H_2 and assume that the H_2O will stay in the amount of nitrogen left. However, now you are not required to consider that case.

Instructions for using T-C

In SSUB the gas is treated with the ideal gas model. The chemical potential of a species *i* is then determined simply by its partial pressure, i.e., P_i=P*y(gas,i). One could thus consider this species as alone and under that pressure.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el H O
 H                        O  DEFINED
TDB_PSUB: rej p *
 GAS:G                    H2O_L                    H2O2_L
   REJECTED
TDB_PSUB: rest p gas
```

```
 GAS:G  RESTORED
TDB_PSUB: rej sp *
 VA                      H                       O
 H1O1                    H1O2                    H2
 H2O1                    H2O2                    O2
 O3  REJECTED
TDB_PSUB: rest sp H2 O2 H2O1
 H2                      O2                      H2O1
   RESTORED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Consider the H2 gas first.

```
POLY_3: s-c T=873 P=101325 V=1 N(O)=0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in            0  s
  37 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) We can now evaluate the amount of H in this gas and the amount of O that it will combine with is half that value.

```
POLY_3: ent-sym var NH=N(H);
POLY_3: ent-sym var NO=.5*N(H);
POLY_3:
```

*) We can also evaluate the Gibbs energy of the H2 gas when in the given surroundings.

```
POLY_3: ent-sym var GH2=U-291*S+101325*V;
POLY_3:
```

*) The partial pressure of the oxygen in the surroundings is 20% of the total.

```
POLY_3: ent-sym var PiO2=.2*101325;
POLY_3:
POLY_3: s-c T=291 P=PiO2 N(H)=0 N(O)=NO V=none
POLY_3: c-e
 Global minimization failed, error code         1034
 NO DIGIT
 . Using normal POLY minimization.
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in            0  s
  49 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) For the O2 gas we get,

```
POLY_3: ent-sym var G1=G+GH2;
```

```
POLY_3:
```

*) Finally we have only H2O at the temperature and partial pressure of the surroundings with its 1.5% H2O.

```
POLY_3: ent-sym var PiH2O=0.015*101325;
POLY_3: s-c T=291 P=PiH2O N(H)=NH N(O)=NO
POLY_3: c-e
 Global minimization failed, error code         1034
 NO DIGIT
 . Using normal POLY minimization.
 Convergence problems, increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: PSUB

 Conditions:
 T=291, P=PIH2O, N(O)=NO, N(H)=NH
 DEGREES OF FREEDOM 0

 Temperature  291.00 K (  17.85 C),  Pressure  1.519875E+03
 Number of moles of components  4.18781E+01,  Mass  2.51475E+02
 Total Gibbs energy -4.28425E+06,  Enthalpy -3.37909E+06,  Volume  2.22222E+01

 Component               Moles      W-Fraction Activity   Potential   Ref.stat
 H                       2.7919E+01 1.1190E-01 6.6145E-20 -1.0685E+05 SER
 O                       1.3959E+01 8.8810E-01 1.8629E-17 -9.3204E+04 SER

 GAS                           Status ENTERED     Driving force  0.0000E+00
 Number of moles 4.1878E+01, Mass 2.5148E+02         Mass fractions:
 O  8.88103E-01  H  1.11897E-01
 Constitution:
 H2O1  1.00000E+00  H2    2.00000E-12  O2    2.00000E-12
POLY_3:
```

*) The very low amounts of H2 and O2 in the result are of no practical importance. This is how POLY here mimics a zero amount. You can thus evaluate the final Gibbs energy and take the difference directly.

```
POLY_3: ent-sym var Exergy=G1-G;
POLY_3: sh Exergy
EXERGY=3417919.8
POLY_3: exit
 CPU time           0  seconds
```

Comments

It should again be emphasized that the amount of exergy used by a piece of equipment depends on how it disposes of the end products.

3.6A. Calculation of equilibrium

Consider a ternary system with three solution phases, e.g. Fe-Cr-C with fcc, bcc and liquid. One may define the conditions by presenting the values of T and P and further require that all three phases take part in the equilibrium. Compute the compositions of the three phases at given values of T and P but without prescribing an average composition of the system. Then, define a composition within the three-phase triangle you have found and determine the solidus and liquidus temperatures for that alloy.

Hint

It is most common to store experimental information in the form of a fundamental equation for the Gibbs energy, using T, P and N_i as the independent state variables. The computation of equilibrium when the values of other state variables are prescribed as conditions must be made by iteration. However, when such a procedure is available in a data bank system, it is not necessarily evident to the user.

There have already been a number of problems involving iteration and here is another one. It may serve to demonstrate the great flexibility that may be available in a data bank system. As an example, one could have evaluated at what temperature the liquid has a particular content or amount.

In complicated cases it may be difficult for the program to locate the equilibrium compositions of the phases. It may then help to give reasonable start values if one has a feeling for the properties of the system. There may also be ways of making the system more efficient in finding good start values for the compositions of the phases. A final possibility could be to start with an alloy composition close to a lower-order system, in this case a binary system.

Instructions for using T-C

In POLY you can prescribe start values with the commands set-start-value, set-all-start-values and set-start-constitution. With the latter one you can give the compositions of the individual phases through their site fractions. When being asked if you prefer automatic start values you may respond **Y**, meaning **yes**, **N**, meaning **no**, or **f** meaning **forced.**

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-sys Fe Cr C
 FE                       CR                       C
   DEFINED
TDB_DFECRC: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L    :C CR FE:
  > This is metallic liquid solution phase, with C species
 FCC_A1      :CR FE:C VA:
 BCC_A2      :CR FE:C VA:
 HCP_A3      :CR FE:VA C:
 SIGMA       :FE:CR:CR FE:
 CEMENTITE   :CR FE:C:
 M3C2        :CR:C:
```

```
 M7C3        :CR FE:C:
 M23C6       :CR FE:CR FE:C:
 GRAPHITE    :C:
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  SIGMA                   CEMENTITE
 M3C2                    M7C3                    M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc liq
 FCC_A1                  BCC_A2                  LIQUID:L
   RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           80
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) The ordinary way to find a required three-phase equilibrium is to **ch**ange the **st**atus of all three **p**hases to **fix 1** and not give N=1. Try T=1750 K.

```
POLY_3: s-c P=101325 T=1750
POLY_3: c-s p fcc bcc liq=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        47705  grid points in           0  s
  48 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) You can inspect the meaning of VWCS and alternatives by pressing ?. The default may be good enough unless you like to have some specific information.

```
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC
```

```
 Conditions:
 P=1.01325E5, T=1750
 FIXED PHASES
 LIQUID=1  BCC_A2=1  FCC_A1=1
 DEGREES OF FREEDOM 0

 Temperature 1750.00 K (1476.85 C),  Pressure  1.013250E+05
 Number of moles of components  3.01448E+00,  Mass  1.65932E+02
 Total Gibbs energy -3.15411E+05,  Enthalpy  1.82160E+05,  Volume  2.32188E-05

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        4.0237E-02 2.9125E-03 1.7764E-03 -9.2150E+04 SER
 CR                       1.6975E-01 5.3191E-02 1.7157E-04 -1.2616E+05 SER
 FE                       2.8045E+00 9.4390E-01 8.1383E-04 -1.0351E+05 SER

 LIQUID                      Status FIXED       Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.4478E+01         Mass fractions:
 FE  9.34869E-01  CR  5.94528E-02  C   5.67797E-03

 BCC_A2                      Status FIXED       Driving force  0.0000E+00
 Number of moles 1.0044E+00, Mass 5.5689E+01         Mass fractions:
 FE  9.47883E-01  CR  5.11575E-02  C   9.59464E-04

 FCC_A1                      Status FIXED       Driving force  0.0000E+00
 Number of moles 1.0100E+00, Mass 5.5765E+01         Mass fractions:
 FE  9.48733E-01  CR  4.91053E-02  C   2.16128E-03
POLY_3:
```

*) The driving force is zero for each one of the phases. They are thus in equilibrium. Their amounts are given as 1 or very close to, as required. There is a slight difference from 1 because the numbers given when fixing the phases refer to number of moles of formula units, The numbers given here refer to number of atoms.

Before the properties of the three phases there is a list for the whole system and there you find the composition of the alloy containing the equal amounts of the phases. Find the solidus and liquidus of that alloy. You don't need to introduce that composition by typing. It is already available.

```
POLY_3: s-c w(cr)
Value /.05319131032/:
POLY_3: s-c w(c)
Value /.002912516306/:
POLY_3:
```

*) To find the solidus you should fix the liquid to the amount of 0 mole. In order not to be in conflict with the overall composition of the alloy, which has now been defined, the other phases should just be entered. When their amounts are given as 1 it will just be start values for the iteration. Instead, their total amount should now be given, e.g. as N=1. Of course, the condition on T must be removed.

```
POLY_3: s-c T=NONE N=1
POLY_3: ch-st p fcc bcc=ent 1
POLY_3: ch-st p liq=fix 0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        47705  grid points in            1  s
  13 ITS,  CPU TIME USED   1 SECONDS
POLY_3: sh T
 T=1737.3341
POLY_3:
```

*) This is the solidus temperature where all liquid has just solidified. Examine this equilibrium in more detail.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, W(CR)=5.31913E-2, W(C)=2.91252E-3, N=1
 FIXED PHASES
 LIQUID=0
 DEGREES OF FREEDOM 0

 Temperature 1737.33 K (1464.18 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.50450E+01
 Total Gibbs energy -1.03462E+05,  Enthalpy  5.53212E+04,  Volume  7.55932E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        1.3348E-02 2.9125E-03 2.4589E-03 -8.6787E+04 SER
 CR                       5.6310E-02 5.3191E-02 1.8831E-04 -1.2390E+05 SER
 FE                       9.3034E-01 9.4390E-01 8.3058E-04 -1.0246E+05 SER

 LIQUID                      Status FIXED       Driving force  0.0000E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 FE  9.27166E-01  CR  6.52974E-02  C   7.53684E-03

 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.5045E+01         Mass fractions:
 FE  9.43896E-01  CR  5.31913E-02  C   2.91252E-03
POLY_3:
```

*) It is evident that this was not a eutectic solidification because fcc is the only phase present when the last of the liquid disappears. The alloy has solidified by a peritectic reaction. Now, find the temperature where the soldification starts, i.e., the liquidus temperature. It is found by fixing the liquid to 1 at the same time as N=1.

```
POLY_3: ch-st p liq=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        47705  grid points in           1  s
  18 ITS,  CPU TIME USED   1 SECONDS
POLY_3: sh T
 T=1775.3927
POLY_3:
```

*) This is the liquidus temperature. List the equilibrium in order to see what solid phase is the first one to form.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, W(CR)=5.31913E-2, W(C)=2.91252E-3, N=1
 FIXED PHASES
 LIQUID=1
 DEGREES OF FREEDOM 0

 Temperature 1775.39 K (1502.24 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.50450E+01
 Total Gibbs energy -1.07093E+05,  Enthalpy  6.99546E+04,  Volume  7.92365E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        1.3348E-02 2.9125E-03 8.3698E-04 -1.0460E+05 SER
```

```
 CR                        5.6310E-02 5.3191E-02 1.5039E-04 -1.2993E+05 SER
 FE                        9.3034E-01 9.4390E-01 7.7421E-04 -1.0575E+05 SER

 LIQUID                       Status FIXED       Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.5045E+01         Mass fractions:
 FE  9.43896E-01  CR  5.31913E-02  C   2.91252E-03

 BCC_A2                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 FE  9.52018E-01  CR  4.74737E-02  C   5.08281E-04
POLY_3:
```

*) Evidently, bcc is the first solid to form. Later on fcc will appear and bcc will disappear before solidification is completed.

```
POLY_3: exit
 CPU time            2  seconds
```

Comments

When requiring that a phase must take part in an equilibrium, you have actually defined a condition and can decrease the number of usual conditions. You may omit either a condition for the overall composition or for a potential as P or T.

3.6B. Calculation of equilibrium

Compute and plot a curve showing what happens to the alloy considered in Problem 3.6A when cooled from pure liquid state down to 500^{o}C.

Hint

Hopefully, your databank system has a special facility for this kind of plotting. The composition of your alloy may have been 0.05319 mass% Cr and 0.002913 mass% C.

Instruction for using T-C

By stepping you may move through several phase fields and in POST it is possible to plot any property obtainable from the states having been computed. With the command **set-lab** there are several options for identifying curves. Option **F** will give you curves for the amounts of the phases and with labels for identification.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-sys Fe Cr C
 FE                      CR                       C
   DEFINED
TDE_DFECRC:
```

*) This time you should keep all the phases available in the system. You like to see which ones will appear and where.

```
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1750 N=1
POLY_3: s-c w(Cr)=.05319131032
POLY_3: s-c w(C)=.002912516306
POLY_3: c-e
 Using global minimization procedure
 Calculated        87414  grid points in            1  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     1  s
POLY_3:
```

*) You have computed the equilibrium for your alloy at one temperature. Now you like to step through a range of temperatures.

```
POLY_3: s-a-v 1 T 773 1873
Increment /27.5/:
POLY_3: step
Option? /NORMAL/:
 looking for miscibility gaps..at:
 QSTEPP   1873.00000000000
 QSTEPP   773.000000000000
 QSTEPP   1323.00000000000
 No new miscibility gap found!

 Phase Region from    1873.00     for:
     LIQUID
 Calculated     6 equilibria

 Phase Region from    1775.39     for:
     LIQUID
```

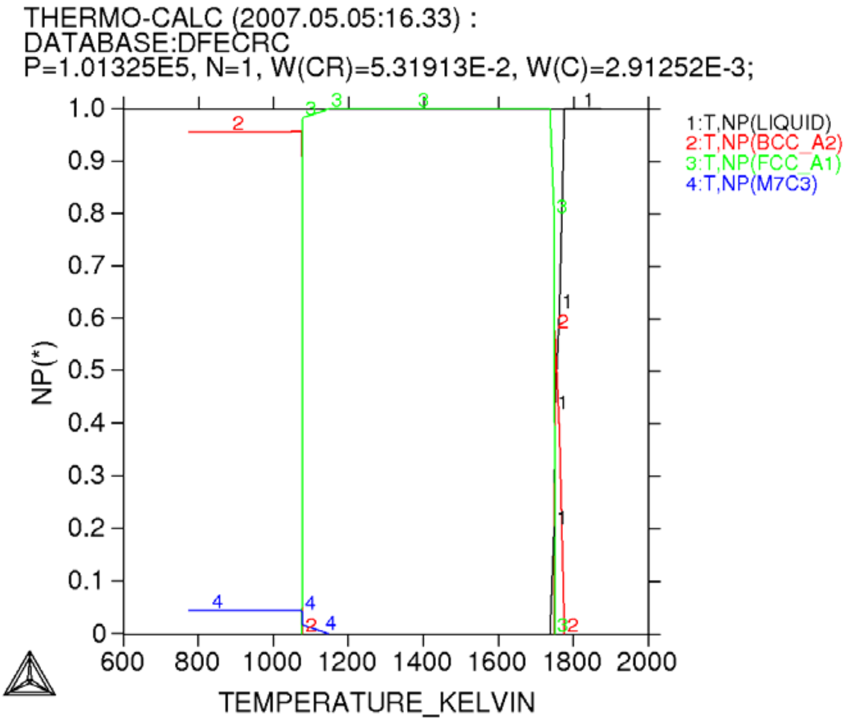
```
     BCC_A2
 Calculated     4 equilibria

 Phase Region from    1750.71     for:
     LIQUID
     BCC_A2
     FCC_A1
 Calculated     3 equilibria

 Phase Region from    1748.89     for:
     LIQUID
     FCC_A1
 Calculated     3 equilibria

 Phase Region from    1737.33     for:
     FCC_A1
 Calculated    25 equilibria

 Phase Region from    1147.20     for:
     FCC_A1
     M7C3
 Calculated     5 equilibria

 Phase Region from    1077.50     for:
     BCC_A2
     FCC_A1
     M7C3
 Calculated     4 equilibria

 Phase Region from    1075.36     for:
     BCC_A2
     M7C3
 Calculated    14 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Go to the postprocessor for plotting. You can stay in that module and plot your data in several ways by just defining new axes.

```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01


 Setting automatic diagram axis

POST: set-lab F
POST:
```

*) **F** was the option mentioned in the instructions. That is all needed.

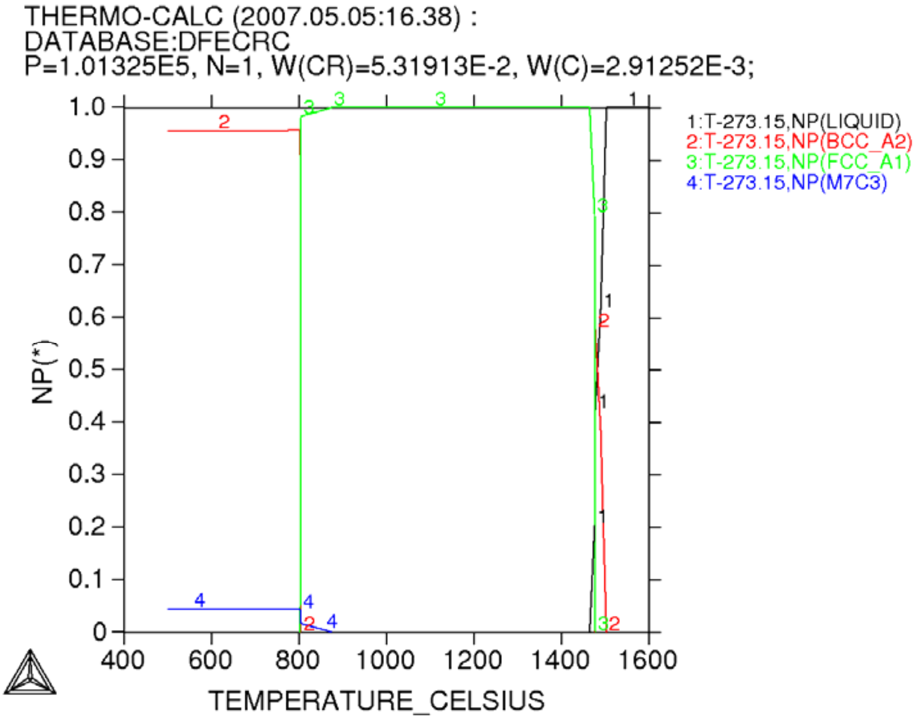
```
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Change the temperature axis to degree Celsius.

```
POST: s-d-a x T-C
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```

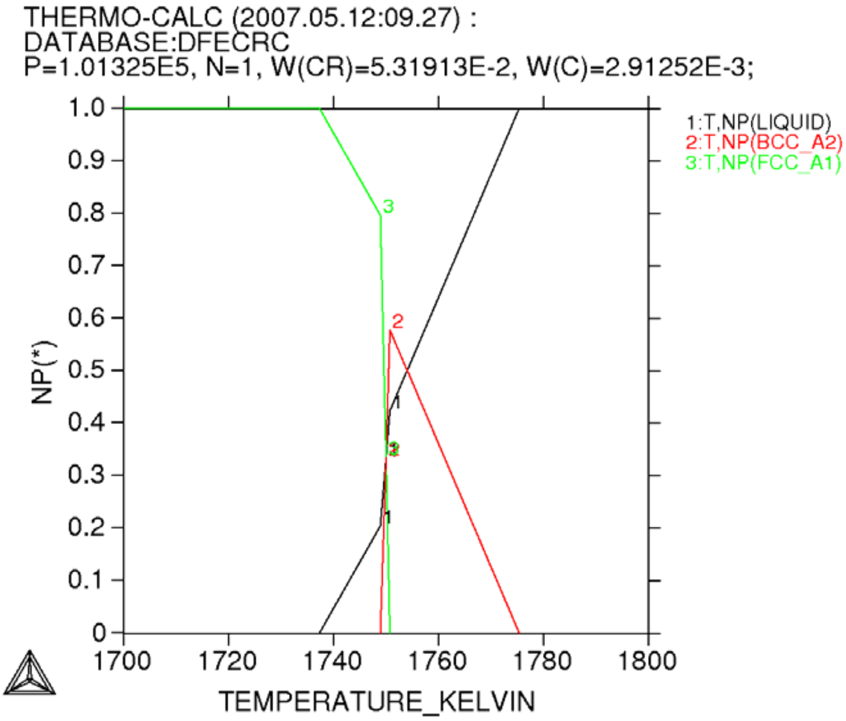


```
POST:
```

*) Make the information more visible between 1700 and 1800 K.

```
POST: s-s-s x
AUTOMATIC SCALING  (Y OR N) /N/:
MIN VALUE : 1700 1800
POST: plot
```

```
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            28  seconds
```

Comments

1) You can change the plotting in several ways. Option **F** gives you the phase fractions. T-C means temperature in degree Celsius.

2) If much information is jammed into a narrow range, you may magnify that range. Thus, the last diagram shows quite clearly how solidification starts by the precipitation of 2(bcc) and the simultaneous decrease of 1(liquid). Then 3(fcc) starts forming and 2(bcc) disappears quickly and the solidification is then completed by a slower growth of 3(fcc).

3) The temperatures for the boundaries between phase regions are given in the list from the stepping. It seems that the liq+bcc+fcc phase field exists only between 1748.89 and 1750.71 K.

3.7. Evaluation of the driving force

Calculate numerically the driving force for the precipitation of a phase from a supersaturated solid solution under three different conditions but all under constant T and P. (a) Consider the formation of the very first, minute amount of the new phase. (b) Consider the situation where the precipitation is halfway. (c) Consider the integrated driving force for the whole reaction. (d) You may finally evaluate the driving force per mole of the new phase averaged for the whole reaction.

Hint

a) This case was considered already in Problem 1.8. It was concluded that the driving force depends on the exact composition of the new phase. In order to predict the rate of nucleation of the new phase one is interested in the composition that yields the largest driving force. That was not done in Problem 1.8. Your data bank system may have a facility for evaluating the driving force for the most favourable composition directly.

b) Here it is necessary first to compute the final equilibrium and evaluate the composition of the parent phase when the reaction is halfway. Then the problem is of the same kind as under (a).

c) Here you should simply compare the Gibbs energy of the initial and the final states. The initial state can be treated as a state of equilibrium if you can require that the new phase cannot form, i.e., as you did under (a).

For convenience you may solve this problem for the system used in Problem 1.8, the Fe-Cr system at 1 atm.

Instructions for using T-C

a) In Problem 1.8 it was demonstrated that POLY automatically gives the driving force for the formation of any phase that has been made dormant and the value refers to the most favourable composition. You may now use that facility directly.

b) When you have found the composition of the parent phase for halfway reaction, you can apply the same method if you consider only the parent phase with its new composition.

c) With POLY you can suspend a phase. By suspending the new phase or making it dormant you may compute the initial state as a state of equilibrium.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr
 FE                     CR  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L               FCC_A1                  BCC_A2
 HCP_A3                 SIGMA  REJECTED
TDB_DFECRC: rest p bcc sigma
 BCC_A2                 SIGMA  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          25
 FUNCTIONS ....
```

```
 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Consider an alloy with 30 mole% Cr at 1 atm and 650°C. Make sigma dormant in order to describe the initial state.

```
POLY_3: s-c P=101325 T=923 N=1 x(Cr)=.3
POLY_3: ch-st p sigma=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) Choose the option **N** in order to see the constitution of phases, **P** in order to see the dormant ones and **X** to get mole fractions.

```
Options /VWCS/:  XNP
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=923, N=1, X(CR)=0.3
 DEGREES OF FREEDOM 0

 Temperature  923.00 K ( 649.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.46917E+01
 Total Gibbs energy -3.77447E+04,  Enthalpy  2.55506E+04,  Volume  7.30301E-06

 Component               Moles      M-Fraction Activity   Potential   Ref.stat
 CR                      3.0000E-01 3.0000E-01 1.0474E-02 -3.4986E+04 SER
 FE                      7.0000E-01 7.0000E-01 6.2676E-03 -3.8927E+04 SER

 BCC_A2                     Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.4692E+01         Mole fractions:
 FE  7.00000E-01  CR  3.00000E-01
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  7.00000E-01  CR  3.00000E-01
 Sublattice  2,  Number of sites  3.0000E+00
 VA  1.00000E+00

 SIGMA                      Status DORMANT     Driving force  1.5819E-02
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 FE  5.33413E-01  CR  4.66587E-01
 Constitution:
 Sublattice  1,  Number of sites  8.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  4.0000E+00
```

```
 CR  1.00000E+00
 Sublattice  3,  Number of sites  1.8000E+01
 CR  5.55422E-01  FE  4.44578E-01
POLY_3:
```

*) For later comparisons you may like to store the driving force by **ent**ering the **sym**bol for a **var**iable named **Da**. Driving forces have the symbol **DGm** but remember that the driving forces are divided by RT when presented by POLY in order to make the values dimensionless. Actually, the driving force for a dormant phase is given already in the list of the state of equilibrium, but not for a suspended phase.

```
POLY_3: ent-sym var Da=8.31451*T*DGM(SIGMA);
POLY_3: ent-sym var Ginit=G;
POLY_3:
```

*) You have thus found G for the initial state and should now go to the final state of equilibrium.

```
POLY_3: ch-st p sigma=ent 0
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXNP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=923, N=1, X(CR)=0.3
 DEGREES OF FREEDOM 0

 Temperature  923.00 K ( 649.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.46917E+01
 Total Gibbs energy -3.77623E+04,  Enthalpy  2.50690E+04,  Volume  6.41242E-06

 Component               Moles      M-Fraction Activity   Potential   Ref.stat
 CR                      3.0000E-01 3.0000E-01 9.8503E-03 -3.5457E+04 SER
 FE                      7.0000E-01 7.0000E-01 6.4135E-03 -3.8750E+04 SER

 BCC_A2                     Status ENTERED     Driving force  0.0000E+00
 Number of moles 7.5534E-01, Mass 4.1456E+01        Mole fractions:
 FE  7.49893E-01  CR  2.50107E-01
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  7.49893E-01  CR  2.50107E-01
 Sublattice  2,  Number of sites  3.0000E+00
 VA  1.00000E+00

 SIGMA                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 2.4466E-01, Mass 1.3236E+01        Mole fractions:
 FE  5.45963E-01  CR  4.54037E-01
 Constitution:
 Sublattice  1,  Number of sites  8.0000E+00
 FE  1.00000E+00
 Sublattice  2,  Number of sites  4.0000E+00
 CR  1.00000E+00
 Sublattice  3,  Number of sites  1.8000E+01
 CR  5.34506E-01  FE  4.65494E-01
POLY_3:
```

*) As expected, the driving force for the formation of sigma is now zero. The Gibbs energy of the final state of equilibrium is now available and you can directly evaluate the integrated driving force by taking the difference and saving it in a variable.

```
POLY_3: ent-sym var Dc=Ginit-G;
POLY_3:
```

*) This driving force is expressed per mole of the whole system. You may also be interested in the value per mole of the new phase. You must divide with its amount which is directly available.

```
POLY_3: ent-sym var Dd=Dc/Np(sigma);
POLY_3:
```

*) You should also evaluate the Cr content of fcc for halfway reaction.

```
POLY_3: ent-sym var CrAver=(.3+x(bcc,Cr))/2;
POLY_3:
```

*) Evaluate the driving force for further precipitation of sigma in this diluted matrix. It is obtained as for the initial state.

```
POLY_3: s-c x(Cr)=CrAver
POLY_3: ch-st p sigma=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution      0 s, total time      0  s
POLY_3: ent-sym var Db=8.31451*T*DGM(SIGMA);
POLY_3: eval
Name(s):
 DA=121.40347
 GINIT=-37744.672
 DC=17.611067
 DD=71.982163
 CRAVER=0.27505334
 DB=71.869315
POLY_3: exit
 CPU time            0  seconds
```

Comments

The driving force is highest from the beginning, Da. At half-way reaction it is much lower, Dd. The driving force averaged over the whole reaction is very low, Dc, but evaluated per mole of the new phase, Db, it is rather close to the value at halfway, Dd.

3.8. Driving force for molecular reactions

Consider a gas mixture of 60% H_2, 30% O_2 and 10% H_2O at 2000 K and 1 bar. (a) What is the driving force for the formation of more H_2O? (b) What is the average driving force per mole of H_2O for the whole reaction?

Hint

Most data bank systems have a facility for the tabulation of properties as functions of temperature, e.g. the Gibbs energy of reaction. However, when applied to reactions such tables generally assume that all the species occur in their standard states, usually the pure form at 1 atm. You would here have to look for another way to obtain the information wanted but it could be different in different systems. Try to use your facility to solve this problem by comparing the Gibbs energy for two states.

Instructions for using T-C

The TAB module in T-C can tabulate properties of a phase in non-equilibrium states. By comparing two states with the same content of atoms, one may study the Gibbs energy difference between them. You may get some inspiration to the present problem from Problem 1.8.

You can easily get the Gibbs energy, G1, of the initial gas mixture from TAB by entering the fractions of the species. TAB thus requires the content of a formula unit and gives back values per mole of formula units, i.e., per mole of species (molecules) for a gas. In the present case you thus get per mole of atoms $Gm1=G1/(2\cdot 0.6+2\cdot 0.3+3\cdot 0.1)=G1/2.1$ and there will be $Nm1=0.1/2.1$ mole of H_2O molecules. Then, compare with G2 for a gas with slightly more H_2O, e.g. 59.90% H_2, 29.95% O_2 and 10.15% H_2O. Per mole of atoms it will have $Gm2=G2/2.1015$ and it will have $Nm2=0.1015$ mole of H_2O molecules. Compared to the initial gas it will thus have $0.1015/2.1015-0.1/2.1$ more H_2O molecules.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TAB:
```

*) This time it is most convenient to define the system through the species.

```
TDB_PSUB: def-sp H2 O2 H2O1
 H2                       O2                       H2O1
   DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 GAS:G       :H2 O2 H2O1:
  > Gaseous Mixture, using the ideal gas model
 H2O_L       :H2O1:
TAB:
```

*) You should reject liquid H_2O. You can here read its proper symbol in the present database.

```
TDB_PSUB: rej p H2O_L
 H2O_L  REJECTED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
```

```
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go tab
TAB:
```

*) TAB can consider only one phase at a time and then it regards a phase as a substance.

```
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /1/:  .6
H2O1 /1/:  .1
Pressure /100000/:
Low temperature limit /298.15/:  2000
High temperature limit /2000/:  2000
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 4.21                          22.40.33

 Phase : GAS                       Pressure :      100000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 2000.00   3.71002E+01   3.26447E+04   2.27632E+02  -4.22618E+05

TAB:
```

*) Go to POLY to save the G value. You should remember that TAB gives values per mole of the substance and for a gas it is the number of molecules, species, that counts. In the present case it means 2.1 moles of atoms.

```
TAB: go pol

 POLY version  3.32,  Aug 2001
POLY_3: ent-sym var Gm1=-4.22618E+05/2.1;
POLY_3: b
TAB:
```

*) Now you should modify the composition of the gas slightly. Use the composition proposed in the instructions. Notice that it is evident that the composition must be given in fractions because you will not be asked for the value of the last component.

```
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.6/:  .5990
H2O1 /.1/:  .1015
Pressure /100000/:
Low temperature limit /2000/:
High temperature limit /2000/:
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 4.21                          22.40.34

 Phase : GAS                       Pressure :      100000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
```

```
 ******************************************************************************
 2000.00   3.71245E+01   3.33092E+04   2.27726E+02  -4.23142E+05

TAB:
```

*) Go to POLY to calculate the driving force per mole of H_2O molecules according to the instructions.

```
TAB: go pol

 POLY version  3.32,  Aug 2001
POLY_3: ent-sym var Da=(Gm1-(-4.23142E+05)/2.1015)/(0.1015/2.1015-0.1/2.1);
POLY_3:
```

*) Now you should compute the equilibrium for the system in order to get the integrated driving force for the whole reaction until equilibrium is reached. You may give its composition using **s**et **i**nitial **a**mounts of the species. Otherwise, in POLY you must give the composition in terms of elements. If you make a mistake, you can **s**et an **i**nitial **a**mount equal to the negative of the incorrect entry. Or you could delete all the entered conditions including the entered amounts with the command **s**et-**c**onditions ***=none**. Or you could **l**ist the **c**onditions and identify what you like to remedy. Finally, you could always **rein**itiate POLY and start the session from the very beginning.

```
POLY_3: s-c T=2000 P=1E5
POLY_3: s-i-a N(H2)=.6
POLY_3: s-i-a N(H2O1)=.1
POLY_3: s-i-a N(O2)=.3
POLY_3:
```

*) You better check the conditions.

```
POLY_3: l-c
 T=2000, P=1E5, N(H)=1.4, N(O)=0.7
 DEGREES OF FREEDOM 0
POLY_3:
```

*) You can see that POLY has immediately transformed the input in terms of elements..

```
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
 Found the set of lowest grid points in            0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You could directly obtain the molar Gibbs energy through the symbol Gm and subtract it from Gm1 because both quantities are expressed per mole of atoms in the system. Thus you obtain the integrated driving force for a system with one mole of atoms. However, next you will need the amount of H_2O molecules in order to know how many has formed, compared to the initial state. You can get the fraction of H_2O molecules through the symbol y(gas,H2O1) and that is the amount per formula unit. It should be multiplied by the number of formula units per atom, which is obtained as Vm/Vf(gas) where Vf(gas) is the symbol for the volume of one mole of formula units.

```
POLY_3: ent-sym var Db=(Gm1-Gm)/(y(gas,H2O1)*Vm/Vf(gas)-0.1/2.1);
POLY_3: sh Da Db
 DA=155491.
 DB=111679.99
POLY_3: exit
 CPU time            0  seconds
```

Comments

Again, the driving force is highest at the beginning, Da, and the average value, Db, obtained from the integrated driving force, is about two thirds.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

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Chapter 4. Practical handling of multicomponent systems

4.1. Partial quantities

Evaluate the diffusion potential in CuZn with 50 mass% Zn at 700^{o}C and 1 atm. Use a direct method, not the one based on the difference of two chemical potentials used in Eq. 4.8 in the textbook.

Hint

It could be evaluated directly if it could be expressed as a partial derivative of G with respect to a state variable while a set of other state variables are kept constant. That is indeed possible.

The diffusion potential is defined as the change of Gibbs energy when a component is exchanged for another. That may be accomplished by adding N_{Zn} and removing the same amount of Cu, $dN_{Cu} = - dN_{Zn}$. The total number of moles, N is thus constant and the diffusion potential is obtained directly as $(\partial G / \partial N_{Zn})_N$. One could also use Eq. 6.43 in the textbook, giving the diffusion potential in our binary as dG_m/dx_{Zn} which is identical to $(\partial G / \partial x_{Zn})_{N=1}$.

Instructions for using T-C

First you must give conditions using the known mass% and N=1. After having computed the equilibrium you can evaluate x_{Zn} and use it as a condition instead of w_{Zn} in a new computation of equilibrium. It will be the same state of equilibrium as before but now it has the correct set of independent variables. You can thus evaluate $(\partial G / \partial x_{Zn})_{N=1}$. Then you can evaluate the value of N_{Zn}, when N=1, which you can then use as a condition together with N=1 for a new computation of the equilibrium. As a check you may finally remove the condition based on N and instead use N_{Cu} and evaluate the two partial derivatives that are equal to the chemical potentials of Zn. and Cu. Take the difference and confirm that the evaluation of the diffusion potential was correct.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
```

```
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw Pbin
 Current database: TCS Public Binary Alloys TDB v1

 VA                       /-  DEFINED
 IONIC_LIQ:Y              L12_FCC                  B2_BCC
 BCC_B2  REJECTED
TDB_PBIN:
```

*) Observe that two bcc phases were automatically rejected. Since you don’t know what phases they are, you should be careful if you later like to restore a bcc phase.

```
TDB_PBIN: def-el Cu Zn
 CU                       ZN  DEFINED
TDB_PBIN: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   ALCU_EPSILON             ALCU_ETA
 CUZN_EPS                 CUZN_GAMMA  REJECTED
TDB_PBIN:
```

*) Now a phase called BCC-A2 was rejected. That is the ordinary bcc phase and when restoring it you should give its full name.

```
TDB_PBIN: rest p bcc
 *** BCC INPUT IGNORED
TDB_PBIN:
```

*) This happened because the phase was not defined well enough.

```
TDB_PBIN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
TDB_PBIN:
```

*) No harm done! Now give the full name.

```
TDB_PBIN: rest p BCC_A2
 BCC_A2  RESTORED
TDB_PBIN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            6
 FUNCTIONS ....

 List of references for assessed data

   91Din 'A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, Vol.15,
       No.4, pp.317-425, (1991)'
   KOW-CUZN 'M Kowalski and P Spencer, J Phase Equil, p 432-438 (1993); CU-ZN'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PBIN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=973 N=1
POLY_3: s-c w(Zn)=.5
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
```

```
POLY_3:
```

*) Introduce as condition the variable to which you like to take the derivative. Start with x_{Zn}. N is already introduced as a condition.

```
POLY_3: s-c w(Zn)=none x(Zn)=
Value /.4928873928/:
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) It is the same state of equilibrium as before but now it is defined with the proper set of independent variables, x_{Zn} and N. You can thus evaluate the diffusion potential.

```
POLY_3: ent-sym var diffp1=Gm.x(Zn);
POLY_3:
```

*) Change from x(Zn) to N(Zn).

```
POLY_3: s-c x(Zn)=none N(Zn)=
Value /.4928873928/:
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var diffp2=G.N(Zn);
POLY_3:
```

*) Now you should change the set of independent variable in order to calculate diffusion potential from the chemical potentials. Remember how the chemical potential is defined. Use N_{Zn} and N_{Cu} as conditions.

```
POLY_3: s-c N=none N(Cu)=
Value /.5071126072/:
POLY_3:
```

*) You better check the set of independent variables.

```
POLY_3: l-c
 P=1.01325E5, T=973, N(ZN)=0.492887, N(CU)=0.507113
 DEGREES OF FREEDOM 0
POLY_3:
```

*) You have the proper set for evaluating the chemical potentials of both Cu and Zn.

```
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var muZn=G.N(Zn);
POLY_3: ent-sym var muCu=G.N(Cu);
POLY_3: ent-sym var diffp3=muZn-muCu;
POLY_3: eval
Name(s):
 DIFFP1=-12679.582
 DIFFP2=-12679.582
 MUZN=-69065.497
 MUCU=-56385.915
 DIFFP3=-12679.582
POLY_3: exit
 CPU time            0  seconds
```

Comments

You should obtain agreement between the two methods of evaluating the diffusion potentials. Always remember to check that you have the correct set of independent state variables when evaluating a partial derivative.

4.2. Relations for partial quantities

Evaluate H_{Mg} for an fcc alloy of Al-2 mass% Mg at 500^{o}C and 1 atm.

Hint

From G = H – TS one can derive $H_{Mg} = G_{Mg} + TS_{Mg} = \mu_{Mg} + TS_{Mg}$. Remember to define the proper set of independent state variables when evaluating partial derivatives.

Instructions for using T-C

Use the given information for setting the conditions. From the equilibrium you get values for the set of independent state variables you need. Use them as new conditions, compute equilibrium and evaluate S_{Mg} and $\mu_{Mg.}$ In evaluating S_{Mg} you need the operator "." when entering the function S_{Mg}=S.N(Mg). Of course, you could evaluate H_{Mg} in the same way. Do that and compare the results.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI:
     *) You are satisfied with this database.
TDB_DALMGSI: def-el Al Mg
 AL                      MG  DEFINED
TDB_DALMGSI: rej p *
 LIQUID:L                FCC_A1                  HCP_A3
 DIAMOND_A4              ALMG_BETA               ALMG_DZETA
 ALMG_UPSILON            AL12MG17  REJECTED
TDB_DALMGSI: rest p fcc
 FCC_A1  RESTORED
TDB_DALMGSI: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'N Saunders, COST project (1994); MG-SI'
```

```
 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DALMGSI: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=773 N=1 w(Mg)=.02
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Introduce the proper set of independent variables but without changing the state of equilibrium. It must still be recomputed with the new set of variables.

```
POLY_3: s-c N=none N(Al)=
Value /.9778459629/:
POLY_3: s-c w(Mg)=none N(Mg)=
Value /.02215403715/:
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Now you can evaluate the proper partial derivatives.

```
POLY_3: ent-sym var SMg=S.N(Mg);
POLY_3: ent-sym var HMg=mu(Mg)+T*SMg;
POLY_3:
```

*) It should also be possible to evaluate H_{Mg} directly as a partial derivative.

```
POLY_3: ent-sym var HMg2=H.N(Mg);
POLY_3: eval
Name(s):
 SMG=94.080297
 HMG=21965.3
 HMG2=21965.3
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The two methods of evaluating H_{Mg} gave the same value.

2) Observe that in POLY you can evaluate G, S and H as well as chemical potentials and some other state variables for a state of equilibrium independent of what set of independent state variables were used in computing the equilibrium. It is only partial derivatives obtained by the use of the "." operator that needs the correct set of independent variables.

4.3. Alternative variables for composition

Calculate the fcc+cementite two-phase equilibrium for an Fe alloy with 4 mass% Cr and 3 mass% C at 800°C and 1 atm, assuming that no other carbide forms. Then, calculate this two-phase phase field in the phase diagram at 800°C and 1 atm. Plot the tie-lines in two diagrams with the axes x_{C},u_{Cr} and x_C,z_{Cr} where $u_{Cr}=x_{Cr}/(x_{Fe}+x_{Cr})$ and $z_{Cr}=x_{Cr}/x_{Fe}$.

Hint

Each data bank system may have its own method of mapping boundaries between phase fields and also different facilities for plotting the results.

Instructions for using T-C

When mapping a phase diagram you must first compute an initial equilibrium using those variables as conditions that you like to use as axes during the mapping.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                     CR                     C
   DEFINED
TDB_DFECRC: rej p *
 LIQUID:L               FCC_A1                 BCC_A2
 HCP_A3                 SIGMA                  CEMENTITE
 M3C2                   M7C3                   M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc cem
 FCC_A1                 CEMENTITE  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           33
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
```

```
POLY_3:
```

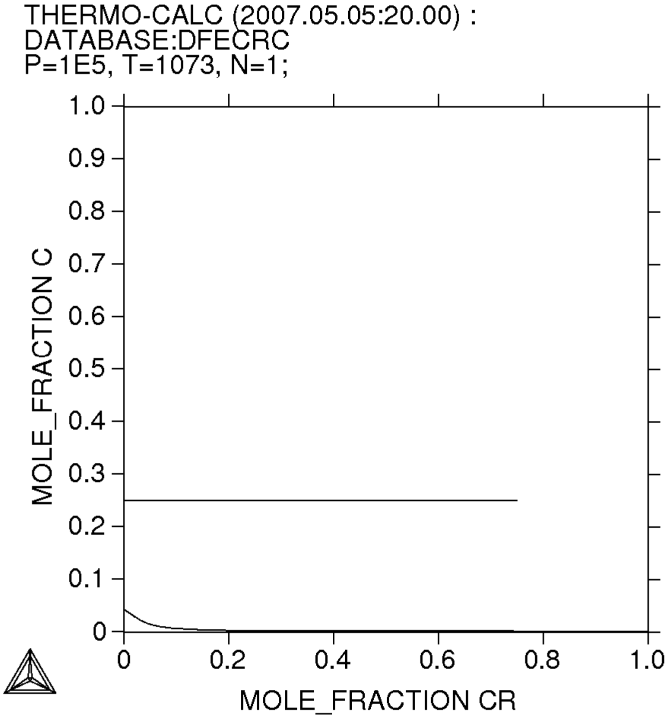
*) Set conditions for the first equilibrium, accepting the values given in mass%.

```
POLY_3: s-c P=101325 T=1073 N=1 w(Cr)=.04 w(C)=.03
POLY_3: c-e
 Using global minimization procedure
 Calculated        19785  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You now have an initial equilibrium but suppose you like to use mole fractions as axes during mapping. Then you must recompute the single equilibrium with proper conditions.

```
POLY_3: s-c w(Cr)=none x(Cr)=
Value /.03861966989/:
POLY_3: s-c w(C)=none x(C)=
Value /.125389332/:
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: s-a-v
Axis number: /1/:
Condition /NONE/:  x(cr)
Min value /0/:
Max value /1/:
Increment /.025/:
POLY_3: s-a-v
Axis number: /2/:
Condition /NONE/:  x(c)
Min value /0/:
Max value /1/:
Increment /.025/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Using ADDED start equilibria
 Global search for miscibility gaps  1  2  3  4  5  6  7 Convergence problems,
increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS

 Found            2  zero phase fraction lines to start mapping

 Phase region boundary   1 at:   9.369E-03  3.655E-02
  ** CEMENTITE
     FCC_A1
 *** Sorry cannot continue ***    4

 Calculated    88 equilibria

 Phase region boundary   2 at:   9.369E-03  3.655E-02
  ** CEMENTITE
     FCC_A1
 Terminating at diagram limit
```

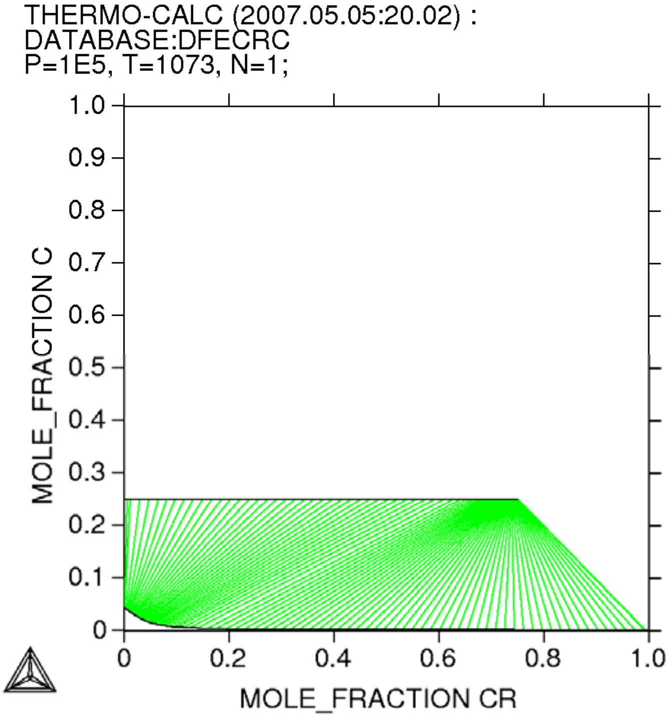
```
 Calculated    11 equilibria
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01


 Setting automatic diagram axis

POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) You must order the tie-lines to be shown if you like them to be. You can decide what fraction of the computed ones you like to see plotted. Now choose all of them (fraction=1).

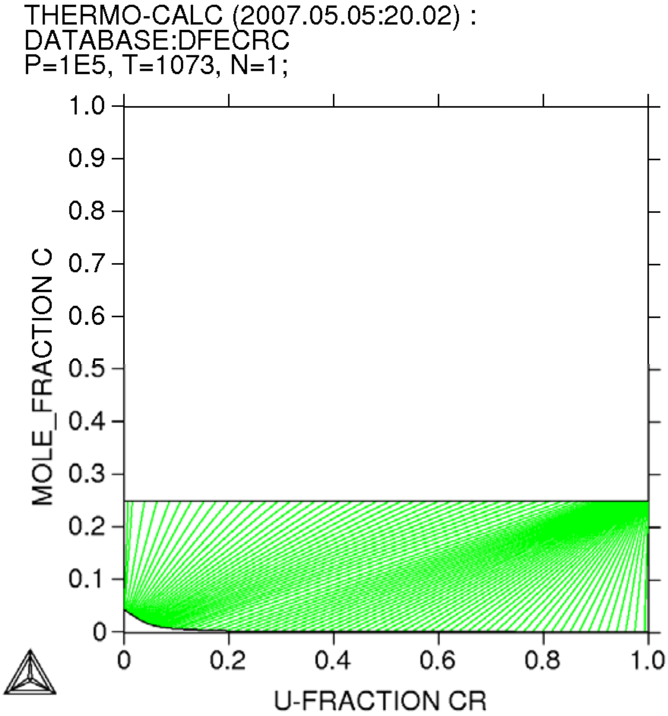
```
POST: s-t-st 1
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) You may like to use a different way of representing the composition. Try the ordinary u fraction.

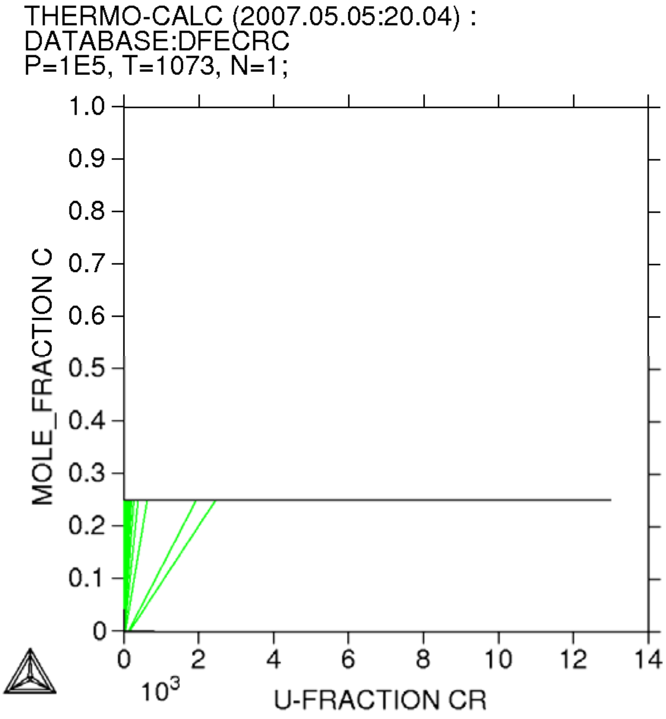
```
POST: s-d-a x u-fr
FOR COMPONENT : Cr
COMPONENTS IN DENOMINATOR : /C CR FE/:  Cr Fe
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Try the z fraction. For POLY it is a kind of u fraction with only one element in the denominator.

```
POST: s-d-a x u-fr
FOR COMPONENT : Cr
COMPONENTS IN DENOMINATOR : /CR FE/:  Fe
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time              3  seconds
```

Comments

1) Here you have learned to compute and plot a very simple phase diagram using the mapping procedure.

2) You have also tried some ways of expressing the composition. With the ordinary u fraction the carbide phase extends across the whole system.

3) With the z fraction the system actually extends to infinity but the computation stops automatically at some limit. Usually it is not interesting to see so much. The last step in the computation is from the last tie-line shown and to the end of the line for the carbide. It would have been more interesting to set the axis from 0 to a few hundred. That could be done using the command **s**et-**s**caling-**s**tatus and answering the questions.

4.5. The tie-line rule

Calculate and plot diagrams similar to Figs. 4.7 (a) and (b) for the liquid Al-Mg phase at 700°C and 1 atm. Furthermore, change the references for Al and Mg to their solid states.

Hint

To be able to use the solid states as references, you should fetch data for those phases from the database.

Instructions for using T-C

Remember to suspend the solid phases. Otherwise, they would interact in the middle of the system.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI:
     *) You are satisfied with this database.
TDB_DALMGSI: def-el Al Mg
 AL                      MG  DEFINED
TDB_DALMGSI: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L     :AL MG:
  > This is metallic liquid solution phase
 FCC_A1       :AL MG:VA:
 HCP_A3       :AL MG:VA:
 DIAMOND_A4  :AL:
 ALMG_BETA   :AL:MG:
 ALMG_DZETA  :AL:MG:
 ALMG_UPSILON :AL:MG:
 AL12MG17    :MG:AL MG:AL MG:
TDB_DALMGSI: rej p *
 LIQUID:L                FCC_A1                  HCP_A3
 DIAMOND_A4              ALMG_BETA               ALMG_DZETA
 ALMG_UPSILON            AL12MG17  REJECTED
TDB_DALMGSI:
     *) Solid Al  is fcc and solid Mg is hcp.
TDB_DALMGSI: rest p liq fcc hcp
 LIQUID:L                FCC_A1                  HCP_A3
   RESTORED
TDB_DALMGSI: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'N Saunders, COST project (1994); MG-SI'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R
```

```
 -OK-
TDB_DALMGSI: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Set conditions for only the liquid phase.

```
POLY_3: s-c P=101325 T=973 N=1 x(Mg)=.3
POLY_3: ch-st p hcp fcc=sus
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You like to step across the whole system.

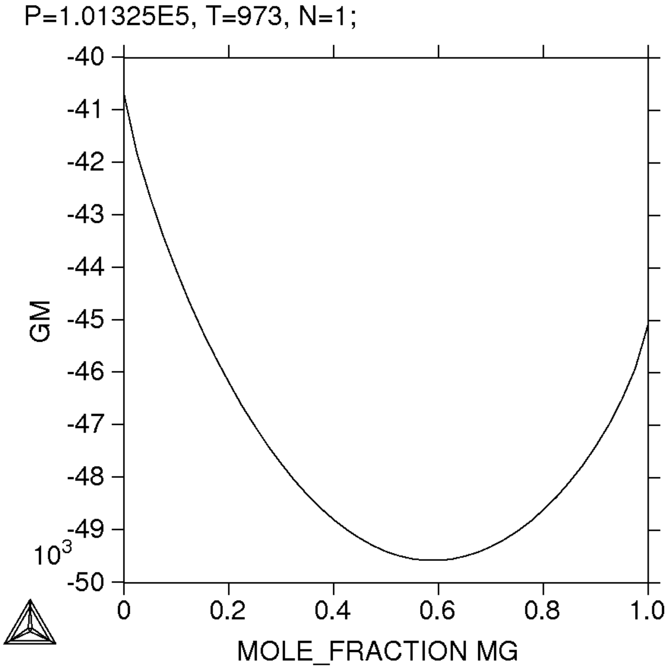
```
POLY_3: s-a-v 1 x(Mg)
Min value /0/:  0
Max value /1/:  1
Increment /.025/:  .025
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from   0.300000     for:
     LIQUID
 Calculated    31 equilibria

 Phase Region from   0.300000     for:
     LIQUID
 Calculated    15 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Now you go to the postprocessor for plotting some property across the system. You can choose any property of the liquid phase. You are asked to choose the molar Gibbs energy.

```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a x m-f Mg
POST:
```

*) m-f stands for mole fraction. In this case it could just as well be written x(Mg).

```
POST: s-d-a y Gm
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



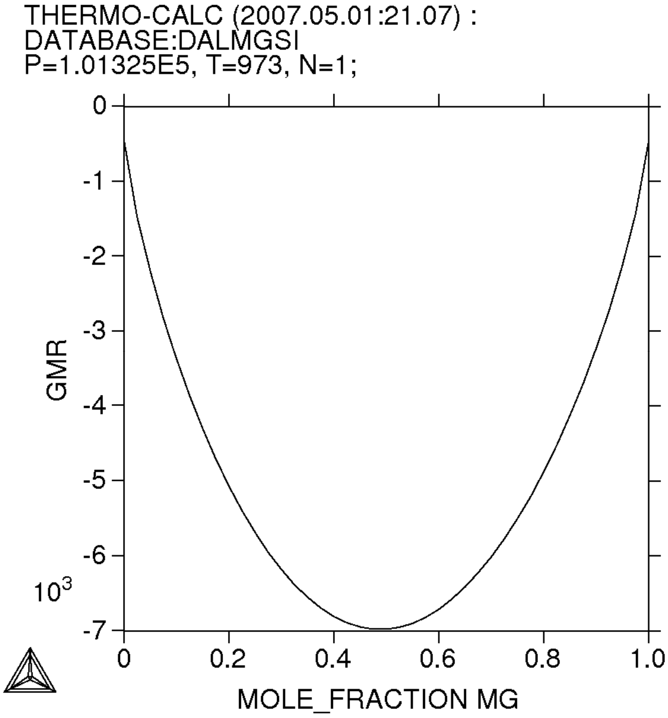
```
POST:
```

*) If you like to give G_m with reference to the pure components at temperature, then you must go back to POLY and **set** new **ref**erences. However, you can only use phases that you have included in the data set. Actually, you did include hcp and fcc and it does not matter that they are suspended at the present time.

```
POST: b
POLY_3: set-ref
Component: Al
Reference phase: fcc
Temperature /*/:  *
Pressure /1E5/:  1E5
POLY_3: set-ref Mg hcp
Temperature /*/:  *
Pressure /1E5/:  1E5
POLY_3: post
POST:
```

*) The new references will be applied if you add the letter **r** to the symbol. You only need to redefine the axis you like to change.

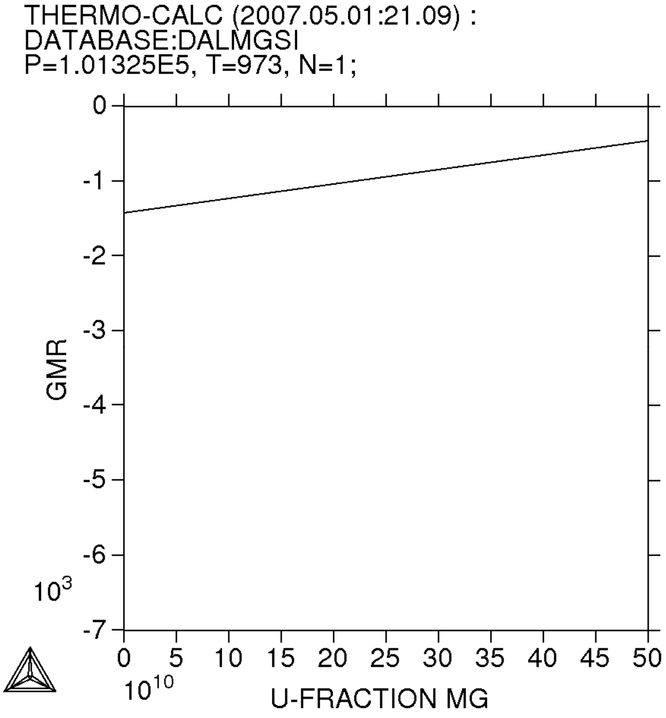
```
POST: s-d-a y Gmr

POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Now change the x axis to the z fraction. In POST it is regarded as a u fraction with only one element in the denominator.

```
POST: s-d-a x u-fr
FOR COMPONENT : Mg
COMPONENTS IN DENOMINATOR : /AL MG/:  Al
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```

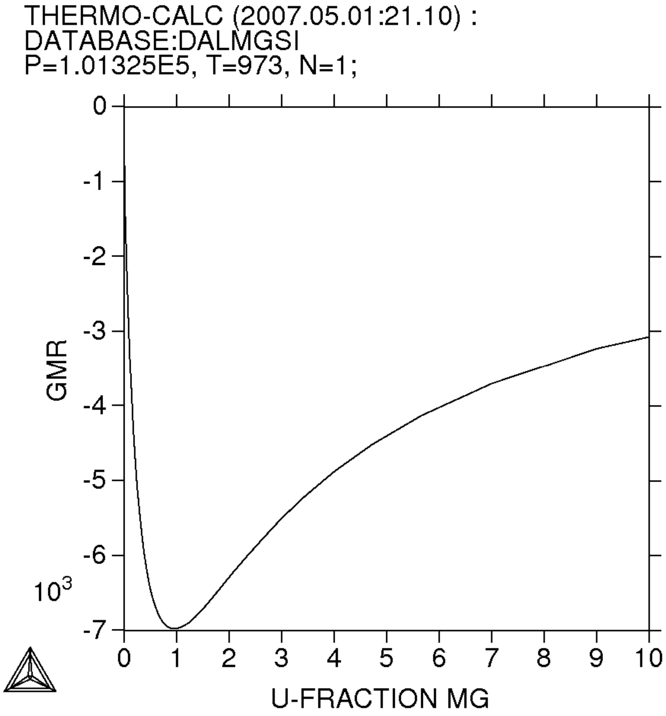


```
POST:
```

*) Here you can see the character of the z variable. It is defined as x_{Mg}/x_{Al}. On the right-hand side of the diagram $x_{Fe}=2\cdot 10^{-12}$, an extremely pure Mg. In the part of the system displayed here, the curve is almost straight and it will continue to infinity. It is not of any practical interest.

If you are not satisfied with a plot, you can always **s**et the **s**caling **s**tatus of an axis differently. The options are Y for yes to automatic scaling which you just had. N means no and you can give the extension of the axis.

```
POST: s-s-s x
AUTOMATIC SCALING  (Y OR N) /N/:
MIN VALUE : 0
MAX VALUE : 10
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            0  seconds
```

Comment

When using the z fraction as an axis variable, you must select the scaling with care.

You may know that a negative curvature of a molar Gibbs energy curve indicates that the system is unstable in that range of composition. A large part of the last diagram shows a negative curvature but the system is the same for which the first diagram showed a positive curvature everywhere. The explanation is that one should not combine the ordinary molar Gibbs energy with the z fraction. Fig. 4.7(b) in the book shows what kind of molar Gibbs energy should be used in combination with the z variable.

4.6. Different sets of components

Explore what facilities your data bank system has for changing the set of components and try it on a gas with the H_2, O_2 and H_2O species.

Hint

In general, the atoms of the elements are defined as the components but there may be a possibility to change this choice. At equilibrium it would be a trivial change because the chemical potential of a species containing several atoms is equal to the sum of the chemical potentials of all the atoms. However, there may sometimes be a practical advantage, e.g. for a system containing a stoichiometric phase or for the gas phase where one may like to treat a species as a component.

Instructions for using T-C

In POLY you can introduce a new set of components with the command "define-components". The whole new set should be given on one line. There is some limitation to this possibility. The new component must already be present as species. Furthermore, one cannot make a change in the middle of a session. A change would automatically erase what has been done so far in POLY.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw Psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-sp O2 H2 H2O1
 O2                      H2                       H2O1
   DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 GAS:G       :H2 O2 H2O1:
  > Gaseous Mixture, using the ideal gas model
 H2O_L       :H2O1:
TDB_PSUB: rej p H2O_L
 H2O_L  REJECTED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R
```

```
 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Here at the beginning of the session in POLY you should define the new components. You should list the complete set of components to be used. The number of components must be the same as before, i.e. the same as the number of elements. In the present case you like to introduce H2O1 as a component and can decide to retain H or O as the second one.

```
POLY_3: def-comp H H2O1
POLY_3:
```

*) Now you must use the new set of components when defining the conditions.

```
POLY_3: s-c P=101325 T=1000 N(H)=2 N(H2O1)=3
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:  NX
 Output from POLY-3, equilibrium =     1, label A0  , database: PSUB

 Conditions:
 P=1.01325E5, T=1000, N(H)=2, N(H2O1)=3
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  5.00000E+00,  Mass  5.60602E+01
 Total Gibbs energy -1.50952E+06,  Enthalpy -6.26674E+05,  Volume  3.28231E-01

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 H                        2.0000E+00 4.0000E-01 7.9613E-05 -7.8475E+04 SER
 H2O1                     3.0000E+00 6.0000E-01 2.8201E-24 -4.5086E+05 SER

 GAS                         Status ENTERED     Driving force  0.0000E+00
 Number of moles 5.0000E+00, Mass 5.6060E+01         Mole fractions:
 H2O1  6.00000E-01  H     4.00000E-01
 Constitution:
 H2O1  7.50000E-01  H2    2.50000E-01  O2    6.72972E-20
POLY_3: sh mu(O2)

 *** ERROR  1622 IN QGSCMA
 *** NO SUCH COMPONENT
POLY_3:
```

*) O2 is not a component and never was.

```
POLY_3: sh mu(O)

 *** ERROR  1622 IN QGSCMA
 *** NO SUCH COMPONENT
POLY_3:
```

*) O was a component initially but was replaced by H2O1. The operation mu(component) only accepts members of the current set of components. The values for other components must be evaluated from those of the current set.

```
POLY_3: ent-sym var muO2=2*mu(H2O1)-4*mu(H)
POLY_3: sh muO2
 MUO2=-587812.38
POLY_3:
```

*) This worked because muO2 is now a symbol, not an operation. Now, try something else.

```
POLY_3: sh mu(O2,gas)
 MU(O2,GAS)=-367045.45
POLY_3:
```

*) This is something different but may easily be mistaken for mu(O2). See the following explanation.

```
POLY_3: ent-sym var RTln=8.31451*T*LOG(y(gas,O2));
POLY_3: sh RTln
 RTLN=-367045.45
POLY_3:
```

*) y(gas,O2) is the fraction of O2 species in the gas. The database uses an ideal gas model and the chemical potential of a species is then equal to RTln(fraction) if the pure species as a gas of the same T and P is used as reference. The difference from the value of the symbol muO2 is thus the chemical potential of pure O2 at the current T and P given with the SER reference.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

A change of components can be justified by the fact that they are the only ones that can be used as independent state variables. Their fractions and amounts can be used to define conditions and also their chemical potentials and other partial derivatives with respect to their amounts. Furthermore, those quantities can be evaluated directly after computing the state of equilibrium.

4.7. Constitution and constituents

Consider an Fe alloy with 5 mass% Cr and 2 mass% C at 1000°C and 1 atm. Compute the equilibrium and evaluate all the state variables that are required for describing (1) the composition and (2) the constitution.

Hint

Of course, one must first compute the equilibrium. The method of showing the composition and the constitution may be different in different data bank systems.

Instructions for using T-C

POLY has several options for listing the compositions and constituents for the state of equilibrium. The purpose of this exercise is to make you familiar with these options and the information they offer.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1
```

```
 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                      CR                      C
   DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  SIGMA                   CEMENTITE
 M3C2                    M7C3                    M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p bcc fcc gra M23 M7
 BCC_A2                  FCC_A1                  GRAPHITE
 M23C6                   M7C3  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           56
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1273 N=1 w(Cr)=.05 w(C)=.02
POLY_3: c-e
 Using global minimization procedure
 Calculated        59082  grid points in            1  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     1  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) C indicates that only the compositions of the phases will be shown, not their constitutions. W indicates that they will be shown as mass fraction of the components.

```
Options /VWCS/: VWCS
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1273, N=1, W(CR)=5E-2, W(C)=2E-2
 DEGREES OF FREEDOM 0
```

```
 Temperature 1273.00 K ( 999.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.18689E+01
 Total Gibbs energy -6.12608E+04,  Enthalpy  3.81695E+04,  Volume  6.77812E-06

 Component                 Moles      W-Fraction Activity   Potential   Ref.stat
 C                         8.6369E-02 2.0000E-02 9.4825E-02 -2.4934E+04 SER
 CR                        4.9878E-02 5.0000E-02 2.1360E-04 -8.9453E+04 SER
 FE                        8.6375E-01 9.3000E-01 2.5358E-03 -6.3265E+04 SER

 FCC_A1                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.3598E-01, Mass 4.4371E+01         Mass fractions:
 FE  9.57428E-01  CR  2.88585E-02  C   1.37132E-02

 M23C6                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.4497E-01, Mass 6.7035E+00         Mass fractions:
 FE  7.89335E-01  CR  1.56923E-01  C   5.37420E-02

 M7C3                         Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.9051E-02, Mass 7.9407E-01         Mass fractions:
 FE  5.84828E-01  CR  3.28724E-01  C   8.64486E-02
POLY_3:
```

*) To the right on the previous line it is confirmed that the composition of each phase is given as mass fraction. This may be convenient for checking with practical experience. e.g. fcc is shown to have 1.37 mass% C, which seems reasonable at 1000°C. Try another option.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/: X
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1273, N=1, W(CR)=5E-2, W(C)=2E-2
 DEGREES OF FREEDOM 0

 Temperature 1273.00 K ( 999.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.18689E+01
 Total Gibbs energy -6.12608E+04,  Enthalpy  3.81695E+04,  Volume  6.77812E-06

 Component                 Moles      M-Fraction Activity   Potential   Ref.stat
 C                         8.6369E-02 8.6369E-02 9.4825E-02 -2.4934E+04 SER
 CR                        4.9878E-02 4.9878E-02 2.1360E-04 -8.9453E+04 SER
 FE                        8.6375E-01 8.6375E-01 2.5358E-03 -6.3265E+04 SER

 FCC_A1                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.3598E-01, Mass 4.4371E+01         Mole fractions:
 FE  9.09942E-01  C   6.05993E-02  CR  2.94585E-02

 M23C6                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.4497E-01, Mass 6.7035E+00         Mole fractions:
 FE  6.53552E-01  C   2.06897E-01  CR  1.39551E-01

 M7C3                         Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.9051E-02, Mass 7.9407E-01         Mole fractions:
 FE  4.36486E-01  C   3.00000E-01  CR  2.63514E-01
POLY_3:
```

*) Now the C content in fcc is given as mole fraction 0.0606, which is easy to compare with the site fraction 0.0645, which will be shown with the next option.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCS/:  N
```

```
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1273, N=1, W(CR)=5E-2, W(C)=2E-2
 DEGREES OF FREEDOM 0

 Temperature 1273.00 K ( 999.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.18689E+01
 Total Gibbs energy -6.12608E+04,  Enthalpy  3.81695E+04,  Volume  6.77812E-06

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        8.6369E-02 8.6369E-02 9.4825E-02 -2.4934E+04 SER
 CR                       4.9878E-02 4.9878E-02 2.1360E-04 -8.9453E+04 SER
 FE                       8.6375E-01 8.6375E-01 2.5358E-03 -6.3265E+04 SER

 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.3598E-01, Mass 4.4371E+01         Mole fractions:
 FE  9.09942E-01  C   6.05993E-02  CR  2.94585E-02
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  9.68641E-01  CR  3.13588E-02
 Sublattice  2,  Number of sites  1.0000E+00
 VA  9.35492E-01  C   6.45085E-02

 M23C6                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.4497E-01, Mass 6.7035E+00         Mole fractions:
 FE  6.53552E-01  C   2.06897E-01  CR  1.39551E-01
 Constitution:
 Sublattice  1,  Number of sites  2.0000E+01
 FE  8.22629E-01  CR  1.77371E-01
 Sublattice  2,  Number of sites  3.0000E+00
 FE  8.33476E-01  CR  1.66524E-01
 Sublattice  3,  Number of sites  6.0000E+00
 C   1.00000E+00

 M7C3                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.9051E-02, Mass 7.9407E-01         Mole fractions:
 FE  4.36486E-01  C   3.00000E-01  CR  2.63514E-01
 Constitution:
 Sublattice  1,  Number of sites  7.0000E+00
 FE  6.23552E-01  CR  3.76448E-01
 Sublattice  2,  Number of sites  3.0000E+00
 C   1.00000E+00
POLY_3:
```

*) With the option **N** the constitution for each phase is given below the composition. The constitution is described with the site fractions for the constituents in each sublattice. E.g. M23C6 is described with three sublattices and Cr resides in two of them. C resides in the third one and is there alone.

In fcc C resides in the second sublattices together with vacancies. The site fraction is y(fcc,C#2)=0.0645. This is the same amount of C that on the first line for fcc is given as 1.37 mass% C. In order to see the close connection of these two values it should be better to use the option **X** instead of **W**.

It is worth noting that the list also gives the number of sites on each sublattice in one formula unit, e.g. 20 and 3 for the two sublattices where Cr resides in M23C6.

```
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXNS/:  P
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC
```

```
 Conditions:
 P=1.01325E5, T=1273, N=1, W(CR)=5E-2, W(C)=2E-2
 DEGREES OF FREEDOM 0

 Temperature 1273.00 K ( 999.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.18689E+01
 Total Gibbs energy -6.12608E+04,  Enthalpy  3.81695E+04,  Volume  6.77812E-06

 Component               Moles      M-Fraction Activity   Potential   Ref.stat
 C                       8.6369E-02 8.6369E-02 9.4825E-02 -2.4934E+04 SER
 CR                      4.9878E-02 4.9878E-02 2.1360E-04 -8.9453E+04 SER
 FE                      8.6375E-01 8.6375E-01 2.5358E-03 -6.3265E+04 SER

 BCC_A2                     Status ENTERED     Driving force -7.1981E-02
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 FE  9.73415E-01  CR  1.78884E-02  C   8.69627E-03
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  9.81955E-01  CR  1.80453E-02
 Sublattice  2,  Number of sites  3.0000E+00
 VA  9.97076E-01  C   2.92419E-03

 FCC_A1                     Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.3598E-01, Mass 4.4371E+01         Mole fractions:
 FE  9.09942E-01  C   6.05993E-02  CR  2.94585E-02
 Constitution:
 Sublattice  1,  Number of sites  1.0000E+00
 FE  9.68641E-01  CR  3.13588E-02
 Sublattice  2,  Number of sites  1.0000E+00
 VA  9.35492E-01  C   6.45085E-02

 GRAPHITE                   Status ENTERED     Driving force -4.5776E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  FE  0.00000E+00  CR  0.00000E+00
 Constitution:
 C  1.00000E+00

 M23C6                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.4497E-01, Mass 6.7035E+00         Mole fractions:
 FE  6.53552E-01  C   2.06897E-01  CR  1.39551E-01
 Constitution:
 Sublattice  1,  Number of sites  2.0000E+01
 FE  8.22629E-01  CR  1.77371E-01
 Sublattice  2,  Number of sites  3.0000E+00
 FE  8.33476E-01  CR  1.66524E-01
 Sublattice  3,  Number of sites  6.0000E+00
 C   1.00000E+00

 M7C3                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.9051E-02, Mass 7.9407E-01         Mole fractions:
 FE  4.36486E-01  C   3.00000E-01  CR  2.63514E-01
 Constitution:
 Sublattice  1,  Number of sites  7.0000E+00
 FE  6.23552E-01  CR  3.76448E-01
 Sublattice  2,  Number of sites  3.0000E+00
 C   1.00000E+00
POLY_3:
```

*) With the option **P** you can also inspect the situation for phases not taking part in the equilibrium. Both bcc and graphite are listed with negative driving forces, confirming that they should not take part in the equilibrium. You should note that the compositions and

constituents given for these unstable phases are their most favourable compositions. If conditions were gradually changed to their advantage, they would thus be able to form as soon as their most favourable compositions make them stable. If a phase has been made dormant, it could show a positive driving force. Then one could expect it to form and it should preferably nucleate with the composition and constitution shown in the list.

```
POLY_3: exit
 CPU time            1  seconds
```

Comments

Here you learned about various options for the presentation of compositions and constituents. However, many other quantities are available, e.g. U, V, H, S, F and G and their molar quantities, U_m etc. In addition, the quantities per mole of formula unit, U_f etc. can be evaluated. By entering a symbol for a variable or function one can evaluate the value of many algebraic expressions involving the simple quantities and also involving the operator "." to give partial derivatives.

4.8. Chemical potentials in a phase with sublattices

Evaluate the equilibrium distribution of Cu and Zn between the two sublattices in an ordered bcc alloy of Cu with 50 mass% Zn at 400^{o}C and 1 atm. Then, apply this distribution to 500^{o}C and evaluate the driving force for redistribution of the elements in the direction of the new equilibrium distribution by evaluating the diffusion potentials in each sublattice and taking the difference.

Hint

The method may be different in different data bank systems.

Instructions for using T-C

There is no quick and safe way to evaluate properties of non-equilibrium states from POLY. You may use the tabulation module TAB, which allows you to define any constitution, even non-equilibrium ones. First you should go to POLY and compute equilibrium at 673 K. When you then go to TAB, the computed constitution will appear as default even if you change the temperature. You can thus tabulate the non-equilibrium properties at 773 K, among which you find G expressed per formula unit. Save the value under the symbol G1. Then you make a minute change of site fractions for one of the sublattices without changing its total amount of atoms. Again, tabulate the properties and save the G value under the symbol G2. The diffusion potential is then obtained as the difference G2-G1, divided by the minute change of site fraction. You should also divide by the stoichiometric coefficient of that sublattice in order to express the potential per mole of atoms. You find them in the listed constitution. Then you make a minute change of the site fractions in the other sublattice and repeat the procedure. Save this G value as G3 and use G3-G1. The driving force for redistribution is the difference between the two results.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
```

```
TDB_DALMGSI: sw Pbin
 Current database: TCS Public Binary Alloys TDB v1

 VA                      /-  DEFINED
 IONIC_LIQ:Y             L12_FCC                 B2_BCC
 BCC_B2  REJECTED
TDB_PBIN: def-el Cu Zn
 CU                      ZN  DEFINED
TDB_PBIN: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  ALCU_EPSILON            ALCU_ETA
 CUZN_EPS                CUZN_GAMMA  REJECTED
TDB_PBIN: rest p bcc_A2 B2
 BCC_A2                  B2_BCC  RESTORED
TDB_PBIN:
```

*) BCC_A2 is the ordinary disordered bcc phase. The present problem concerns ordered bcc, which means that the compositions are different on two sublattices that did not have to be considered in the disordered bcc. In the present database, the ordered bcc is described with an addition to the disordered one. That addition has the symbol B2_BCC. By restoring both you get a complete description of the ordered bcc, which has the crystallographic symbol B2.

```
TDB_PBIN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            8
 FUNCTIONS ....

 List of references for assessed data

   91Din 'A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, Vol.15,
       No.4, pp.317-425, (1991)'
   KOW-CUZN 'M Kowalski and P Spencer, J Phase Equil, p 432-438 (1993); CU-ZN'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PBIN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=673 N=1 w(Zn)=.5
POLY_3: c-e
 Using global minimization procedure
 Calculated        19648  grid points in            1  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     1  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:  N
 Output from POLY-3, equilibrium =     1, label A0  , database: PBIN

 Conditions:
 P=1.01325E5, T=673, N=1, W(ZN)=0.5
 DEGREES OF FREEDOM 0

 Temperature  673.00 K ( 399.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  6.44500E+01
 Total Gibbs energy -4.20109E+04,  Enthalpy -2.31663E+02,  Volume  0.00000E+00
```

```
 Component                 Moles      W-Fraction Activity   Potential   Ref.stat
 CU                        5.0711E-01 5.0000E-01 1.3757E-03 -3.6869E+04 SER
 ZN                        4.9289E-01 5.0000E-01 2.1321E-04 -4.7301E+04 SER

 B2_BCC                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 6.4450E+01         Mass fractions:
 CU  5.00000E-01  ZN  5.00000E-01
 Constitution:
 Sublattice  1,  Number of sites  5.0000E-01
 CU  2.53268E-01  ZN  7.46732E-01
 Sublattice  2,  Number of sites  5.0000E-01
 CU  7.60957E-01  ZN  2.39043E-01
 Sublattice  3,  Number of sites  3.0000E+00
 VA  1.00000E+00
POLY_3:
```

*) Where the list gives the constitution, it starts by giving the number of sites in each sublattice and that define the formula unit used in the database and thus in the tabulation module, $(Cu,Zn)_{0.5}(Cu,Zn)_{0.5}$. The third sublattice is for interstitials and does not apply here.

You have now established a constitution, which will represent a non-equilibrium when the temperature is soon changed to 773 K. That must be done in the tabulation module. In POLY the constitution would change to a new equilibrium.

```
POLY_3: go tab
TAB:
```

*) The name of the bcc phase is here B2_BCC

```
TAB: tab-sub B2
SPECIFY SUBLATTICE (0 FOR ALL) /0/:
 FRACTIONS IN SUBLATTICE           1
CU /.2532682732/:  .2532682732
 FRACTIONS IN SUBLATTICE           2
CU /.7609569413/:  .7609569413
Pressure /101325/:
Low temperature limit /298.15/:  773
High temperature limit /2000/:  773
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T  F R O M  T H E R M O - C A L C
               2007. 3.28                           18.33.19



 Phase : B2_BCC                      Pressure :      101325.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
   773.00   2.91794E+01   2.64468E+03   6.60623E+01  -4.84215E+04
   773.00   2.91794E+01   2.64468E+03   6.60623E+01  -4.84215E+04

TAB:
```

*) You go back to POLY just to be able to store the Gibbs energy value for the initial constitution. Then you return to TAB and study the effect of a slight change of the constitution.

```
TAB: b
POLY_3: ent-sym var G1=-4.84215E+04;
POLY_3: b
```

```
TAB:
```

*) Now, increase the Cu fraction on sublattice #1 by 0.001.

```
TAB: tab-sub B2
SPECIFY SUBLATTICE (0 FOR ALL) /0/:
 FRACTIONS IN SUBLATTICE            1
CU /.2532682732/:  .2542682732
 FRACTIONS IN SUBLATTICE            2
CU /.7609569413/:
Pressure /101325/:
Low temperature limit /773/:
High temperature limit /773/:
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 3.28                           18.33.19



 Phase : B2_BCC                     Pressure :      101325.00
 Specie: *

 *******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 *******************************************************************************
  773.00   2.91778E+01   2.65049E+03   6.60631E+01  -4.84163E+04
  773.00   2.91778E+01   2.65049E+03   6.60631E+01  -4.84163E+04

TAB: b
POLY_3: ent-sym var G2=-4.84163E+04;
POLY_3: b
TAB:
```

*) Now, increase the Cu fraction on sublattice #2 by .001.

```
TAB: tab-sub B2
SPECIFY SUBLATTICE (0 FOR ALL) /0/:
 FRACTIONS IN SUBLATTICE            1
CU /.2542682732/:  .2532682732
 FRACTIONS IN SUBLATTICE            2
CU /.7609569413/:  .7619569413
Pressure /101325/:
Low temperature limit /773/:
High temperature limit /773/:
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 5.25                           13.41.28



 Phase : B2_BCC                     Pressure :      101325.00
 Specie: *

 *******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 *******************************************************************************
  773.00   2.91778E+01   2.64423E+03   6.60538E+01  -4.84154E+04
  773.00   2.91778E+01   2.64423E+03   6.60538E+01  -4.84154E+04
```

```
TAB: b
POLY_3: ent-sym var G3=-4.84154E+04;
POLY_3:
```

*) The increase of the Cu content by 0.001, and a corresponding decrease of the Zn content, has thus given a larger change for sublattice #1 than for sublattice #2. There would thus be a driving force for an exchange between the two sublatices. Evaluate the diffusion potentials for the two sublattices and obtain the driving force for a change of the constitution towards a new equilibrium from their difference. Remember how the formula unit was defined, , $(Cu,Zn)_{0.5}(Cu,Zn)_{0.5}$, To make the result apply to one mole you should divide with the stoichiometric coefficient, 0.5 for both sublattices.

```
POLY_3: ent-sym var diffP1=(G2-G1)/.001/0.5;
POLY_3: ent-sym var diffP2=(G3-G1)/.001/0.5;
POLY_3: ent-sym var drivF=diffP2-diffP1;
POLY_3: eval
Name(s):
 G1=-48421.5
 G2=-48416.3
 G3=-48415.4
 DIFFP1=10400.
 DIFFP2=12200.
 DRIVF=1800.
POLY_3: exit
 CPU time            1  seconds
```

Comments

1) The Gibbs energy of non-equilibrium constitutions can be obtained from the tabulation module.

2) The driving force for changing back towards the equilibrium constitution is obtained from the difference in diffusion potential for the two sublattices.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

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Chapter 5. Thermodynamics of processes

Problem 5.1A. Thermodynamic treatment of kinetics of internal processes
Problem 5.1B. Thermodynamic treatment of kinetics of internal processes
Problem 5.5. Chemical reaction

5.1A. Thermodynamic treatment of kinetics of internal processes

Evaluate the thermodynamic force for the solidification of pure liquid Mo to bcc at 2800 K and 1 atm. The melting point of Mo is 2896 K. Suppose the reaction is so rapid that there is no heat exchange with the surroundings.

Hint

1) The first law gives $dH=dQ+VdP=0$ in this case and the second law gives $dS=dQ/T+d_{ip}S= d_{ip}S=(d_{ip}S/df)df=Xdf$ where X is the thermodynamic force. Suppose a small fraction, Δf , solidifies. Some heat of melting will be deliberated and will heat the system to a temperature determined by the condition that H is constant. After finding that temperature you may evaluate $X = d_{ip}S / df = dS / df \cong \Delta S / \Delta f$.

2) The new temperature may be found by introducing Δf and guessing a value of the adiabatic T and evaluating ΔH there. By extrapolation you can then find the correct temperature where $\Delta H = 0$. Then you can evaluate S at that temperature and obtain $X \cong \Delta S / \Delta f$.

Instruction for using T-C

Normally, POLY cannot give properties of a non-equilibrium state. However, if the non-equilibrium concerns the relation between two phases but does not concern the internal structure of the individual phases, then POLY can give the properties of each one of the phases and you can then add them.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PURE4
 Current database: SGTE Unary (Pure Elements) TDB v4

 VA                      /-  DEFINED
TDB_PURE4: def-el Mo
 MO  DEFINED
```

```
TDB_PURE4: rej p *
 BCC_A2                  FCC_A1                  HCP_A3
 LIQUID:L  REJECTED
TDB_PURE4: rest p bcc liq
 BCC_A2                  LIQUID:L  RESTORED
TDB_PURE4: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.4), developed by
      SGTE (Scientific Group Thermodata Europe), 1991-2003, and provided by
      TCSAB (Aug. 2003). '

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PURE4: go pol

 POLY version  3.32,  Aug 2001
POLY_3: ch-st p bcc=dor
POLY_3: s-c P=101325 T=2800 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var S1=S;
POLY_3: ent-sym var H1=H;
POLY_3:
```

*) Introduce the amount of liq in a two-phase state with 0.001 mole fraction solid.

```
POLY_3: s-c N=.999
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
POLY_3:
```

*) Save H for the liquid constituent at 2800 K and continue with the solid constituent.

```
POLY_3: ent-sym var HL2=H;
POLY_3: s-c N=.001
POLY_3: ch-st p bcc=ent 1
POLY_3: ch-st p liq=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3:
```

*) Evaluate and save H for this two-phase state at 2800 K.

```
POLY_3: ent-sym var H2=H+HL2;
POLY_3:
```

*) Guess the adiabatic temperature and evaluate H for the same state at that temperature, starting with the solid constituent.

```
POLY_3: s-c T=2801
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var HS3=H;
```

```
POLY_3: s-c N=0.999
POLY_3: ch-st p bcc=dor
POLY_3: ch-st p liq=ent 1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in           0  s
POLY_3: ent-sym var H3=H+HS3;
POLY_3:
```

*) Now you could evaluate the difference in H between the pure liquid at 2800 K, H1, and the two-phase state at 2801 K. The difference should be zero for the actual adiabatic temperature. Your guess of 2801 K was thus good but not good enough. You find the real adiabatic temperature by interpolation.

```
POLY_3: ent-sym var T4=2800+1*(H2-H1)/(H2-H3);
POLY_3: sh T4
 T4=2800.912
POLY_3:
```

*) It remains to evaluate S for the two-phase non-equilibrium state at the adiabatic temperature. Again you have to find H for each constituent separately and add them.

```
POLY_3: s-c T=T4
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in           0  s
POLY_3: ent-sym var SL4=S;
POLY_3: s-c N=.001
POLY_3: ch-st p bcc=ent 1
POLY_3: ch-st p liq=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in           0  s
POLY_3: ent-sym var S4=S+SL4;
POLY_3:
```

*) Finally, you can evaluate the thermodynamic force under adiabatic conditions, using the relation give in the hint.

```
POLY_3: ent-sym var TFad=(S4-S1)/.001;
POLY_3: sh S4 TFad
 S4=109.41408
 TFAD=0.44710169
POLY_3: exit
 CPU time            0  seconds
```

Comment

You should realize that the driving force is equal to T times the thermodynamic force under isothermal conditions. However, there is no such relation in the present case where the temperature is not fixed. The concept of driving force, as we have defined it, does not apply to non-isothermal cases. However, compare with Problem 5.1B that gives a different aspect.

5.1B. Thermodynamic treatment of kinetics of internal processes

Do the same under isothermal conditions. Compare the results and explain.

Hint

For the isothermal case you can start by evaluating the driving force, DF, from the difference in Gibbs energy. Then you get the thermodynamic force TF=DF/T.

Instructions for using T-C

Again you can get the properties of the individual phases by treating each of them as a separate system, considering its amount.

Prompts, commands and responses

```
sys: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PURE4
 Current database: SGTE Unary (Pure Elements) TDB v4

 VA                      /-  DEFINED
TDB_PURE4: def-el Mo
 MO  DEFINED
TDB_PURE4: rej p *
 BCC_A2                  FCC_A1                  HCP_A3
 LIQUID:L  REJECTED
TDB_PURE4: rest p bcc liq
 BCC_A2                  LIQUID:L  RESTORED
TDB_PURE4: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.4), developed by
      SGTE (Scientific Group Thermodata Europe), 1991-2003, and provided by
      TCSAB (Aug. 2003). '

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PURE4: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Investigate the initial purely liquid state and store its G.

```
POLY_3: ch-st p bcc=dor
POLY_3: s-c P=101325 T=2800 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var G1=G;
POLY_3:
```

*) Investigate a two-phase state and for convenience you may again choose a mole fraction of 0.001 solid constituent. This is a non-equilibrium state and the properties must be obtained by

adding the contributions from the individual phases. Start with the liquid because the solid is already dormant.

```
POLY_3: s-c N=.999
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
POLY_3: ent-sym var GL2=G;
POLY_3:
```

*) Continue with the solid constituent.

```
POLY_3: ch-st p bcc=ent 1
POLY_3: ch-st p liq=dor
POLY_3: s-c N=.001
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var GS2=G;
POLY_3: ent-sym var G2=GS2+GL2;
POLY_3:
```

*) Finally, you can evaluate the driving force and the thermodynamic force.

```
POLY_3: ent-sym var DF=(G1-G2)/.001;
POLY_3: ent-sym var TFiso=DF/2800;
POLY_3: sh TFiso DF
 TFISO=0.44942638
 DF=1258.3939
POLY_3: exit
 CPU time            0  seconds
```

Comment

1) Problem 5.1A gave a thermodynamic force of TFad = 0.44710169 under adiabatic conditions. Within the accuracy expected when one takes the difference between quantities of almost the same magnitude, this is an excellent agreement with the thermodynamic force under isothermal conditions, TFiso, obtained here. This is a confirmation of the arguments in Section 3.6 where it was claimed that the driving force for a change is a function of the state itself and not of how its conditions are controlled. Those conditions influence where the system is going but have no effect on the very first stage of the internal process when it cannot yet "feel" what external constraints (conditions) are applied on the system.

2) Even for a process that will change the temperature, it is thus possible to evaluate the thermodynamic force by first evaluating the driving force using the Gibbs energy at constant temperature and then just divide by the initial temperature.

5.5. Chemical reactions

Evaluate the driving force for the formation of more H_2O molecules in a gas with the constitution 5 mol% H_2O, 40 mol% H_2 and 55 mol% O_2 at 1 atm and 2000 K.

Hint

The driving force for the formation per mole of more H_2O is $\mu_{H_2} + 0.5 \cdot \mu_{O_2} - \mu_{H_2O}$ according to Eq. 5.62. The question is how your data bank system can give you values for the chemical potentials of a non-equilibrium gas.

Instructions for using T-C

POLY can only give properties for states of equilibrium. The database for the gas treats it as an ideal gas where the chemical potential of a species is given by its partial pressure, i.e., as if it were a pure gas of a pressure equal to its partial pressure. You can thus evaluate the chemical potential of a species by requiring that it is the only species present and give its partial pressure as the value to the total pressure.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PSUB
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el H O
 H                      O  DEFINED
TDB_PSUB: rej p *
 GAS:G                  H2O_L                  H2O2_L
   REJECTED
TDB_PSUB: rest p gas
 GAS:G  RESTORED
TDB_PSUB: rej sp *
 VA                     H                      O
 H1O1                   H1O2                   H2
 H2O1                   H2O2                   O2
 O3  REJECTED
TDB_PSUB: rest sp H2 O2 H2O1
 H2                     O2                     H2O1
   RESTORED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go tab
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /1/:  1
H2O1 /1/:  0
```

*) This will thus be pure H_2. It is not necessary to give the fraction of the last constituent. Give its partial pressure as the total pressure.

```
Pressure /100000/:  40000
Low temperature limit /298.15/:  2000
High temperature limit /2000/:
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 5.11                           22.27.19


 Phase : GAS                         Pressure :       40000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)       (Joule/K)     (Joule)
 ******************************************************************************
 2000.00   3.43045E+01   5.29300E+04   1.96016E+02  -3.39103E+05

TAB:
```

*) Go to POLY and save the value of G in the last column as the chemical potential for the H_2 constituent. Then, go back to TAB and do the same for O_2.

```
TAB: go pol

 POLY version  3.32,  Aug 2001
POLY_3: ent-sym var muH2=-3.39103E+05;
POLY_3: b
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /1/:  0
H2O1 /0/:  0
```

*) This gas has no H_2 and no H_2O. It is thus pure O_2. Give its partial pressure as the total pressure.

```
Pressure /40000/:  55000
Low temperature limit /2000/:
High temperature limit /2000/:
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 5.11                           22.27.19


 Phase : GAS                         Pressure :       55000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G
   (K)    (Joule/K)     (Joule)       (Joule/K)     (Joule)
 ******************************************************************************
 2000.00   3.78262E+01   5.91909E+04   2.73724E+02  -4.88258E+05

TAB: b
POLY_3: ent-sym var muO2=-4.88258E+05;
POLY_3:
```

*) This was the chemical potential of O_2. Finally, do the same for the H_2O constituent.

```
POLY_3: b
TAB: tab-sub gas
```

```
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /0/:  0
H2O1 /0/:  1
Pressure /55000/:  5000
Low temperature limit /2000/:
High temperature limit /2000/:
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 5.11                           22.27.20



 Phase : GAS                        Pressure :        5000.00
 Specie: *

 ******************************************************************************
    T      Cp             H             S             G
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 2000.00   5.16962E+01  -1.68705E+05   2.89916E+02  -7.48537E+05

TAB: b
POLY_3:
```

*) Now you can directly evaluate and store the difference in chemical potentials as the driving force.

```
POLY_3: ent-sym var D=muH2+.5*muO2-(-7.48537E+05);
POLY_3: sh D
 D=165305
POLY_3: exit
 CPU time             0  seconds
```

Comment

The positive driving force means that the reaction actually goes in the direction of forming more H_2O, which is not self-evident because the dissociation of H_2O into H_2 and O_2 is not negligible at such a high temperature.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

---

Chapter 6. Stability

6.5A. Limit of stability

Compare numerically the values of $(\partial T / \partial S)_{V,N}$ and $(\partial T / \partial S)_{P,N}$ for pure diamond at 1000 K and 1 atm. Both expressions are used for defining stability.

Hint

The only difference between the two partial derivatives is that different quantities are kept constant. They are thus based on different sets of independent state variables.

Instructions for using T-C

T-C has a special operator for the evaluation of partial derivatives with respect to a state variable that could be either a potential or an extensive variable. Sometimes it works best with the potential in the denominator. Try both ways in the present cases.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pgeo
 Current database: Saxena Pure Minerals Database v1

 O                        VA  DEFINED
 STEAM                    OXYGEN                   HYDROGEN
   REJECTED
 CARBON_MONOXIDE          CARBON_DIOXIDE           METHANE
   REJECTED
TDB_PGEO:
```

*) Notice that this database is mainly for oxides and O is thus defined automatically. However, you don't want to include O.

```
TDB_PGEO: rej-el O
 O  REJECTED
```

```
TDB_PGEO: def-el C
 C  DEFINED
TDB_PGEO: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 DIAMOND     :C1:
 GRAPHITE    :C1:
TDB_PGEO: rej p gra
 GRAPHITE  REJECTED
TDB_PGEO: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            1
 FUNCTIONS ....
 -OK-
TDB_PGEO: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You must define the system as given. That will directly give the correct set of independent variables for one of the derivatives.

```
POLY_3: s-c P=101325 T=1000 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var derP1=1/S.T;
```

*) In order to take the derivative with respect to S, that variable must be included in the set of independent variables, i.e., it must have been used as a condition for the state of equilibrium.

```
POLY_3: s-c T=none S=
Value /19.84063161/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var derP2=T.S;
```

*) You change to a new set of independent variables by introducing V instead of P.

```
POLY_3: s-c P=none S=none T=1000 V=
Value /3.436459517E-06/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            1  grid points in            0  s
   7 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var derV1=1/S.T;
POLY_3:
```

*) Finally, you should again introduce S as an independent variable.

```
POLY_3: s-c T=none S=
Value /19.84063161/:
POLY_3: ent-sym var derV2=T.S;
POLY_3: eval
Name(s):
 DERP1=46.544542
 DERP2=46.544542
 DERV1=47.169399
 DERV2=47.169399
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The two derivatives derV and derP have different values simply because there is a difference in what variables are kept constant.

2) They are both used for defining stability but it is known that the one using a potential as constant, instead of the conjugate extensive variable, should be smaller according to Eq. 6.30. That is indeed demonstrated by derP being smaller than derV.

3) It is interesting to see that $(\partial Y / \partial X) = 1/(\partial X / \partial Y)$ but in order to get this satisfactory result you must use different sets of independent variables by including X in the first case and Y in the second.

6.5B. Limit of stability

Evaluate the stability of a supersaturated fcc alloy of Fe with 20 mol% C at 1200 and 1000 K and 1 atm.

Hint

A system is least stable against fluctuations of one extensive state variable while all but one of the other conjugate pairs are represented by the potential. The exception is one that has been chosen to define the size of the system, e.g. N_i where *i* is the main component. The preferable expression for the stability of the system would thus be $B = 2(\partial\mu_c / \partial N_c)_{T,P,\mu_2,\ldots,\mu_{c-1},N_1}$. However, it should be remembered that inside an unstable region this quantity may again turn positive while other expressions of stability have turned negative. It should thus be used only inside a stable region and when approaching an unstable region.

Instructions for using T-C

T-C offers the possibility of evaluating the partial derivative of a state variable under constant values of a set of independent state variables. The first state variable may then be regarded as a state function, function of that set of variables. You can make that evaluation by using those constant values as conditions for the equilibrium.

When the partial derivative represents a stability condition, then the denominator is an extensive variable and in order to define the size of the system one of the variables to be kept constant must also be extensive and one may choose the amount of the main component, N_1. For a binary case one may choose T and P as the remaining independent variables. Usually, one may thus have a proper set of independent variables from the beginning and for a binary system one may thus evaluate the stability without changing the set of variables.

For a binary A-B system you can directly use the given T, P, N_A and N_B as conditions and that would be a complete set of independent variables.

Prompts, commands and responses

```
SYS: go da
```

```
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C
   DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE
GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc
 FCC_A1  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          29
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Remember not to give the composition of the system with x_C and N. You need N_C and N_{Fe} when later evaluating the partial derivative.

```
POLY_3: s-c P=101325 T=1200 N(C)=.2 N(Fe)=.8
POLY_3: c-e
 Using global minimization procedure
 Calculated        19648  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Introduce a function for the stability because you will use it several times.

```
POLY_3: ent-sym fun stab=mu(C).N(C);
POLY_3: sh stab

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
```

```
 If possible enter derivatives as VARIABLES instead

 STAB=153193.58
POLY_3: s-c T=1000
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: sh stab

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STAB=142107.57
POLY_3: s-c T=800
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: sh stab

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STAB=131021.55
POLY_3:
```

*) You have thus found that the stability decreases at lower temperatures. Can that be taken as an indication that you are approaching a miscibility gap that exists at higher C contents that widens towards lower temperatures? Examine the stability for higher C contents at 800 K.

```
POLY_3: s-c N(C)=.3 N(Fe)=.7
POLY_3: c-e
POLY_3: sh stab

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STAB=137861.05
POLY_3: s-c N(C)=.4 N(Fe)=.6
POLY_3: c-e
POLY_3: sh stab

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STAB=165457.06
POLY_3: exit
 CPU time            4  seconds
```

Comments

1) The stability for this C content decreases at lower temperatures but that is not a sign of a miscibility gap at higher C contents and lower temperatures.

2) It is not possible to step in N(C) in order to get a curve for the stability as function of the C content. The reason is that one would also have to adjust the value of N(Fe), which is not possible in POLY's stepping procedure. To set the condition for Fe as N=1 does not help because the stability can be evaluated only if N(Fe) is used as a condition, i.e. as an independent variable.

6.5C. Limit of stability

The stability can be defined in many ways. Each method expresses the stability in its own way and the resulting values for the same case may differ appreciably. However, there are two general principles. 1) A method using a set of independent variables containing a potential gives a lower value than a method using the conjugate extensive variable. 2) At the limit of stability all methods using potentials except for two extensive variables give the value zero. Test if your data bank system can confirm the first principle. The second one will be tested in Problem 6.5D.

Hint

You may consider the bcc phase in the Fe-Cr-C system at 1 atm and 700 K and for 1 mol% C and 5 mol% Cr.

Instructions for using T-C

1) Always start by first computing the equilibrium for the given composition and then changing the condition for one of the contents to a condition for another variable. Then you should compute the same equilibrium with this new definition and finally evaluate the stability using the "." operator.

2) Start by examining methods based on $\partial\mu_{Cr} / \partial N_{Cr}$ where T, P and two quantities related to Fe and C are kept constant. Try the combinations (N_C;N_{Fe}), (N_C;x_{Fe}), (N_C;μ_{Fe}), (μ_C;μ_{Fe}), (x_C;μ_{Fe}) and (x_C;x_{Fe}).

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                       CR                       C
   DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   SIGMA                    CEMENTITE
```

```
 M3C2                    M7C3                    M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           33
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You like to know the stability at a given composition. You are not interested in looking for a composition with a lower Gibbs energy. You could thus inactivate the global minimization procedure.

```
POLY_3: set-min
 Settings for global minimization:
 Use global minimization /Y/: N
 Settings for general calculations:
 Force positive definite Phase Hessian /N/:
 Control minimization step size /N/:
POLY_3: s-c P=101325 T=700 N(Cr)=.05 N(C)=.01 N(Fe)=.94
POLY_3: c-e
 Global equilibrium calculation turned off, you can turn it on with
 SET_MINIMIZATION_OPTIONS Y,,,,
   8 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym fun stabCr=mu(Cr).N(Cr);
POLY_3: sh stabCr
 STABCR=94553.346
POLY_3: s-c N(Fe)=none x(Fe)=
Value /.94/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh stabCr
 STABCR=52753.451
POLY_3:
```

*) One could possibly expect to get the same result here since N(Fe) and x(Fe) are both equal to 0.94. However, when N(Cr) is increased during a derivation, N(Fe) must also increase if x(Fe) should stay constant. The effect on mu(Cr) will thus be less.

```
POLY_3: s-c x(Fe)=none mu(Fe)=
Value /-24676.72301/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh stabCr
 STABCR=11570.964
POLY_3:
```

*) This is a lowest stability value in agreement with Eq. 6.30.

```
POLY_3: s-c N(C)=none mu(C)=
Value /29447.02461/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh stabCr
 STABCR=0
POLY_3:
```

*) This result is expected from the Gibbs-Duhem relation because mu(Cr) cannot vary when all the other potentials are constant.

```
POLY_3: s-c mu(C)=none x(C)=
Value /.00999999969/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh stabCr
 STABCR=-2.3453967E-12
POLY_3:
```

*) This is practically zero considering the limited accuracy of the numerical calculations. The explanation is that N(Cr) is here the only quantity defining the size. It does not affect the composition and mu(Cr) cannot vary with N(Cr).

```
POLY_3: s-c mu(Fe)=none x(Fe)=
Value /.9400000018/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh stabCr
 STABCR=2.2458789E-10
POLY_3:
```

*) This is also practically zero and here it is more immediately evident that the composition cannot vary with N(Cr) since x(C) and x(Fe) are already given and, consequently, x(C) cannot vary, nor mu(Cr).

```
POLY_3: exit
 CPU time            0  seconds
```

Comment

1) A stability expression based on two extensive variables kept constant will get more severe, i.e., get a lower numerical value, if one of those variables is replaced by its conjugate intensive variable.

2) In all partial derivatives, expressing stability, there must be at least one extensive variable in addition to the one used in the derivative.

6.5D. Limit of stability

Test the second principle defined in Problem 6.5C.

Hint

As for Problem 6.5C you may again consider the bcc phase in the Fe-Cr-C system at 1 atm and 700 K and for 1 mol% C. There is a bcc miscibility gap and the stability limit, i.e., the spinodal, falls close to 6 mol% Cr. You may thus examine the stability for 5, 6 and 7 mol% Cr.

Instructions for using T-C

1) For each alloy you should first compute the equilibrium for the given composition and then change one of the contents to the chemical potential of the same compound. Then you should compute the same equilibrium with this new definition and can finally evaluate a stability using the "." operator.

2) For all three alloys use $\partial\mu_{Cr}/\partial N_{Cr}$ with μ_{C} and N_{Fe} and $\partial\mu_C/\partial N_C$ with μ_{Cr} and N_{Fe} as independent variables but also the quantity QF that POLY can evaluate directly for any state of equilibrium.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                      CR                      C
   DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  SIGMA                   CEMENTITE
 M3C2                    M7C3                    M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           33
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
```

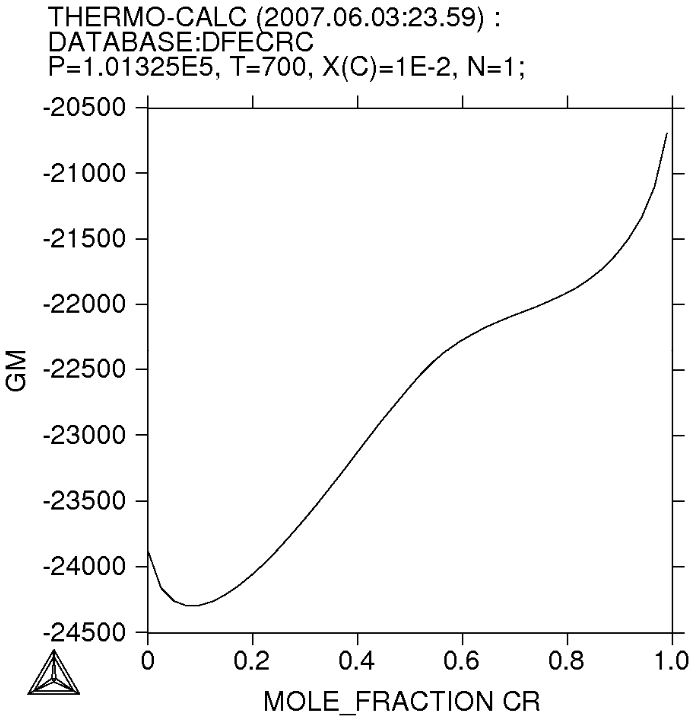
```
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You should prevent POLY from reacting to the miscibility gap and split alloys into two phases. You should thus omit the global minimization procedure.

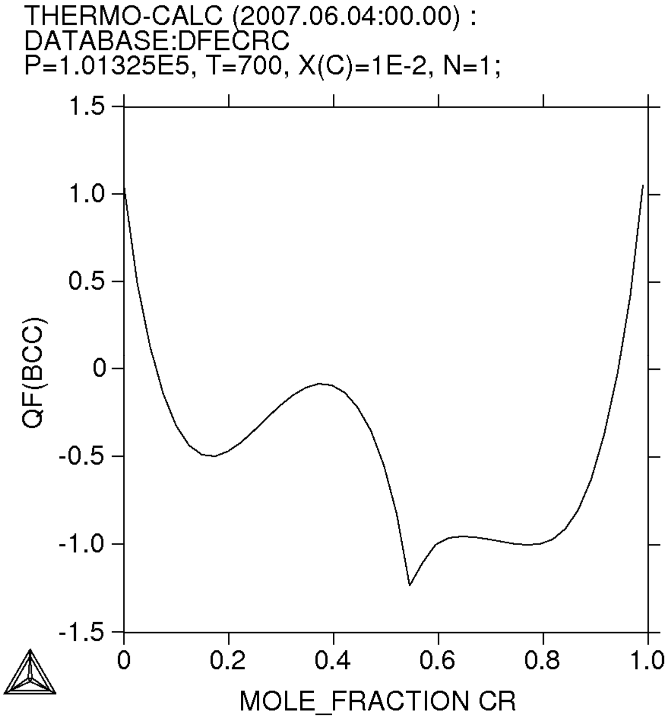
```
POLY_3: set-min N
 Settings for global minimization:
 Settings for general calculations:
 Force positive definite Phase Hessian /N/:
 Control minimization step size /N/:
POLY_3: s-c P=101325 T=700 x(Cr)=.05 x(C)=.01 N=1
POLY_3: c-e
 Global equilibrium calculation turned off, you can turn it on with
 SET_MINIMIZATION_OPTIONS Y,,,,
   8 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) You like to step across the system and then plot Gm and QF as functions of the Cr content.

```
POLY_3: s-a-v 1 x(Cr) 0 .99
Increment /.02475/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one          0

 Phase Region from   0.500000E-01 for:
     BCC_A2
 Calculated    41 equilibria

 Phase Region from   0.500000E-01 for:
     BCC_A2
 Calculated     6 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a x m-f Cr
POST: s-d-a y Gm
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: s-d-a y QF(bcc)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3:
```

*) Start again from the initial alloy. The Cr content has been varied during the stepping procedure and should be restored.

```
POLY_3: s-c x(Cr)=.05
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
```

```
POLY_3:
```

*) Now you should introduce the set of independent variables for the first partial derivative.

```
POLY_3: s-c x(Cr)=none N(Cr)=.05 N=none N(Fe)=.94
POLY_3: s-c x(C)=none mu(C)=
Value /29447.02446/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) You will evaluate partial derivatives several times and should thus defined functions for them. In order to save the value from an evaluation, you should further save it as a variable.

```
POLY_3: ent-sym fun stabCr=mu(Cr).N(Cr);
POLY_3: ent-sym var stCr05=stabCr;
POLY_3: s-c mu(C)=none N(C)=.01 N(Cr)=none mu(Cr)=
Value /-27169.30695/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym fun stabC=mu(C).N(C);
POLY_3: ent-sym var stC05=stabC;
POLY_3: sh stCr05 stC05 QF(bcc)

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STCR05=14288.414

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STC05=92759.74
 QF(BCC_A2)=0.12733409
POLY_3:
```

*) All these quantities are positive and agree that this alloy is not in a region of instability. Now, do the same for the next alloy. Start with its composition.

```
POLY_3: s-c N(C)=none x(C)=.01 mu(Cr)=none x(Cr)=.06 N(Fe)=.93
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: s-c x(Cr)=none N(Cr)=.06 x(C)=none mu(C)=
Value /27201.66822/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var stCr06=stabCr;
POLY_3: s-c mu(C)=none N(C)=.01 N(Cr)=none mu(Cr)=
Value /-26297.18603/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var stC06=stabC;
POLY_3: sh stCr06 stC06 QF(bcc)

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STCR06=779.57015

 Warning: All functions are evaluated for this command and as there are
```

```
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STC06=6313.5985
 QF(BCC_A2)=8.4326953E-3
POLY_3:
```

*) The values of all these quantities have decreased considerably. You are approaching the limit of stability. Continue to the third alloy.

```
POLY_3: s-c N(C)=none x(C)=.01 mu(Cr)=none x(Cr)=.07 N(Fe)=.92
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: s-c x(Cr)=none N(Cr)=.07 x(C)=none mu(C)=
Value /25010.47882/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var stCr07=stabCr;
POLY_3: s-c mu(C)=none N(C)=.01 N(Cr)=none mu(Cr)=
Value /-25583.61545/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var stC07=stabC;
POLY_3: sh stCr07 stC07 QF(bcc)

 Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STCR07=-7473.93

Warning: All functions are evaluated for this command and as there are
 one or more functions with a derivative which may be irrelevant
 for this equilibrium some functions may have wrong values.
 If possible enter derivatives as VARIABLES instead

 STC07=-73357.28
 QF(BCC_A2)=-9.5413995E-2
POLY_3:
```

*) This time all the values are negative and this alloy is thus inside the region of instability.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) You have confirmed that the three methods of expressing the stability give very different values but they agree on the limit of stability.

2) The QF symbol represents a further method of expressing the stability that has been normalized in order to give comparable values under different conditions. The sharp break in the middle of the diagram indicates that there was a change of method. It will be further discussed in Problem 6.6.

3) If you draw a double tangent to the G_m curve you may find that the miscibility gap starts above about 20 mol% Cr. And the curve indicates that the inflection point falls at about 40 mol% Cr. However, then you found that the limit of stability falls at about 7 mol% Cr. The explanation is

that the system is really three-dimensional and the double tangent in your section at a constant value of 1 mol% C cannot be used.

6.6. Limit of stability of alloys

Compare the value of $\begin{vmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{vmatrix}$ with $(\partial\mu_2/\partial N_2)_{T,P,\mu_3,N_1}$ and $(\partial\mu_3/\partial N_3)_{T,P,\mu_2,N_1}$ for the fcc phase in an Fe alloy with 1 mol% C and 5 mol% Cr at 1200 K and 1 atm.

Hint

The determinant is equal to $G_{22}G_{33} - G_{23}G_{32}$ where G_2 is identical to $\mu_2 = (\partial G/\partial N_2)_{T,P,N_3,N_1}$ in a ternary system. The set of independent variables are thus T, P, N_1, N_2 and N_3 for all the quantities in the determinant. Each partial derivative involves a chemical potential.

Instructions for using T-C

Of course, the G_{ij} quantities can also be expressed as partial derivatives, $G_{ij} = (\partial\mu_i/\partial N_j)_{T,P,N_i,N_k}$, where the subscript k represents all the other components. Notice that G_{ij}=G_{ji}. All the quantities required for solving this problem are thus available with the operator "." but you must be careful with the choices of conditions, which will define the set of independent variables.

POLY can directly give information on the stability through a quantity available under the symbol QF(phase).

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                     CR                     C
   DEFINED
TDB_DFECRC: rej p *
TDB_DFECRC: rest p bcc
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data
```

```
  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: set-min N
 Settings for global minimization:
 Settings for general calculations:
 Force positive definite Phase Hessian /N/:
 Control minimization step size /N/:
POLY_3: s-c P=101325 T=700 N(Fe)=.94 N(C)=.01 N(Cr)=.05
POLY_3: c-e
 Global equilibrium calculation turned off, you can turn it on with
 SET_MINIMIZATION_OPTIONS Y,,,,
   7 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Start by evaluating and saving all the G_{ij} etc. but omitting all with i<j due to symmetry.

```
POLY_3: ent-sym var GFeFe=mu(Fe).N(Fe);
POLY_3: ent-sym var GCC=mu(C).N(C);
POLY_3: ent-sym var GCrCr=mu(Cr).N(Cr);
POLY_3: ent-sym var GFeC=mu(Fe).N(C);
POLY_3: ent-sym var GFeCr=mu(Fe).N(Cr);
POLY_3: ent-sym var GCCr=mu(C).N(Cr);
POLY_3: ent-sym var detFeC=GFeFe*GCC-GFeC**2;
POLY_3: ent-sym var detFeCr=GFeFe*GCrCr-GFeCr**2;
POLY_3: ent-sym var detCCr=GCC*GCrCr-GCCr**2;
POLY_3: ent-sym var stab=QF(bcc);
POLY_3:
```

*) Change a condition in order to evaluate $(\partial\mu_2 / \partial N_2)_{T,P,\mu_3,N_1}$, where 1 stands for Fe, 2 stands for C and 3 for Cr. You should thus use μ_{Cr} as a condition.

```
POLY_3: s-c N(Cr)=none mu(Cr)=
Value /-27169.30695/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var BCCFe=mu(C).N(C);
POLY_3: ent-sym var BFeFeC=mu(Fe).N(Fe);
POLY_3: s-c mu(Cr)=none N(Cr)=.05 N(C)=none mu(C)=
Value /29447.02446/:
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var BCrCrFe=mu(Cr).N(Cr);
POLY_3: ent-sym var BFeFeCr=mu(Fe).N(Fe);
POLY_3: s-c mu(C)=none N(C)=.01 N(Fe)=none mu(Fe)=
Value /-24676.72301/:
POLY_3: c-e
```

```
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var BCrCrC=mu(Cr).N(Cr);
POLY_3: ent-sym var BCCCr=mu(C).N(C);
POLY_3:
```

*) As explained in the comments, you are also asked to evaluate the following products.

```
POLY_3: ent-sym var pCrCrFe=BCrCrFe*GCC;
POLY_3: ent-sym var pCCFe=BCCFe*GCrCr;
POLY_3: ent-sym var pFeFeCr=BFeFeCr*GCC;
POLY_3: ent-sym var pCCCr=BCCCr*GFeFe;
POLY_3: ent-sym var pFeFeC=BFeFeC*GCrCr;
POLY_3: ent-sym var pCrCrC=BCrCrC*GFeFe;
POLY_3: eval
Name(s):
 GFEFE=85.78498
 GCC=613836.07
 GCRCR=94553.346
 GFEC=5276.6037
 GFECR=-2668.0784
 GCCR=-221967.36
 DETFEC=2.4815368E7
 DETFECR=992614.73
 DETCCR=8.7707438E9
 STAB=0.12733409
 BCCFE=92759.74
 BFEFEC=10.497933
 BCRCRFE=14288.414
 BFEFECR=40.426703
 BCRCRC=11570.964
 BCCCR=289274.1
 PCRCRFE=8.7707438E9
 PCCFE=8.7707438E9
 PFEFECR=2.4815368E7
 PCCCR=2.4815373E7
 PFEFEC=992614.73
 PCRCRC=992614.93
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) In this exercise you were primarily interested in the three determinants because each one of them treated two components in equivalent ways. Indeed they are all positive in the present case but their values differ much. Next you were interested in the six B-quantities which were supposed to express the stability as based on partial derivatives. All of them are also positive but again they differ much. However, when they were multiplied by the correct second derivative of G, their values were modified to agree in pairs and each pair agrees with one of the determinants. The reason of this agreement is given by Eq. 6.35 where the second factor is identical to a second derivative of G for a ternary system and there are no more factors.

2) One may wonder what method of expressing the stability of an alloy should be preferred. It may seem that the partial derivatives have the most direct thermodynamic basis but unfortunately they give different values. The method based on a determinant may be preferred because it treats both solutes in the same way. However, it does not have the same value if constructed with different pairs of components. It must be accepted that the stability has different values depending on what kind of fluctuation one considers. However, all the alternatives discussed identify the same limit of stability.

3) The particular stability function QF(phase) that POLY can give directly has been normalized in a very approximate way, comparable to multiplying by x1x2/RT for a binary system. It is not comparable to any of the stabilities discussed here but it also predicts the same limit of stability.

6.9. Le Chatelier's principle

Consider the internal process $2H_2 + O_2 \rightarrow 2H_2O$ when a gas with 2 mole of H and 1 mole of O from the equilibrium at 1800 K and 1 atm is (a) compressed adiabatically to 10 bar so rapidly that no reaction can occur. Evaluate T and the molar volume, V_m. Then, suppose (b) there is time for the process to go to a new equilibrium under 10 bar but still without any exchange of heat. Finally suppose (c) the temperature will eventually return to 1800 K but still under 10 bar. Evaluate the final V_m. Compare the resulting T and V_m with initial values and discuss how the results can be used as examples of Le Chatelier's principle.

Hint

(a) For the adiabatic compression, S is not changed because there is no internal reaction. That can be used as a condition for finding the new state after compression. However, it is a frozen-in state and would have to be evaluated from a module that can handle states of non-equilibrium. S will change during (b) due to the internal process but not H because there is no exchange of enthalpy with the surroundings during an isobaric adiabatic change. The final state (c) is easily found as the state of equilibrium at 1800 K.

Instructions for using T-C

When using the TAB module in T-C you should remember that it gives properties per mole of formula units, in this case mole of species, not mole of atoms. POLY normally works with mole per atom or component but can deliver extensive quantities per formula unit under symbols with the subscript *f* instead of *m*.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw psub
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-sp O2 H2 H2O1
 O2                      H2                      H2O1
   DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 GAS:G        :H2 H2O1 O2:
 H2O1_L       :H2O1:
TDB_PSUB: rej p H2O_L
 H2O_L  REJECTED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
```

```
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=1800
POLY_3:
```

*) The proportions of H and O are such that they correspond exactly to 1 mole of H_2O and you could just as well enter that as the **i**nitial **a**mount.

```
POLY_3: s-i-a N(H2O1)=1
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
```

*) Choose option **N** in order to see the constitution.

```
Options /VWCS/:  N
 Output from POLY-3, equilibrium =     1, label A0  , database: PSUB

 Conditions:
 P=1.01325E5, T=1800, N(H)=2, N(O)=1
 DEGREES OF FREEDOM 0

 Temperature 1800.00 K (1526.85 C),  Pressure  1.013250E+05
 Number of moles of components  3.00000E+00,  Mass  1.80148E+01
 Total Gibbs energy -6.46092E+05,  Enthalpy -1.78445E+05,  Volume  1.47835E-01

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 H                        2.0000E+00 1.1190E-01 2.9517E-06 -1.9057E+05 SER
 O                        1.0000E+00 8.8810E-01 2.0475E-08 -2.6496E+05 SER

 GAS                         Status ENTERED     Driving force  0.0000E+00
 Number of moles 3.0000E+00, Mass 1.8015E+01         Mass fractions:
 O  8.88103E-01  H  1.11897E-01
 Constitution:
 H2O1  9.97337E-01  H2    1.77564E-03  O2    8.87822E-04
POLY_3:
```

*) You can see that there is a slight dissociation into H_2 and O_2. Record the essentials of the state. For the entropy, obtain the value per formula unit to be used in TAB.

```
POLY_3: ent-sym var T1=T;
POLY_3: ent-sym var Vm1=Vm;
POLY_3: ent-sym var Hm1=Hm;
POLY_3: ent-sym var Sm1=Sm;
POLY_3: ent-sym var Sf1=Sf(gas);
POLY_3: eval
```

```
Name(s):
 T1=1800
 VM1=4.9278451E-2
 HM1=-59481.526
 SM1=86.601345
 SF1=259.57338
POLY_3: go tab
TAB:
```

*) In addition to the usual properties given in the table, you like to add the volume.

```
TAB: ent-fun
Name: Vfroz
Function: V;
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.001775644781/:
H2O1 /.9973365328/:
Pressure /101325/:  1E6
Low temperature limit /298.15/:  1800
High temperature limit /2000/:  3000
Step in temperature /100/:
Output file /SCREEN/:

               O U T P U T   F R O M   T H E R M O - C A L C
               2007. 5. 5                          21.58.19


 Column 6: Vfroz    V

 Phase : GAS                        Pressure :     1000000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G            Vfroz
   (K)    (Joule/K)     (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 1800.00   5.00803E+01  -1.78286E+05   2.40538E+02  -6.11254E+05   1.49661E-02
 1900.00   5.08907E+01  -1.73237E+05   2.43268E+02  -6.35446E+05   1.57976E-02
 2000.00   5.16530E+01  -1.68110E+05   2.45898E+02  -6.59905E+05   1.66290E-02
 2100.00   5.23693E+01  -1.62908E+05   2.48435E+02  -6.84622E+05   1.74605E-02
 2200.00   5.30413E+01  -1.57637E+05   2.50887E+02  -7.09589E+05   1.82919E-02
 2300.00   5.36703E+01  -1.52301E+05   2.53259E+02  -7.34797E+05   1.91234E-02
 2400.00   5.42574E+01  -1.46905E+05   2.55556E+02  -7.60238E+05   1.99548E-02
 2500.00   5.48034E+01  -1.41451E+05   2.57782E+02  -7.85906E+05   2.07863E-02
 2600.00   5.53089E+01  -1.35945E+05   2.59941E+02  -8.11792E+05   2.16177E-02
 2700.00   5.57746E+01  -1.30391E+05   2.62037E+02  -8.37892E+05   2.24492E-02
 2800.00   5.62021E+01  -1.24792E+05   2.64074E+02  -8.64198E+05   2.32806E-02
 2900.00   5.66195E+01  -1.19150E+05   2.66053E+02  -8.90705E+05   2.41121E-02
 3000.00   5.70243E+01  -1.13468E+05   2.67979E+02  -9.17407E+05   2.49435E-02

TAB:
```

*) The wanted value of Sf1 =259.57338 is found very close to 2600 K. Increase the precision.

```
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /.001775644781/:
H2O1 /.9973365328/:
Pressure /1000000/:
Low temperature limit /1800/:  2550
High temperature limit /3000/:  2600
Step in temperature /100/:  5
Output file /SCREEN/:
```

```
              O U T P U T   F R O M   T H E R M O - C A L C
              2007. 5. 5                        21.58.19


 Column 6: Vfroz    V

 Phase : GAS                      Pressure :     1000000.00
 Specie: *

 ******************************************************************************
    T      Cp            H             S             G            Vfroz
   (K)    (Joule/K)      (Joule)      (Joule/K)      (Joule)
 ******************************************************************************
 2550.00   5.50612E+01  -1.38705E+05   2.58870E+02  -7.98822E+05   2.12020E-02
 2555.00   5.50864E+01  -1.38429E+05   2.58977E+02  -8.00117E+05   2.12436E-02
 2560.00   5.51115E+01  -1.38154E+05   2.59085E+02  -8.01412E+05   2.12851E-02
 2565.00   5.51365E+01  -1.37878E+05   2.59193E+02  -8.02707E+05   2.13267E-02
 2570.00   5.51615E+01  -1.37602E+05   2.59300E+02  -8.04004E+05   2.13683E-02
 2575.00   5.51863E+01  -1.37326E+05   2.59407E+02  -8.05300E+05   2.14099E-02
 2580.00   5.52110E+01  -1.37050E+05   2.59514E+02  -8.06598E+05   2.14514E-02
 2585.00   5.52356E+01  -1.36774E+05   2.59621E+02  -8.07896E+05   2.14930E-02
 2590.00   5.52602E+01  -1.36498E+05   2.59728E+02  -8.09194E+05   2.15346E-02
 2595.00   5.52846E+01  -1.36222E+05   2.59835E+02  -8.10493E+05   2.15762E-02
 2600.00   5.53089E+01  -1.35945E+05   2.59941E+02  -8.11792E+05   2.16177E-02

TAB:
```

*) You may choose T=2585 and go to POLY in order to use the values of H and Vfroz, both of which are per formula unit.

```
TAB: b
POLY_3: ent-sym var Ta=2585;
POLY_3: ent-sym var Vma=2.14930E-02*Sm1/Sf1;
POLY_3: ent-sym var Hma=-1.36774E+05*Sm1/Sf1;
POLY_3:
```

*) Compute the equilibrium according to (b). You can use the value of Hfa as condition.

```
POLY_3: s-c P=1E6 T=none Hm=Hma
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated         8409  grid points in            0  s
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var Tb=T;
POLY_3: ent-sym var Vmb=Vm;
```

*) Compute the equilibrium according to (c).

```
POLY_3: s-c Hm=none T=1800
POLY_3: c-e
 Using global minimization procedure
 Calculated         8409  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: ent-sym var Vmc=Vm;
POLY_3: eval
Name(s):
 T1=1800
 VM1=4.9278451E-2
 HM1=-59481.526
 SM1=86.601345
 SF1=259.57338
 TA=2585
 VMA=7.1706996E-3
 HMA=-45631.846
```

```
 TB=2505.3707
 VMB=7.0103201E-3
 VMC=4.9907737E-3

POLY_3: exit
 CPU time            0  seconds
```

Comments

1) This case concerns the effect of an increased P. The conjugate variable to –P is V and for the first change you find dV/d(-P)=(0.00717-0.04928)/(-10-(-1))=0.004679. It is a positive value as expected for a stable system. The total change after the internal process has reached equilibrium is dV/d(-P)=(0.00701-0.04928)/(-10-(-1))=0.004697. The change has thus increased further by the internal process. This is as expected theoretically because the variable that was primarily changed was a potential and the effect concerned an extensive variable.

2) Usually it is expected that LeChatelier's principle should predict a reversal of the first effect, called LeChatelier's modification. However, that applies when the variable that is primarily changed is an extensive variable and the effect is then studied on a potential.

3) You may think that the temperature obeys LeChatelier's principle because it is first increased from 1800 to 2585 K and then decreased (modified) to 2505 K as an effect of the internal process. However, T is not the conjugate variable to –P and the principle should not be applied to such a combination of variables.

Chapter 7. Applications of molar Gibbs energy diagrams

7.2. Instability of binary solutions

Calculate and plot a molar Gibbs energy diagram for the bcc phase in the Fe-Cr system at 500^{o}C under 1 atm.

Hint

1) Since pure Fe and Cr are both bcc, there will be only one phase to be fetched from the database. From your first run you may get a Gm curve with two minima. The bcc phase should thus have a miscibility gap at this low temperature and your equilibration module may have a procedure for identify two bcc phases, an Fe rich phase, bcc#1, and a Cr rich phase, bcc#2. Try to accomplish this if it does not happen automatically.

2) Use the pure elements at the actual temperature as references.

Instructions for using T-C

When searching for the state of equilibrium by minimizing the Gibbs energy, it is possible to find a local minimum and stop there. In POLY this can be prevented by applying a global minimization procedure, which searches for an even lower Gibbs energy by scanning over a wide range of compositions or constitutions. That procedure can be turned off or activated by the command set-min followed by options. When there is a miscibility gap in a phase, this procedure will find the other side of the miscibility gap and then consider two phase, #1 and #2. By turning this procedure off and on you can thus obtain different results. As default, this procedure is normally turned on and a miscibility gap will be found automatically.

It may be instructive to see the two minima. If you don't get them on your first run, try to inactivate the automatic procedure.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr
 FE                      CR  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  SIGMA  REJECTED
TDB_DFECRC: rest p bcc
 BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           34
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Compute an equilibrium using as one condition a value of the variable you like to vary, e.g. x(Cr).

```
POLY_3: s-c P=101325 T=673 N=1 x(Cr)=.1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Creating a new composition set BCC_A2#2
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Observe the note: "Creating a new composition set BCC_A2#2". POLY has thus detected the miscibility gap. Now you can start stepping and preferably across the whole system.

```
POLY_3: s-a-v
Axis number: /1/:
Condition /NONE/:  x(Cr)
Min value /0/:
Max value /1/:
Increment /.025/:
```

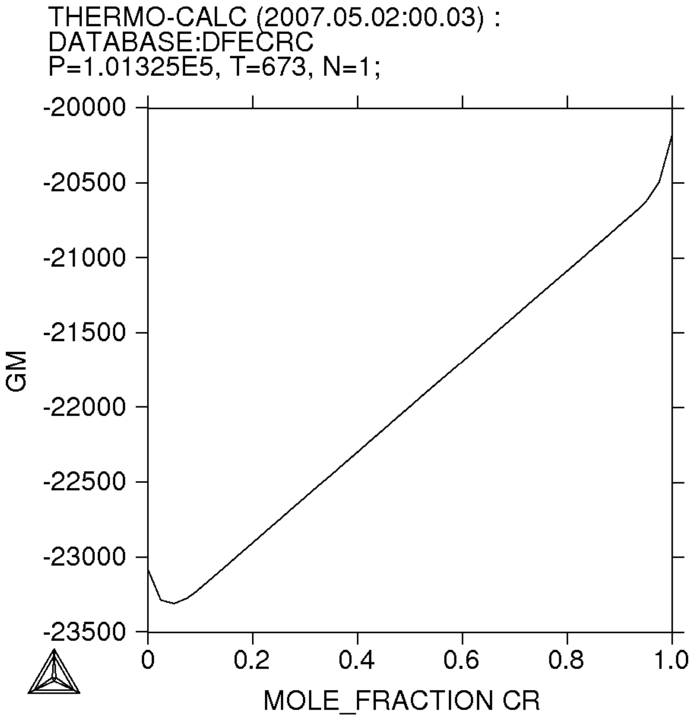
```
POLY_3: step
Option? /NORMAL/:

 Phase Region from   0.100000     for:
     BCC_A2#1
     BCC_A2#2
 Calculated    36 equilibria

 Phase Region from   0.939244     for:
     BCC_A2#2
 Calculated     6 equilibria

 Phase Region from   0.100000     for:
     BCC_A2#1
     BCC_A2#2
 Calculated     3 equilibria

 Phase Region from   0.934860E-01 for:
     BCC_A2#1
 Calculated     7 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Time to go to the postprocessor for plotting a diagram.

```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a x m-f Cr
POST:
```

) The symbol m-f Cr stands for "mass fraction of Cr", which is usually denoted by x(Cr). Sometimes one likes to specify the values for individual phases and uses x(bcc,Cr) or more generally x(,Cr). M-f Cr is identical to the latter symbol.

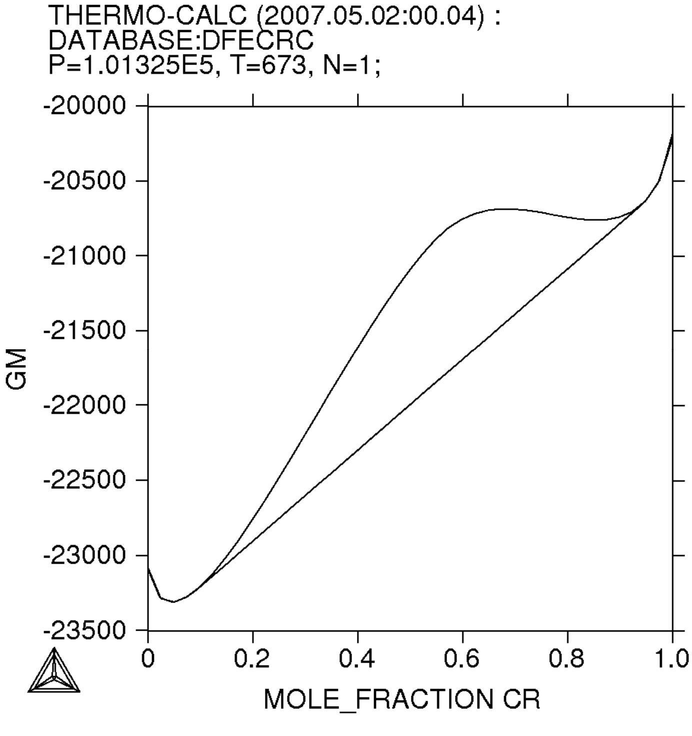
```
POST: s-d-a y Gm
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) The two-phase states in the central part of the diagram are represented by a straight line, the common tangent. If you also like to see the metastable and unstable parts of the Gibbs energy of the homogeneous phase, you have to step through the computations again with an option “separate”.

```
POST: b
POLY_3: step
Option? /NORMAL/:  sep
 Convergence problems, increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS

 Phase Region from   0.497537     for:
     BCC_A2#1
     BCC_A2#2

 Phase Region from   0.497537     for:
     BCC_A2#1
     BCC_A2#2
 *** Buffer saved on file *** USERPROFILE\RESULT.POLY3
POLY_3: post
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```

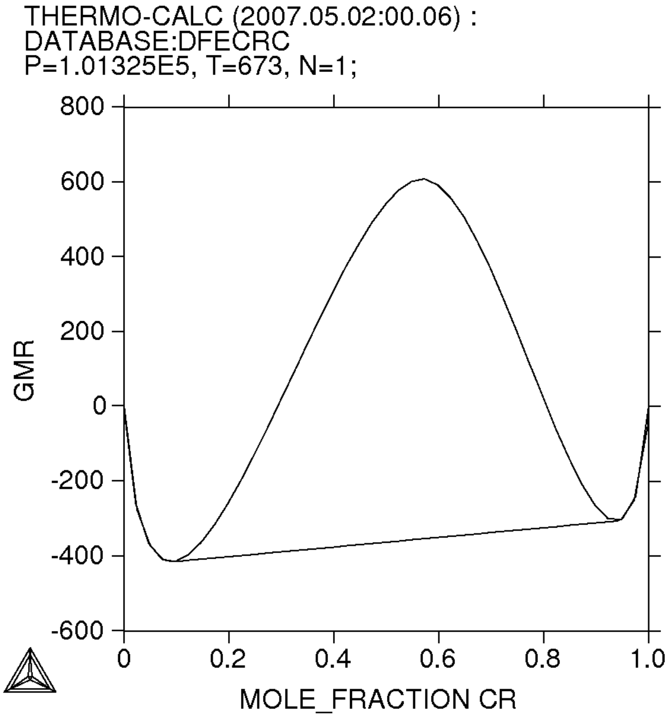


```
POST:
```

*) G_m is here given relative to the SER references. You may prefer to use the pure elements at the current temperature. You can then introduce them by going back to POLY. If you then like to use them in POST, you call for Gmr instead of Gm.

```
POST: b
POLY_3: set-ref Fe bcc
Temperature /*/:
Pressure /1E5/:
POLY_3: set-ref Cr bcc
Temperature /*/:
```

```
Pressure /1E5/:
POLY_3: post
POST: s-d-a y Gmr
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            0  seconds
```

Comments

POLY can automatically find the other side of a miscibility gap.

7.3. Illustration of the Gibbs-Duhem relation.

Define a system at 1000 K and 1 atm, with the elements Fe, Cr and C and with the phases bcc, graphite and cementite, $(Fe,Cr)_3C$. Then, define Fe_3C_1 and Cr_3C_1 as new components instead of Fe and Cr. Make bcc and graphite dormant and compute the equilibrium between cementite, with equal amounts of Fe and Cr, and graphite. Evaluate the potential of a hypothetical component Fe_1Cr_1. Finally, evaluate the same potential if the C activity is just half as high as for graphite. Evaluate the difference in Fe_1Cr_1 potential with what one should expect. Fig. 7.6 can be used as an illustration.

Hint

1) Equilibrium with graphite simply means that the C activity is 1, if graphite is used as reference. The second case can then be treated in exactly the same way but with a C activity of 0.5.

2) The potential of Fe for an equilibrium is equal to the potential of Fe_3C_1 minus the potential of C and divided by 3. Similarly for Cr and the potential for Fe_1Cr_1 is the sum of the two.

Instructions for using T-C

1) The new components must be introduced as the first action in POLY.

2) One should get the correct value for Fe_1Cr_1 in SER if SER is used for cementite and graphite. However, the choice of reference has no effect on the difference in a potential.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                       CR                       C
   DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   SIGMA                    CEMENTITE
 M3C2                     M7C3                     M23C6
 GRAPHITE  REJECTED
TDB_DFECRC: rest p bcc gra cem
 BCC_A2                   GRAPHITE                 CEMENTITE
   RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           37
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R
```

```
 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Now at the beginning of the session on POLY, you should define the whole new set of components.

```
POLY_3: def-comp Fe3C1 Cr3C1 C
POLY_3: set-ref C gra
Temperature /*/:
Pressure /1E5/:
POLY_3: ch-st p gra=dor
POLY_3: ch-st p bcc=dor
POLY_3: s-c P=1E5 T=1000 N(Fe3C1)=1 N(Cr3C1)=1 acr(C)=1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          137  grid points in           0  s
  15 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1E5, T=1000, N(FE3C1)=1, N(CR3C1)=1, ACR(C)=1
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.000000E+05
 Number of moles of components  2.00000E+00,  Mass  3.47551E+02
 Total Gibbs energy -3.48499E+05,  Enthalpy  1.44449E+05,  Volume  2.40157E-05

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 FE3C1                    1.0000E+00 5.1662E-01 1.0043E-08 -1.5312E+05 SER
 CR3C1                    1.0000E+00 4.8338E-01 6.2354E-11 -1.9538E+05 SER
 C                        0.0000E+00-1.0222E-17 1.0000E+00  0.0000E+00 GRAPHITE

 CEMENTITE                   Status ENTERED     Driving force  0.0000E+00
 Number of moles 2.0000E+00, Mass 3.4755E+02         Mass fractions:
 FE3C1  5.16621E-01  CR3C1  4.83379E-01  C      0.00000E+00

 GRAPHITE                    Status DORMANT     Driving force  0.0000E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 C      1.00000E+00  FE3C1  0.00000E+00  CR3C1  0.00000E+00
```

*) According to the Hint, the potential of Fe_1Cr_1 is given as follows. Observe that mu(C) is the symbol when SER is used. A few lines earlier when ACR(C) was used, the letter R indicates that the special reference was used.

```
POLY_3: ent-sym fun muFeCr=(mu(Fe3C1)+mu(Cr3C1)-2*mu(C))/3;
POLY_3:
```

*) When you are going to use an expression for a symbol several times, then you should define it as a function. If you then like to store the current value you should define that as a variable.

```
POLY_3: ent-sym var mu1=muFeCr;
POLY_3:
```

*) Next, use a different value of acr(C) as a condition.

```
POLY_3: s-c acr(C)=.5
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
```

```
 Using already calculated grid
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Everytime you call for the function muFeCr, it will be evaluated from the current conditions. mu2 on the next line will thus get a different value than the earlier mu1.

```
POLY_3: ent-sym var mu2=muFeCr;
POLY_3: ent-sym var diff=mu2-mu1;
POLY_3: sh diff
 DIFF=3842.1194
POLY_3: exit
 CPU time            0  seconds
```

Comments

The value 3842.1194 is the difference in chemical potential of Fe_1Cr_1 in the Fe-Cr cementite due to the two C activities. The change in activity gives a change in potential of RTln(1/0.5). Comparison with Fig. 7.9 shows that one should divide by 3 because of the composition of cementite, M_3C but one should also multiply by 2 because the hypothetical component Fe_1Cr_1 was here defined for two atoms. (3/2)RTln(1/0.5) = 3842.1194.

7.4. Two-phase equilibria in binary systems

The database lists four carbides in the Cr-C system, Cr23C6, Cr3C Cr7C3 and Cr3C2, and together with the end-members, bcc-Cr and graphite, it makes six phases. Examine the phase equilibria by computing the equilibrium for alloy compositions in all the regions between phases.

Hint

For all the alloy compositions, let all the phases be present and note the degree of instability, i.e. the negative value of the driving force for formation, of all the phases not taking part in the equilibrium.

Instructions for using T-C

If you get problems when computing equilibrium, try set-all-start values and respond F for Forced instead of N, which stands for No.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Cr C
 CR                     C  DEFINED
TDB_DFECRC: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 LIQUID:L    :C CR:
  > This is metallic liquid solution phase, with C species
 FCC_A1      :CR:C VA:
```

```
 BCC_A2      :CR:C VA:
 HCP_A3      :CR:VA C:
 CEMENTITE   :CR:C:
 M3C2        :CR:C:
 M7C3        :CR:C:
 M23C6       :CR:CR:C:
 GRAPHITE    :C:
TDB_DFECRC: rej p fcc hcp
 FCC_A1                  HCP_A3  REJECTED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           45
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: set-ref C gra
Temperature /*/:
Pressure /1E5/:
POLY_3: s-c T=1000 P=101325 N=1 x(C)=.2
POLY_3: c-e
 Using global minimization procedure
 Calculated         279  grid points in            0  s
 Found the set of lowest grid points in            0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:  XP
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5, N=1, X(C)=0.2
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  4.39990E+01
 Total Gibbs energy -4.50781E+04,  Enthalpy  8.16011E+03,  Volume  2.45960E-07

 Component                 Moles      M-Fraction Activity   Potential   Ref.stat
 C                         2.0000E-01 2.0000E-01 3.5879E-04 -6.5957E+04 GRAPHITE
 CR                        8.0000E-01 8.0000E-01 1.2116E-02 -3.6694E+04 SER
```

```
 LIQUID                      Status ENTERED     Driving force -1.5219E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.66620E-01  C   3.33803E-02

 BCC_A2                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 3.3333E-02, Mass 1.7332E+00         Mole fractions:
 CR  1.00000E+00  C   1.25040E-07

 CEMENTITE                   Status ENTERED     Driving force -2.6056E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status ENTERED     Driving force -7.9328E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 9.6667E-01, Mass 4.2266E+01         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status ENTERED     Driving force -1.1456E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status ENTERED     Driving force -2.7210E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3:
```

*) Bcc and M23C6 are stable. Cr3C(cementite) falls between them and cannot form as a stable phase. Show the C activity relative to graphite.

```
POLY_3: sh acr(C)
 ACR(C)=3.5878726E-4
POLY_3:
```

*) Insert a slightly higher C content.

```
POLY_3: s-c x(C)=.23
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5, N=1, X(C)=0.23
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  4.27995E+01
 Total Gibbs energy -4.57743E+04,  Enthalpy  6.99316E+03,  Volume  0.00000E+00

 Component                 Moles      M-Fraction Activity   Potential   Ref.stat
 C                         2.3000E-01 2.3000E-01 3.6431E-03 -4.6685E+04 GRAPHITE
 CR                        7.7000E-01 7.7000E-01 6.6186E-03 -4.1721E+04 SER

 LIQUID                      Status ENTERED     Driving force -1.8784E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
```

```
 CR  8.68080E-01  C   1.31920E-01

 BCC_A2                      Status ENTERED     Driving force -6.0466E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  1.00000E+00  C   2.49139E-09

 CEMENTITE                   Status ENTERED     Driving force -1.3459E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status ENTERED     Driving force -5.6149E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status ENTERED     Driving force  0.0000E+00
 Number of moles 7.5185E-01, Mass 3.2873E+01         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status ENTERED     Driving force -5.8124E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 2.4815E-01, Mass 9.9261E+00         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3:
```

*) M23C6 and M7C3 are stable. Cr3C does not form in spite of the fact that the alloy composition was here chosen close to the composition of Cr3C.

```
POLY_3: sh acr(C)
 ACR(C)=3.6431395E-3
POLY_3: s-c x(C)=.35
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5, N=1, X(C)=0.35
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  3.80012E+01
 Total Gibbs energy -4.54726E+04,  Enthalpy  4.21182E+03,  Volume  0.00000E+00

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        3.5000E-01 3.5000E-01 2.1305E-01 -1.2856E+04 GRAPHITE
 CR                       6.5000E-01 6.5000E-01 1.1574E-03 -5.6219E+04 SER

 LIQUID                      Status ENTERED     Driving force -2.4604E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.40466E-01  C   2.59534E-01

 BCC_A2                      Status ENTERED     Driving force -2.3481E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.99926E-01  C   7.40201E-05
```

```
 CEMENTITE                   Status ENTERED     Driving force -4.2521E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status ENTERED     Driving force -1.5462E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status ENTERED     Driving force -5.4116E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 5.0000E-01, Mass 1.8001E+01         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 5.0000E-01, Mass 2.0000E+01         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3:
```

*) M7C3 and M3C2 are stable.

```
POLY_3: sh acr(C)
 ACR(C)=0.21305078
POLY_3: s-c x(C)=.45
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5, N=1, X(C)=0.45
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  3.40028E+01
 Total Gibbs energy -4.13308E+04,  Enthalpy  4.45886E+03,  Volume  4.49815E-07

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        4.5000E-01 4.5000E-01 1.0000E+00  0.0000E+00 GRAPHITE
 CR                       5.5000E-01 5.5000E-01 4.1286E-04 -6.4790E+04 SER

 LIQUID                      Status ENTERED     Driving force -2.7618E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  6.93947E-01  C   3.06053E-01

 BCC_A2                      Status ENTERED     Driving force -3.3777E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.99652E-01  C   3.47717E-04

 CEMENTITE                   Status ENTERED     Driving force -8.1176E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status ENTERED     Driving force  0.0000E+00
 Number of moles 8.3333E-02, Mass 1.0009E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00
```

```
 M23C6                       Status ENTERED     Driving force -1.0388E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00        Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status ENTERED     Driving force  0.0000E+00
 Number of moles 9.1667E-01, Mass 3.3002E+01        Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status ENTERED     Driving force -2.5770E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00        Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3:
```

*) M3C2 and graphite are stable.

```
POLY_3: sh acr(C)
 ACR(C)=1
POLY_3:
```

*) Cr3C(cementite) is never stable in this system. Force it to be in equilibrium with bcc.

```
POLY_3: ch-st p *=dor
POLY_3: ch-st p bcc cem=fix 1
POLY_3: s-c N=none x(C)=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          138  grid points in           0  s
  17 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh acr(C)
 ACR(C)=1.0173557E-3
POLY_3:
```

*) Force Cr3C to be in equilibrium with M23C6.

```
POLY_3: ch-st p bcc=dor
POLY_3: ch-st p m23=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            2  grid points in           0  s
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  M23C6=1
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  3.30000E+01,  Mass  1.43597E+03
 Total Gibbs energy -1.49568E+06,  Enthalpy  2.47366E+05,  Volume  0.00000E+00

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        7.0000E+00 2.1212E-01 4.3347E-02 -2.6095E+04 GRAPHITE
 CR                       2.6000E+01 7.8788E-01 3.4690E-03 -4.7092E+04 SER

 LIQUID                      Status DORMANT     Driving force -1.9908E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00        Mole fractions:
 CR  7.93565E-01  C   2.06435E-01
```

```
 BCC_A2                      Status DORMANT     Driving force -1.2506E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.99985E-01  C   1.51053E-05

 CEMENTITE                   Status FIXED       Driving force  0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status DORMANT     Driving force -3.1385E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status FIXED       Driving force  0.0000E+00
 Number of moles 2.9000E+01, Mass 1.2680E+03         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status DORMANT     Driving force  2.1708E-02
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status DORMANT     Driving force  2.9071E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3: sh acr(C)
 ACR(C)=4.3347127E-2
POLY_3:
```

*) Now M3C2 and M7C3 have positive driving forces and would like to form. Force Cr3C to be in equilibrium with M7C3.

```
POLY_3: ch-st p m23=dor
POLY_3: ch-st p m7=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            2  grid points in            0  s
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  M7C3=1
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.40000E+01,  Mass  5.68004E+02
 Total Gibbs energy -6.50110E+05,  Enthalpy  6.82607E+04,  Volume  0.00000E+00

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        4.0000E+00 2.8571E-01 5.5357E-04 -6.2352E+04 GRAPHITE
 CR                       1.0000E+01 7.1429E-01 1.4841E-02 -3.5007E+04 SER

 LIQUID                      Status DORMANT     Driving force -1.3105E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.58864E-01  C   4.11358E-02

 BCC_A2                      Status DORMANT     Driving force  2.0286E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  1.00000E+00  C   1.92922E-07
```

```
 CEMENTITE                   Status FIXED      Driving force  0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status DORMANT    Driving force -7.4991E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status DORMANT    Driving force  2.5061E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status DORMANT    Driving force -8.5041E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status FIXED      Driving force  0.0000E+00
 Number of moles 1.0000E+01, Mass 4.0001E+02         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3: sh acr(C)
 ACR(C)=5.5356977E-4
POLY_3:
```

*) The list shows that bcc and M23C6 have positive driving forces for this equilibrium.

```
POLY_3: ch-st p m7=dor
POLY_3: ch-st p m3=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            2  grid points in            0  s
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  M3C2=1
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  9.00000E+00,  Mass  3.48009E+02
 Total Gibbs energy -3.99718E+05,  Enthalpy  4.09174E+04,  Volume  0.00000E+00

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        3.0000E+00 3.3333E-01 3.8889E-02 -2.6998E+04 GRAPHITE
 CR                       6.0000E+00 6.6667E-01 3.5968E-03 -4.6792E+04 SER

 LIQUID                      Status DORMANT    Driving force -1.9843E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.96628E-01  C   2.03372E-01

 BCC_A2                      Status DORMANT    Driving force -1.2145E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.99986E-01  C   1.35518E-05

 CEMENTITE                   Status FIXED      Driving force  0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01
```

```
 GRAPHITE                    Status DORMANT     Driving force -3.2471E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status DORMANT     Driving force  6.2378E-03
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status FIXED       Driving force  0.0000E+00
 Number of moles 5.0000E+00, Mass 1.8001E+02         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status DORMANT     Driving force  2.8347E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3: sh acr(C)
 ACR(C)=3.8888654E-2
POLY_3:
```

*) The list shows that M23C6 and M7C3 have now positive driving forces. Finally, study the equilibrium between graphite and Cr3C.

```
POLY_3: ch-st p m3=dor
POLY_3: ch-st p gra=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            2  grid points in           0  s
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 T=1000, P=1.01325E5
 FIXED PHASES
 CEMENTITE=1  GRAPHITE=1
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  5.00000E+00,  Mass  1.80010E+02
 Total Gibbs energy -1.92689E+05,  Enthalpy  3.37377E+04,  Volume  5.39778E-06

 Component                Moles      M-Fraction Activity   Potential   Ref.stat
 C                        2.0000E+00 4.0000E-01 1.0000E+00  0.0000E+00 GRAPHITE
 CR                       3.0000E+00 6.0000E-01 1.2186E-03 -5.5791E+04 SER

 LIQUID                      Status DORMANT     Driving force -2.0004E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.13137E-01  C   2.86863E-01

 BCC_A2                      Status DORMANT     Driving force -2.2957E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  9.99652E-01  C   3.47730E-04

 CEMENTITE                   Status FIXED       Driving force  0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02         Mole fractions:
 CR  7.50000E-01  C   2.50000E-01

 GRAPHITE                    Status FIXED       Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 1.2011E+01         Mole fractions:
```

```
 C   1.00000E+00  CR  0.00000E+00

 M23C6                       Status DORMANT     Driving force -1.8037E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.93103E-01  C   2.06897E-01

 M3C2                        Status DORMANT     Driving force  6.4941E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  6.00000E-01  C   4.00000E-01

 M7C3                        Status DORMANT     Driving force  4.9994E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mole fractions:
 CR  7.00000E-01  C   3.00000E-01
POLY_3: sh acr(C)
 ACR(C)=1
POLY_3:
```

*) Cr3C2 and M7C3 have now positive driving forces.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

It may seem strange that bcc got a positive driving force for the equilibrium Cr3C(cementite)+M7C3 although it is never stable in this system. It is related to the very low C activity for that equilibrium, which is connected to a higher Cr activity, according to the Gibbs-Duhem relation.

7.5. Allotropic phase boundaries

Fcc and bcc Fe have the same Gibbs energy at 1 atm and 911^{o}C. That phase equilibrium represents an end-point of a T_o line that extends into all binary Fe-X phase diagram. Compute and plot that line for the Fe-C system up to 1 mass% C.

Hint

The T_o line is sometimes regarded as an allotropic phase boundary. In principle, it is evaluated from the condition G_m(fcc) = G_m(bcc) but different data bank systems may have different methods of computing that kind of equilibrium.

Instructions for using T-C

T-C has a special procedure for the computation of T_o lines.

Prompts, commands and responses

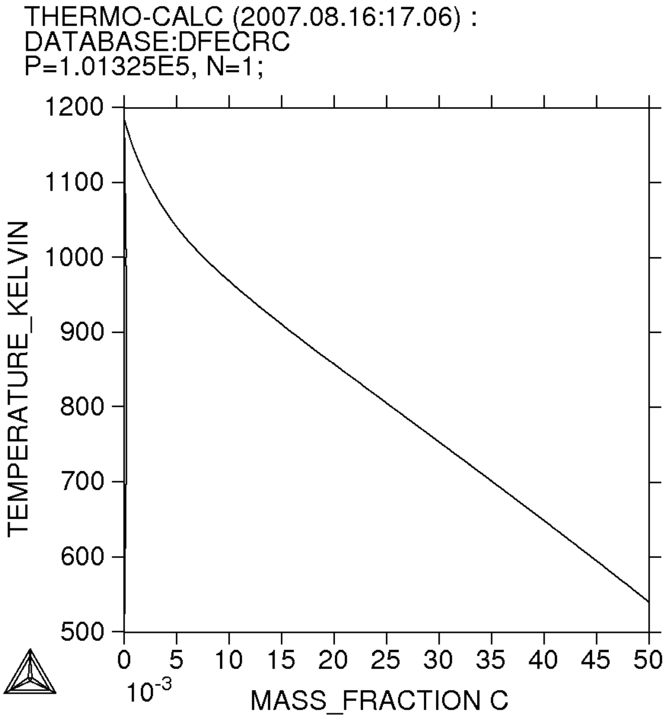
```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
```

```
TDB_DFECRC: def-el Fe C
 FE                      C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  CEMENTITE               M7C3
 M23C6                   GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc
 FCC_A1                  BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           37
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Start with an initial equilibrium and map the phase diagram.

```
POLY_3: s-c P=101325 T=1000 N=1 w(C)=.003
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: s-a-v 1 w(C) 0 .05
Increment /.00125/:
POLY_3: s-a-v 2 T 500 1200
Increment /17.5/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Using ADDED start equilibria
 Global search for miscibility gaps  1  2  3  4  5  6  7  8  9 10 11 12
 Found            2  zero phase fraction lines to start mapping

 Phase region boundary   1 at:   1.902E-04  1.000E+03
     BCC_A2
```

```
  ** FCC_A1
 Calculated   100 equilibra, continuing
 Calculated   200 equilibra, continuing
 Mapping terminated 1
 Calculated   226 equilibria

 Phase region boundary   2 at:   1.902E-04  1.000E+03
     BCC_A2
  ** FCC_A1
 Mapping terminated 1
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3:
```

*) POLY has a special stepping option for T_o lines. You start by setting the x axis variable as for normal stepping. Here you must also give the second axis variable as none since it was entered in the previous plot.

```
POLY_3: s-a-v 1 w(c) 0 .02
Increment /5E-04/:
POLY_3: s-a-v 2 none
POLY_3: step
Option? /NORMAL/:
```

*) Inspect the options.

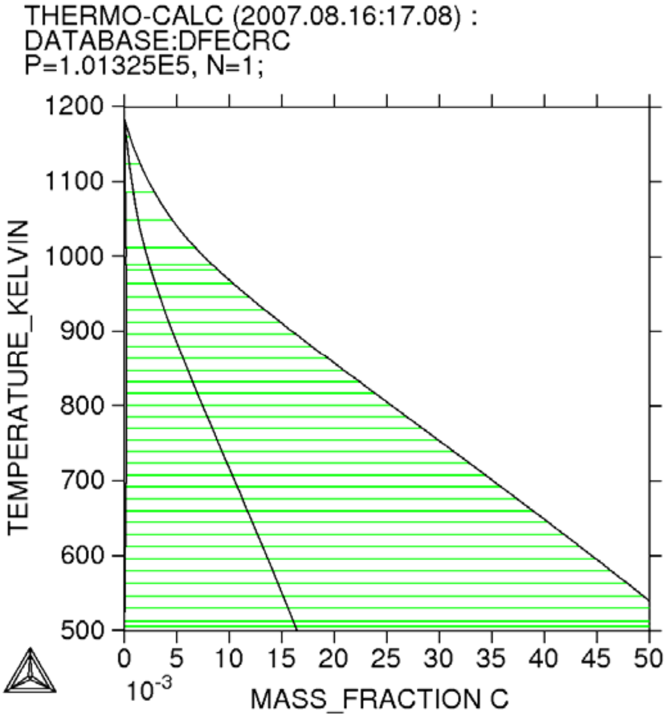
```
Option? /NORMAL/:  ?
 The following options are available:
 NORMAL             Stepping with given conditions
 INITIAL_EQUILIBRIA An initial equilibrium stored at every step
 EVALUATE           Specified variables evaluated after each step
```

```
 SEPARATE_PHASES    Each phase calculated separately
 T-ZERO             T0 line calculation
 PARAEQUILIBRIUM    Paraequilibrium diagram
 MIXED_SCHEIL       Scheil with fast diffusing elements
Option? /NORMAL/:  T-zero
Name of first phase: bcc
Name of second phase: fcc

 Phase Region from   0.300000E-02 for:
     BCC_A2
     FCC_A1
   3.000000E-03         962.48
   2.500000E-03         984.59
   2.000000E-03        1009.05
   1.500000E-03        1037.79
   1.000000E-03        1074.51
   5.000000E-04        1121.53
   5.000000E-10        1184.79

 Phase Region from   0.227025E-03 for:
     BCC_A2
     FCC_A1
   2.270245E-04        1153.42
   7.270245E-04        1098.63
   1.227025E-03        1056.76
   1.727025E-03        1023.98
   2.227025E-03         997.57
   2.727025E-03         974.33
   3.227025E-03         952.97
   3.727025E-03         932.87
   4.227025E-03         913.68
   4.727025E-03         895.17
   5.227025E-03         877.17
   5.727025E-03         859.58
   6.227025E-03         842.31
   6.727025E-03         825.30
   7.227025E-03         808.47
   7.727025E-03         791.81
   8.227025E-03         775.26
   8.727025E-03         758.80
   9.227025E-03         742.40
   9.727025E-03         726.03
   1.022702E-02         709.68
   1.072702E-02         693.32
   1.122702E-02         676.92
   1.172702E-02         660.49
   1.222702E-02         644.00
   1.272702E-02         627.42
   1.322702E-02         610.76
   1.372702E-02         593.99
   1.422702E-02         577.09
   1.472702E-02         560.05
   1.522702E-02         542.85
   1.572702E-02         525.48
   1.622702E-02         507.93
   1.672702E-02         490.16
   1.722702E-02         472.17
   1.772702E-02         453.92
   1.822702E-02         435.41
   1.872702E-02         416.60
   1.922702E-02         397.47
```

```
   1.972702E-02         377.99
   2.000000E-02         367.19
 *** Buffer saved on file USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) In order to indicate that the three lines in the diagram are not just any lines, it may be helpful to identify the phase boundaries by **s**etting the **t**ie-line **st**atus and accepting every third one, for instance.

```
POST: s-t-st 3
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            1  seconds
```

Comments

It is worth noting that the T_o line does not necessarily fall close to the middle of the two phase boundaries.

7.6. Effect of a pressure difference on a two-phase equilibrium

Compute the effect of a pressure increase to 100 atm on the bcc phase when in equilibrium with fcc of 1 atm in the Fe-C system at 1000°C.

Hint

One way to compute the equilibrium between two phases, when only one of them is under an increased pressure, would be to go to the module where the properties are stored and change the molar volume of the other phase to zero. With T-C you have another possibility.

Instructions for using T-C

In POLY there is a special option "set-phase-addition" that allows you to make an addition to the Gibbs energy of an individual phase, α. One could thus account for the effect of an increased pressure on that phase, e.g. caused by the surface energy of a curved interface to another phase, by adding the term $V^{\alpha} \cdot \Delta P$ to the expression for G^{α} stored in the database. Of course, the volume must be expressed for the same amount of phase as the Gibbs energy in the database, i.e., for one formula unit. That would correctly give the effect if the α phase is incompressible, which is a reasonable approximation for condensed phases. For a gas phase in a bubble inside a condensed α phase one would have to evaluate the change of constitution caused by the increased pressure. That would also have an effect on the Gibbs energy.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                  BCC_A2
 HCP_A3                   CEMENTITE               M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc
 FCC_A1                   BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          37
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
```

```
   'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
        C-FE'
   'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
       Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

  The list of references can be obtained in the Gibbs Energy System also
  by the command LIST_DATA and option R

  -OK-
TDB_DFECRC: go pol

  POLY version  3.32,  Aug 2001
POLY_3:
```

*) Start with an ordinary equilibrium between the two phases.

```
POLY_3: s-c P=101325 T=1000 N=1 w(C)=.003
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1000, N=1, W(C)=3E-3
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.52422E+01
 Total Gibbs energy -4.18471E+04,  Enthalpy  2.65541E+04,  Volume  7.22976E-06

 Component               Moles      W-Fraction Activity   Potential   Ref.stat
 C                       1.3798E-02 3.0000E-03 2.6736E-01 -1.0968E+04 SER
 FE                      9.8620E-01 9.9700E-01 6.1890E-03 -4.2279E+04 SER

 BCC_A2                     Status ENTERED     Driving force  0.0000E+00
 Number of moles 6.1420E-01, Mass 3.4277E+01        Mass fractions:
 FE  9.99810E-01  C   1.90214E-04

 FCC_A1                     Status ENTERED     Driving force  0.0000E+00
 Number of moles 3.8580E-01, Mass 2.0965E+01        Mass fractions:
 FE  9.92406E-01  C   7.59399E-03
POLY_3:
```

*) You would be interested in studying the effect of a pressure increase in the bcc phase on the equilibrium composition of the fcc phase. The term $V^{bcc}(P-P_0)$ should thus be added to the Gibbs energy of bcc from the database. You should realize that G is expressed for one formula unit in the database and V should be evaluated for the same unit. It can be obtained from POLY using the symbol Vf, where f stands for formula unit, followed by the name of the phase.

```
POLY_3: ent-sym var wCfcc1=w(fcc,C);
POLY_3: ent-sym var VdelP=(100-1)*101325*Vf(bcc);
POLY_3:
```

*) With the command **special options** you can choose the **set-ph**ase-**add**ition command and thus add the value of VdelP to the G function obtained from the database.

```
POLY_3: special options
Which option? /SET_MISCIBILITY_GAP/:  ?
 No such option, use one of
```

```
    SET_MISCIBILITY_GAP
    SET_MAJOR_CONSTITUENTS
    MISC_GAP_TEST_INTERVAL
    SET_PHASE_ADDITION
    LIST_PHASE_ADDITION
    SET_BREAK_CONDITION
    SET_PRESENT_PHASE
    OUTPUT_AT_MAP_AND_STEP
    T-ZERO TEMPERATURE
    PARAEQUILIBRIUM
    STABILITY_CHECK
    NEVER_ADJUST_MINIMUM_Y
    TOGGLE_ALTERNATE_MODE
    SHOW_OUTPUT_FILE

Which option? /SET_MISCIBILITY_GAP/:  set-ph-add
Phase with addition: bcc
Addition to G per mol formula unit: VdelP
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1000, N=1, W(C)=3E-3
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.52422E+01
 Total Gibbs energy -4.18054E+04,  Enthalpy  2.69429E+04,  Volume  7.21888E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        1.3798E-02 3.0000E-03 2.0159E-01 -1.3316E+04 SER
 FE                       9.8620E-01 9.9700E-01 6.2452E-03 -4.2204E+04 SER

 BCC_A2                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 5.1669E-01, Mass 2.8840E+01         Mass fractions:
 FE  9.99856E-01  C   1.43596E-04

 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 4.8331E-01, Mass 2.6402E+01         Mass fractions:
 FE  9.93880E-01  C   6.12020E-03
POLY_3:
```

*) Save the new composition of the fcc phase.

```
POLY_3: ent-sym var wCfcc2=w(fcc,C);
POLY_3: eval
Name(s):
 WCFCC1=7.5939899E-3
 VDELP=73.338681
 WCFCC2=6.1202042E-3
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) The mass fraction of C in fcc has thus decreased from WCFCC1=0.007594 to WCFCC2=0.006120. Those values were given already in the two lists of the states of equilibrium.

2) POLY can directly give extensive quantities per formula unit using symbols with an f instead of m, e.g. V_f instead of V_m. However, this works only for a phase. Even if there is only one phase in the system, you should thus write V_f(phase).

7.7. Driving force for the formation of a new phase

An fcc phase of Fe with 1.5 mass% C at 1000°C and 1 atm is supersaturated with respect to graphite and cementite. Compute the driving forces for their nucleation. Plot the driving forces as functions of the C content of fcc up to 2 mass% C.

Hint

You should remember the difference between the driving force for the first stage of formation, the so-called nucleation, and the driving force for the whole reaction until equilibrium has been established, i.e. the integrated driving force. See Section 7.7 in the textbook.

Instructions for using T-C

POLY automatically gives the driving force for each dormant phase but as a dimensionless quantity by dividing with RT.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE                M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc gra cem
 FCC_A1                   GRAPHITE                 CEMENTITE
   RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           31
 FUNCTIONS ....
```

```
 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Start by computing the equilibrium for the supersaturated fcc alone in order later to be able to evaluate its driving forces for nucleation. The other phases should thus be dormant.

```
POLY_3: s-c P=101325 T=1000 N=1 w(C)=.015
POLY_3: ch-st p cem gra=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1000, N=1, W(C)=1.5E-2
 DEGREES OF FREEDOM 0

 Temperature 1000.00 K ( 726.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.29484E+01
 Total Gibbs energy -4.00586E+04,  Enthalpy  3.03308E+04,  Volume  7.03164E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        6.6125E-02 1.5000E-02 7.4084E-01 -2.4941E+03 SER
 FE                       9.3388E-01 9.8500E-01 5.8705E-03 -4.2718E+04 SER

 CEMENTITE                   Status DORMANT     Driving force  2.1434E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 FE  9.33106E-01  C   6.68943E-02

 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.2948E+01         Mass fractions:
 FE  9.85000E-01  C   1.50000E-02

 GRAPHITE                    Status DORMANT     Driving force  1.2225E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 C   1.00000E+00  FE  0.00000E+00

POLY_3:
```

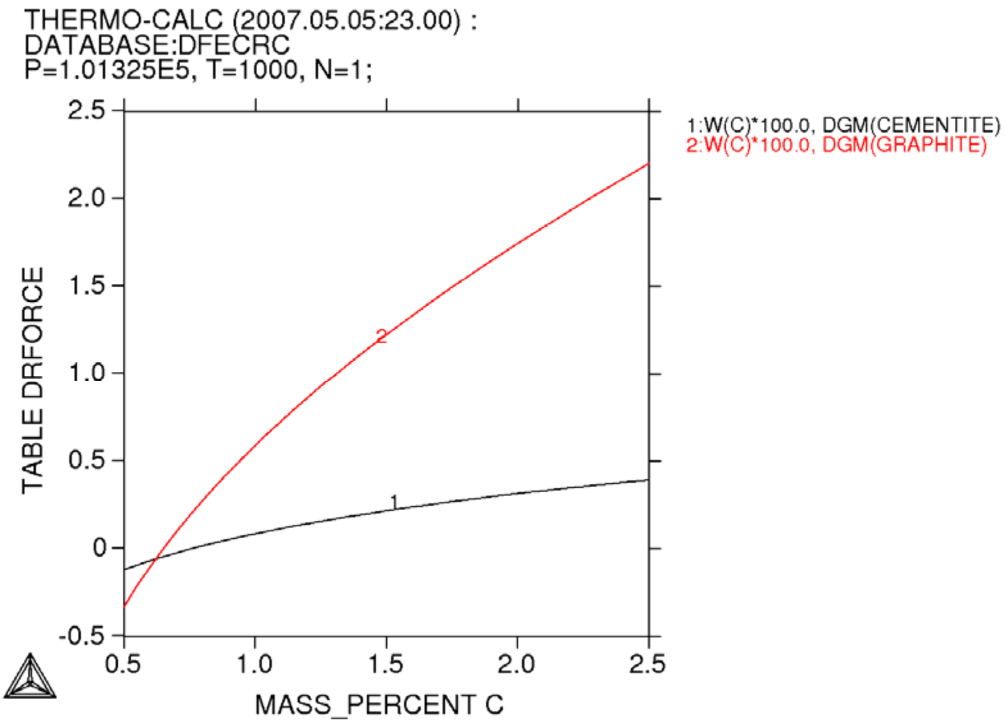
*) Step in order to obtain the properties of the supersaturated fcc over the range of composition.

```
POLY_3: s-a-v
Axis number: /1/:
Condition /NONE/:  w(C)
Min value /0/:  .005
```

```
Max value /1/:  .025
Increment /5E-04/:
POLY_3: step
Option? /NORMAL/:
 looking for miscibility gaps..at:
 QSTEPP  2.500000000000000E-002
 QSTEPP  5.000000000000000E-003
 QSTEPP  1.500000000000000E-002
 No new miscibility gap found!

 Phase Region from   0.250000E-01 for:
     FCC_A1
 Calculated    43 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) All the necessary computations have now been done because for any equilibrium that has been computed, POLY can give you the driving force of a dormant phase through the symbol DGm.

```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01


POST: s-d-a x w-p C
POST: ent-sym tab DrForce=dgm(cem),dgm(gra);
POST: s-d-a y DrForce
COLUMN NUMBER /*/:
POST: set-lab f
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time             0  seconds
```

Comments

The driving force for graphite turns positive above about 0.65 mass% C, for cementite not until about 0.75 mass% C. Cementite is thus a metastable phase. At increasing C contents the driving force for graphite increases much faster than for cementite. The reason is that the mole fraction of C is much higher in graphite. You may illustrate that effect with a molar Gibbs energy diagram. Place the three curves such that the common tangent to cementite and graphite is parallel to the tangent to the fcc curve at a mass percent of about 0.6 where the two curves intersect. Then draw tangents for higher C contents in fcc.

7.8. Partitionless transformation under local equilibrium

Consider the partitionless solidification of an Al-Mg alloy with 2 mass% Mg under 1 atm. Suppose heat conduction is very efficient and the system is thin enough to be kept at a homogeneous temperature, which is decreased until the right temperature for partitionless solidification has been established. Compute the driving force for diffusion in the liquid between the solidification front and the interior of the liquid.

Hint

1) You must first find the temperature where the conditions for partitionless solidification are fulfilled. It is required that the new phase should grow with the composition of the bulk of the liquid. You should thus start by computing at what temperature the solid phase with that composition is in equilibrium with liquid. That should also yield the composition of the liquid at the interface. Then it is easy to take the difference in Mg content inside the liquid, i.e., between the interface to solid and the bulk, which has the initial content.

2) The potential for interdiffusion in a certain position is the difference between the local values of the chemical potentials. In connection to Eq. 4.8 it was also regarded as the driving force for diffusion which was not correct. The driving force for diffusion is the gradient of the diffusion potential. In the present case you are asked to consider the driving force for diffusion between two localities which might mean the difference in potentials.

Instructions for using T-C

In T-C it is convenient to require that a one-phase system of known composition should be in equilibrium with another phase. Apply the command “ch-st p <name>=fix 0” to the solid phase that has formed with the correct composition for partitionless growth.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: def-el Al Mg
 AL                       MG  DEFINED
TDB_DALMGSI: rej p *
 LIQUID:L                 FCC_A1                   HCP_A3
```

```
 DIAMOND_A4               ALMG_BETA                ALMG_DZETA
 ALMG_UPSILON             AL12MG17  REJECTED
TDB_DALMGSI:
```

*) Al has the fcc structure. You should thus restore fcc together with the liquid phase.

```
TDB_DALMGSI: rest p liq fcc
 LIQUID:L                 FCC_A1  RESTORED
TDB_DALMGSI: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            2
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'N Saunders, COST project (1994); MG-SI'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DALMGSI: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Equilibrium with liquid without any material going into the liquid is defined by **liq=fix 0**. You can thus define a system of fcc with the correct composition for partitionless solidification and compute at what temperature it is in equilibrium with the liquid.

```
POLY_3: s-c P=101325 N=1 w(Mg)=.05
POLY_3: ch-st p liq=fix 0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in            0  s
  19 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=853.05611
POLY_3:
```

*) Store the values of the chemical potentials of this two-phase equilibrium because they apply at the interface.

```
POLY_3: ent-sym var muMgInt=mu(Mg);
POLY_3: ent-sym var muAlInt=mu(Al);
POLY_3:
```

*) Now you should evaluate the chemical potentials in the bulk of the liquid, i.e. with fcc as dormant, assuming that the bulk is at the same temperature as the interface. Its composition is already given as a condition.

```
POLY_3: s-c T=
Value /853.0561072/:
POLY_3: ch-st p fcc=dor
POLY_3: ch-st p liq=ent 1
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
```

```
POLY_3:
```

*) The driving force for diffusion is given by the difference in diffusion potential between the two positions in the liquid.

```
POLY_3: ent-sym var drf=mu(Al)-mu(Mg)-muAlInt+muMgInt;
POLY_3: eval
Name(s):
 MUMGINT=-52533.273
 MUALINT=-33518.471
 DRF=8843.7844
POLY_3: exit
 CPU time            0  seconds
```

Comments

Notice that “partitionless” could be “diffusionless” but not necessarily. In the present case there is local equilibrium and diffusion in the pile-up of Mg in front of the advancing interface.

7.9. Activation energy for a fluctuation

Long ago one had the idea that a small coherent particle could precipitate by a fluctuation in the parent phase first reaching the correct composition and size for a nucleus and then transforming without any diffusion. Consider an fcc Fe alloy with 0.5 mass% C at 1000 K and 1 bar and calculate the activation energy for such a fluctuation being a precursor of a critical nucleus of the new phase.

Hint

You have to know the composition and size of the fcc fluctuation. Suppose they have the same values as the critical nucleus of the new phase according to ordinary nucleation theory. You should then start by evaluating the critical nucleus. 1 J/m^2 may be a reasonable value for the specific surface energy.

Instructions for using T-C

The pressure in the critical nucleus is obtained from its driving force, which POLY calculates for all phases not suspended. If you are not sure what phase would nucleate, you can examine the driving forces for possible phases if you have made them dormant. Remember that POLY gives the dimensionless driving force by dividing its actual value with RT. Thus, $2\sigma / r = \Delta P = -\Delta G_m / V_m^{new} = (RT / V_m^{new}) \cdot D / RT$. Its content of material would be $4\pi r^3 / 3V_m^{new}$ and the fcc fluctuation should contain the same amount of material. Neglect the possible "surface" energy between the fcc fluctuation and the fcc bulk. Its Gibbs energy would then be $(4\pi r^3 / 3V_m^{new}) \cdot G_m(fcc)$ and this material has been taken from the bulk fcc with its chemical potentials.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
```

```
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE                M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC:
```

*) If you have no experience with the Fe-C system, it may seem reasonable to keep fcc, bcc, cementite and graphite.

```
TDB_DFECRC: rest p fcc bcc cem gra
 FCC_A1                   BCC_A2                   CEMENTITE
 GRAPHITE  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           41
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Start with the initial fcc alloy. Compute it as a state of equilibrium in order to get its properties. Set all the other phases dormant in order to obtain their driving forces.

```
POLY_3: s-c P=101325 T=1050 N=1 w(C)=.004
POLY_3: ch-st p bcc cem gra=dor
POLY_3: c-e
 Using global minimization procedure
 Calculated          137  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:  P
 Output from POLY-3, equilibrium =     1, label A0  , database: DFECRC

 Conditions:
 P=1.01325E5, T=1050, N=1, W(C)=4E-3
 DEGREES OF FREEDOM 0
```

```
 Temperature 1050.00 K ( 776.85 C),  Pressure  1.013250E+05
 Number of moles of components  1.00000E+00,  Mass  5.50434E+01
 Total Gibbs energy -4.52242E+04,  Enthalpy  3.05639E+04,  Volume  7.17737E-06

 Component                Moles      W-Fraction Activity   Potential   Ref.stat
 C                        1.8331E-02 4.0000E-03 8.6832E-02 -2.1335E+04 SER
 FE                       9.8167E-01 9.9600E-01 5.3467E-03 -4.5670E+04 SER

 BCC_A2                      Status DORMANT     Driving force  2.7134E-03
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 FE  9.99877E-01  C   1.22812E-04

 CEMENTITE                   Status DORMANT     Driving force -2.3017E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 FE  9.33106E-01  C   6.68943E-02

 FCC_A1                      Status ENTERED     Driving force  0.0000E+00
 Number of moles 1.0000E+00, Mass 5.5043E+01         Mass fractions:
 FE  9.96000E-01  C   4.00000E-03

 GRAPHITE                    Status DORMANT     Driving force -8.5079E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00         Mass fractions:
 C   1.00000E+00  FE  0.00000E+00
POLY_3:
```

*) Bcc is the only phase with a tendency to form. You should thus consider a critical nucleus of bcc. Evaluate its radius and size.

```
POLY_3: ent-sym var critr=2*1*Vm(bcc)/8.31451/T/DGM(bcc);
POLY_3: sh critr
 CRITR=6.183278E-7
POLY_3: ent-sym var critN=4*3.14*critr**3/3/Vm(bcc);
POLY_3:
```

*) Now you find the activation energy for the formation of the critical bcc nucleus.

```
POLY_3: ent-sym var Q=DGM(bcc)*8.31451*T*critN;
POLY_3: eval
Name(s):
 CRITR=6.183278E-7
 CRITN=1.3514482E-13
 Q=3.2013704E-12
POLY_3:
```

*) You cannot yet evaluate the Gibbs energy of the fluctuation but you can evaluate the Gibbs energy of that material before the formation of the fluctuation.

```
POLY_3: ent-sym var G0=(x(bcc,C)*mu(C)+x(bcc,Fe)*mu(Fe))*critN;
POLY_3: ent-sym var wbccC=w(bcc,C);
POLY_3:
```

*) In order to find the Gibbs energy of the fluctuation, you must compute the fcc phase with the correct composition as a state of equilibrium.

```
POLY_3: s-c w(C)=wbccC
POLY_3: c-e
 Using global minimization procedure
 Using already calculated grid
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Finally you get the activation energy for the fluctuation before it transforms into the new bcc structure.

```
POLY_3: ent-sym var deltaG=critN*Gm-G0;
POLY_3: eval
Name(s):
 CRITR=6.183278E-7
```

```
 CRITN=1.3514482E-13
 Q=3.2013704E-12
 G0=-6.1702231E-9
 WBCCC=1.2281177E-4
 DELTAG=2.0727424E-11
POLY_3: exit
 CPU time            0  seconds
```

Comments

It is interesting to compare the activation energy for the fcc fluctuation, deltaG, with the activation energy for the critical bcc nucleus, Q. DeltaG is about 10 times as large. It would thus be cheaper to start the formation of the bcc phase by changing the structure first and then let the minute bcc nucleus grow to and above the critical size.

Chapter 8. Phase equilibria and potential diagrams

8.1. Gibbs' phase rule

CaO and MgO are both stoichiometric and they can form a solution (Ca,Mg)O. Evaluate the chemical potential of MgO in a 50/50 alloy at 1500 K and 1 atm, using pure MgO as the reference.

Hint

For a data bank specialized to oxide systems it would be possible to use only oxides as components. The present system would then have two components. A more general kind of data bank should be capable of combining information on different kinds of systems. It is then essential also to describe chemical potentials of elements. It may be an advantage to build such a data bank on an algorithm based on the chemical potentials of the elements. That does not prevent the use of compounds as components but the number of components must be the same as the number of elements.

Instructions for using T-C

T-C is a general kind of data bank and requires three components in a ternary system even in the present case, which is quasi-binary. The problem may be solved by introducing a third component, e.g. O together with MgO and CaO. The chemical potential of O would have no effect if the CaO-MgO system were truly quasi-binary but the basic algorithm is such that it must be free to consider the O potential. One can thus choose any μ_O as a condition, i.e, to keep it constant during the computation of equilibrium and evaluation of μ_{MgO}.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pgeo
 Current database: Saxena Pure Minerals Database v1

 O                       VA  DEFINED
 STEAM                   OXYGEN                  HYDROGEN
   REJECTED
```

```
 CARBON_MONOXIDE         CARBON_DIOXIDE          METHANE
   REJECTED
TDB_PGEO:
```

*) Remember that O is automatically defined in this database.

```
TDB_PGEO: def-el Mg Ca
 MG                      CA  DEFINED
TDB_PGEO: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 GAS:G       :O2:
  > Gaseous Mixture with C-H-O species, using ideal gas model
 CAO         :CA1O1:
 PERICLASE   :MG1O1:
TDB_PGEO: rej p gas
 GAS:G  REJECTED
TDB_PGEO: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            1
 FUNCTIONS ....
 -OK-
TDB_PGEO: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You should define the new set of components at the beginning of the session on POLY. Give the complete set, including O, which was one of the components already before the change.

```
POLY_3: def-comp MgO CaO O
POLY_3:
```

*) Compute the equilibrium, which is only one phase. In order to obey the Gibbs phase rule, that governs the degrees of freedom, you must **s**et a **c**ondition for O. You can give its chemical potential any value, say 1.

```
POLY_3: s-c P=101325 T=1500 N(MgO)=1 N(CaO)=1 mu(O)=1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            2  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh mu(MgO) mu(CaO) mu(O)
 MU(MGO)=-698026.08
 MU(CAO)=-751328.74
 MU(O)=1
POLY_3:
```

*) These chemical potentials could thus be evaluated directly because they concern defined components. That is no longer true for Mg.

```
POLY_3: sh mu(Mg)

 *** ERROR  1622 IN QGSCMA
 *** NO SUCH COMPONENT
POLY_3:
```

*) The chemical potential of Mg must be derived from those of the chosen components. You could define a **fun**ction for the evaluation of the chemical potential of Mg if you are going to use it again later on.

```
POLY_3: ent-sym fun muMg=mu(MgO)-mu(O);
POLY_3: sh muMg
```

```
 MUMG=-698027.08
POLY_3:
```

*) Try to force quite a different value of the chemical potential of O upon the system.

```
POLY_3: s-c mu(O)=1000
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Using already calculated grid
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Check if this large change of mu(O) had any effect on the description of properties of the "real" (Mg,Ca)O system.

```
POLY_3: sh mu(MgO)
 MU(MGO)=-698026.08
```

*) This is the previous value. The change had no effect.

```
POLY_3: exit
 CPU time            0  seconds
```

Comments

1) For the description of a solution phase with a stoichiometric constraint it is necessary to work with a component although one cannot vary its content. The reason is that POLY requires that the Gibbs phase rule must be satisfied. The presence of this "extra" component has no effect on the properties within the stoichiometric solution phase.

2) The problem discussed here is closely related to systems with a compositional degeneracy, to be discussed in Section 13.8. There the solution to the problem will be the same. A new, hypothetical phase is introduced and it is chosen as an arbitrary state of one of the elements. That corresponds to introducing O with an arbitrary chemical potential in the present case.

8.2. Fundamental property diagram

Plot the complete property diagram T,P,μ_{Fe} for pure fcc Fe in order to show that it is convex.

Hint

In principle, it should be a trivial matter to compute equilibrium over a T,P area and to evaluate a property, e.g. μ_{Fe}, for each point. In order to plot the result one should place those points along a series of constant T or P values. One would thus get two series of more or less parallel curves but in order to see the shape of the surface in a two-dimensional diagram, one should redefine the axes. The result should resemble Fig. 8.2 or 8.4. Any point for $\mu(T,P)$ should be placed at (XX,YY) where $XX = T - AA \cdot P$ and $YY = \mu_{Fe} - BB \cdot P$ where the values of AA and BB may be obtained by trial and error. Reasonable starting values could be $AA = 0.2(T_{\max} - T_{\min})/(P_{\max} - P_{\min})$ and $BB = 0.9(\mu_{\max} - \mu_{\min})/(P_{\max} - P_{\min})$.

Instructions for using T-C

In the postprocessor you can easily change the numerical factors in AA and BB for improved visibility. You can make any number of attempts with the same results from POLY.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe
 FE  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3  REJECTED
TDB_DFECRC: rest p fcc
 FCC_A1  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           12
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) For the stepping procedure you need to define the limits of the variables on the axes. You understand how to choose the limits for T and P but not for the chemical potential. You may start by computing two extreme states of equilibrium and read the chemical potentials from them.

```
POLY_3: s-c P=1E5 T=1500 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var mumin=mu(Fe);
POLY_3: s-c P=400E8 T=300
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: ent-sym var mumax=mu(Fe);
POLY_3:
```

*) It is time to define the new axes.

```
POLY_3: ent-sym var AA=(1500-300)/400E8;
POLY_3: ent-sym var BB=(mumax-mumin)/400E8;
POLY_3: ent-sym fun XX=T-.2*AA*P;
POLY_3: ent-sym fun YY=mu(Fe)-.9*BB*P;
```

```
POLY_3:
```

*) Produce the first isobar at a low P, starting with an initial equilibrium and then apply stepping.

```
POLY_3: s-c P=1E5 T=500
POLY_3: c-e
 Using global minimization procedure
 Calculated            1  grid points in            0  s
POLY_3: s-a-v 1 T 300 1500
Increment /30/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Now you may realize that it could be justified to try to save computing time. By default, POLY applies a global minimization procedure in order to make sure that the computation does not stop at a local minimum of Gibbs energy. That may not be a necessary safety procedure in the present case with only one component. You may thus suspend it.

```
POLY_3: set-min
 Settings for global minimization:
 Use global minimization /Y/:  N
 Settings for general calculations:
 Force positive definite Phase Hessian /N/:
 Control minimization step size /N/:
POLY_3:
```

*) Take a step in P and compute a new isobar.

```
POLY_3: s-c P=50E8
POLY_3: c-e
 Global equilibrium calculation turned off, you can turn it on with
 SET_MINIMIZATION_OPTIONS Y,,,,
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Continue with a series of isobars up to 400E8.

```
POLY_3: s-c P=100E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0
```

```
 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c P=150E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c P=200E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c P=250E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c P=300E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0
```

```
 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c P=350E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c P=400E8
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    37 equilibria

 Phase Region from    500.000     for:
     FCC_A1
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

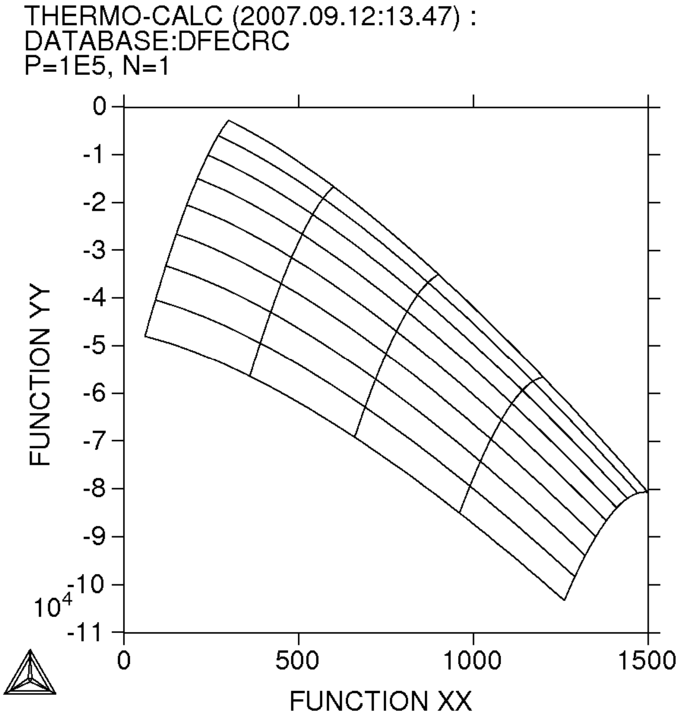
*) Now you should make a similar series of isotherms starting at 300 K and continuing to 1500 K. For the first equilibrium you may choose 1 bar and then step up to 400E8.

```
POLY_3: s-c T=300 P=1E5
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: s-a-v 1 P 1E5 400E8
Increment /999997500/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    100000.     for:
     FCC_A1
 Calculated    43 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c T=600
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0
```

```
 Phase Region from    100000.     for:
     FCC_A1
 Calculated    43 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c T=900
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    100000.     for:
     FCC_A1
 Calculated    43 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c T=1200
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    100000.     for:
     FCC_A1
 Calculated    43 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: s-c T=1500
POLY_3: c-e
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    100000.     for:
     FCC_A1
 Calculated    43 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Time to go to the postprocessor.

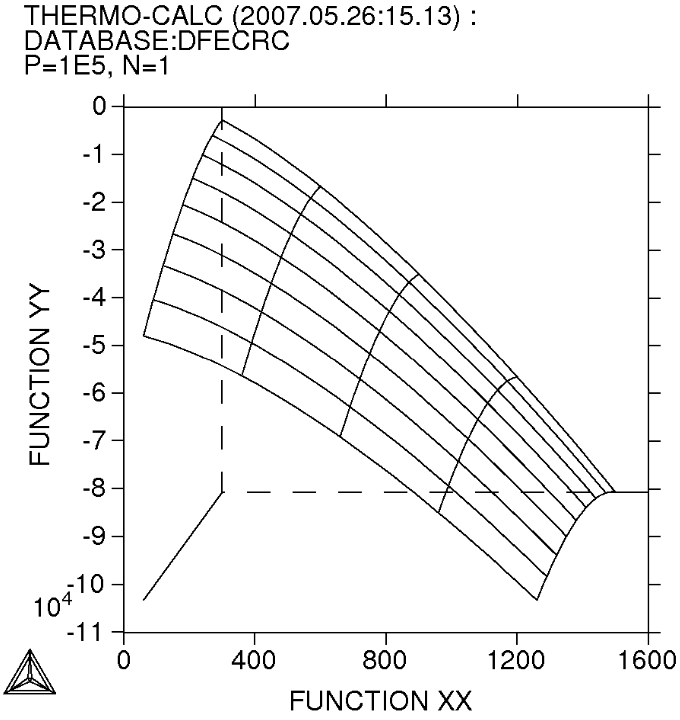
```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST: s-d-a x XX
POST: s-d-a y YY
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) If you like to increase the visibility you may add a coordinate system. To help you, a file with the correct coordinate system has been prepared, the file name is 8.2.exp. To append the coordinate system on top of your calculation you should use the command "**app**end-experimental-data".

```
POST: app
USE EXPERIMENTAL DATA (Y OR N) /N/:  Y 8.2.exp
PROLOGUE NUMBER: /0/:  1
DATASET NUMBER(s): /-1/:  1
POST: s-s-s x n 0 1600
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            0  seconds
```

8.4. Potential phase diagrams in binary and multinary systems

Examine if there is any combination (T,P) where the invariant four-phase equilibrium bcc/fcc/Fe_3C/graphite exists in the Fe-C system? If you find it, examine the region around it. In principle, it should be similar to Fig. 8.11 but instead of constructing a three-dimensional diagram, you may show projections from three directions.

Hint

When mapping the region around the invariant equilibrium, it may be difficult to start from the invariant equilibrium, which cannot be followed. It may be better to start from a point on a three-phase line.

Instructions for using T-C

If you have difficulties finding the invariant point, you may have to try defining better start values.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1
```

```
 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE                M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc cem gra
 FCC_A1                   BCC_A2                   CEMENTITE
 GRAPHITE  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           41
 FUNCTIONS ....

 List of references for assessed data

   'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
       -425, also in NPL Report DMA(A)195 Rev. August 1990'
   'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
        C-FE'
   'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
       Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) To find the four-phase equilibrium you should fix all four phases. You cannot prescribe any values for T or P because they have unique values for the four-phase equilibrium and you don't know them.

```
POLY_3: ch-st p *=fix 1
POLY_3: c-e
 Global minimization failed, error code         1313
 TEMPERATURE NOT SET
 . Using normal POLY minimization.
 Convergence problems, increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
 Old start values kept
 Old start values kept

 *** ERROR  1611 IN QEQUIL
 *** TOO MANY ITERATIONS
 Give the command INFO TROUBLE for help
```

*) It is often difficult to find an invariant equilibrium There are several ways to try to overcome the difficulty. The simplest is to try **c-e** again. The next simplest is to **s**et-**a**ll-**s**tart values and choose the option **F**orced.

```
POLY_3: s-a-s
T /996.5525772/:
P /5487395.871/:
Automatic start values for phase constituents? /N/:  F
```

```
 Forcing automatic start values
 Automatic start values will be set
POLY_3: c-e
 Global minimization failed, error code         1313
 TEMPERATURE NOT SET
 . Using normal POLY minimization.
 Testing POLY result by global minimization procedure
 Calculated          276  grid points in            0  s
  18 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Inspect the equilibrium.

```
POLY_3: sh T P mu(Fe) mu(C)
 T=996.20822
 P=5.5784971E8
 MU(FE)=-37956.434
 MU(C)=-9579.0729
POLY_3:
```

*) You have thus obtained an initial equilibrium and you could in principle start mapping. However, it is often difficult to make the mapping procedure work if the single equilibrium is invariant. POLY cannot start mapping by following that equilibrium! Get another single equilibrium very close the invariant one. Change the status of the phases from **fix**ed to **ent**ered and give values of **T** and **P** and **N=1**.

```
POLY_3: ch-st p *=ent 0
POLY_3: s-c N=1 T=1000 P=6E8
POLY_3: l-c
 N=1, T=1000, P=6E8
 DEGREES OF FREEDOM 1
POLY_3:
```

*) You must enter another condition. You could enter the Fe or C content but would not know what would be a convenient value. Since you are just interested in the potentials it may be more logical instead to take back one of the phases as fixed.

```
POLY_3: ch-st p gra=fix 0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          276  grid points in            0  s
  20 ITS,  CPU TIME USED   0 SECONDS
POLY_3: s-a-v 1 T 900 1100
Increment /5/:
POLY_3: s-a-v 2 P 1E8 1E9 2*
 Logarithmic step set
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   9.903E+02  6.000E+08
  ** BCC_A2
     CEMENTITE
     GRAPHITE
 Calculated     6 equilibria

 Phase region boundary   2 at:   9.962E+02  5.578E+08
  ** BCC_A2
```

```
    CEMENTITE
    FCC_A1
    GRAPHITE

 Phase region boundary   3 at:   9.962E+02  5.578E+08
  ** BCC_A2
     FCC_A1
     GRAPHITE
 Calculated     9 equilibria

 Phase region boundary   4 at:   9.962E+02  5.578E+08
     CEMENTITE
  ** FCC_A1
     GRAPHITE
 Calculated    28 equilibria

 Phase region boundary   5 at:   9.903E+02  6.000E+08
  ** BCC_A2
     CEMENTITE
     GRAPHITE
 Calculated    14 equilibria
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

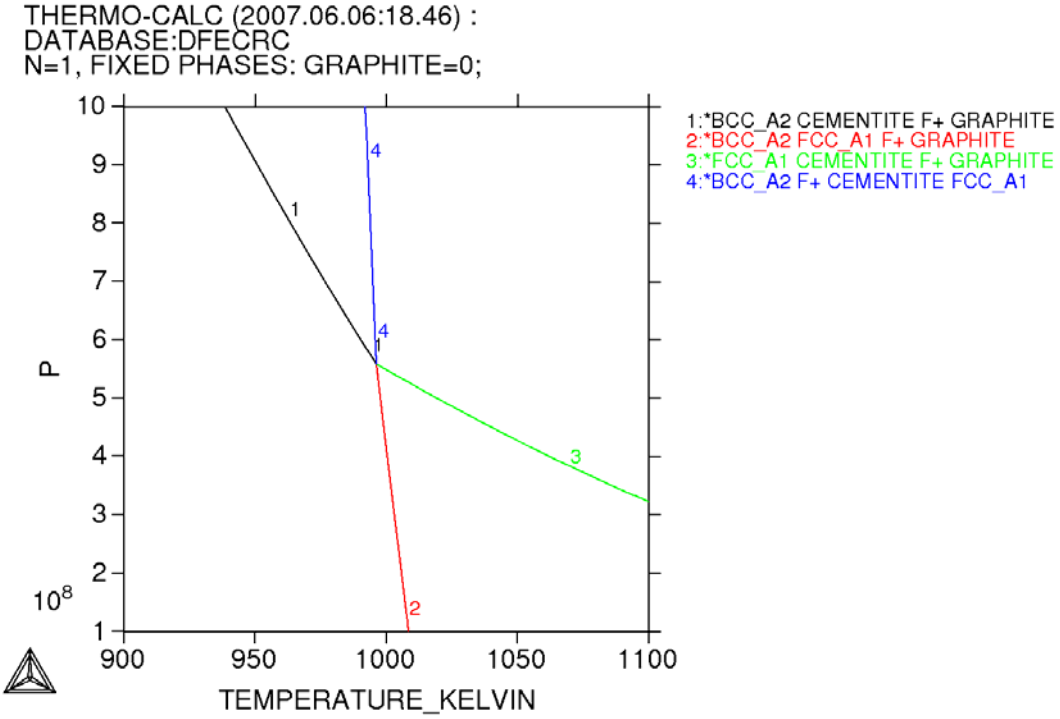
*) Of course, you obtained only equilibria containing graphite because you had the condition **gra=fix**. Introduce a new single equilibrium to start a new mapping with **gra**phite **ent**ered and **cem**entite **fix 0**. Note that fix 1 is not convenient when you have now given N=1. Furthermore, POLY will not repeat the equilibria already computed.

```
POLY_3: ch-st p gra=ent 0
POLY_3: ch-st p cem=fix 0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          276  grid points in            0  s
  20 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) You don't need to define the axes again.

```
POLY_3: map

 Organizing start points

 No initial equilibrium added, trying to fix one

 Phase region boundary   1 at:   9.959E+02  6.000E+08
  ** BCC_A2
     CEMENTITE
     FCC_A1
 Terminating at known equilibrium
 Calculated     3 equilibria

 Phase region boundary   2 at:   9.959E+02  6.000E+08
  ** BCC_A2
     CEMENTITE
     FCC_A1
 Outside axis limits
 Calculated     6 equilibria
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01
```

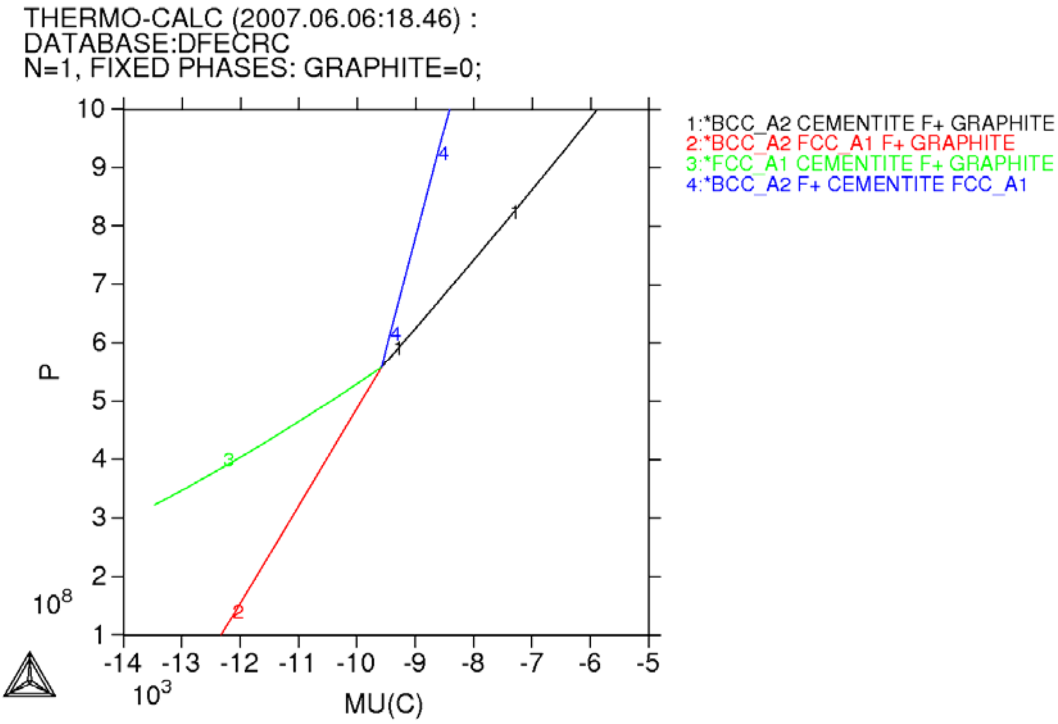
```
 Setting automatic diagram axis

POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



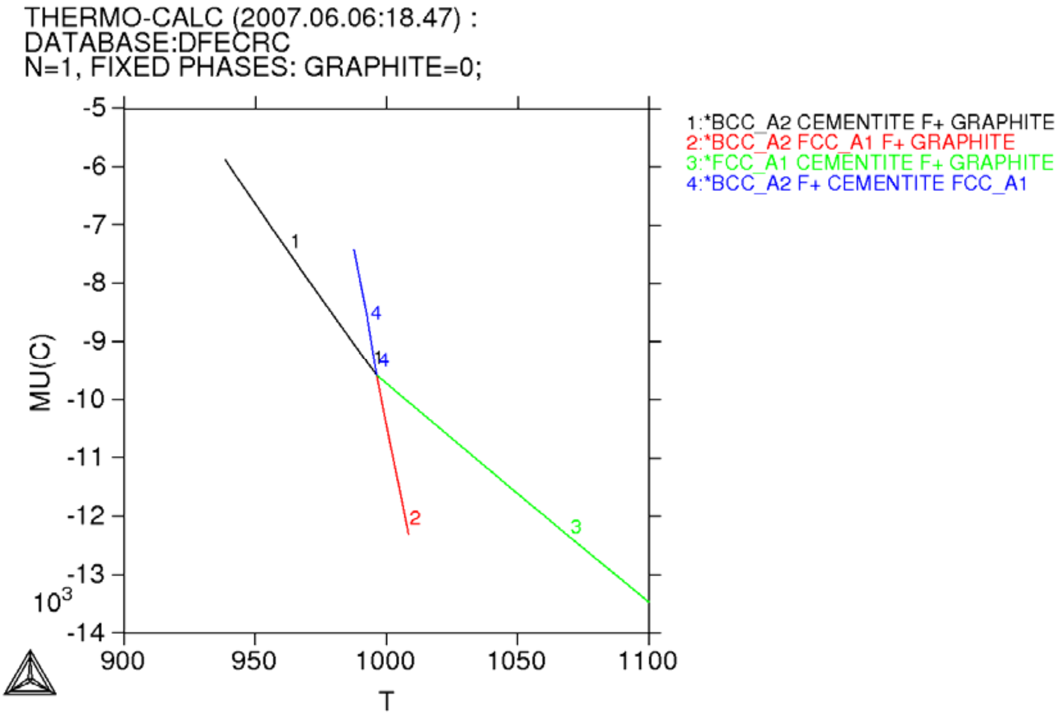
```
POST:
```

*) There is a third potential axis in the complete potential phase diagram, either mu(Fe) or mu(C). The remaining one will make the diagram a fundamental property diagram. Try other combinations of axes.

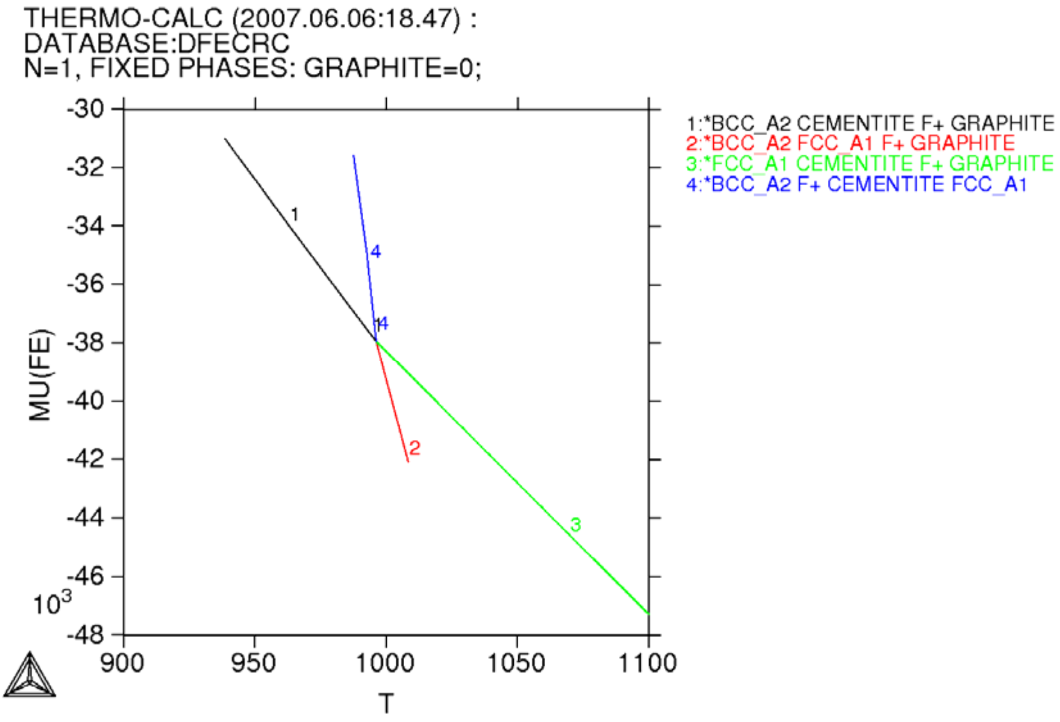
```
POST: s-d-a x mu(C)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: s-d-a x T
POST: s-d-a y mu(C)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: s-d-a y mu(Fe)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time                  0  seconds
```

Comments

You have a three-dimensional description of the system. The complete potential diagram could be inscribed in a cube and the three first diagrams show how it looks from the three sides. You thus have full information on its three-dimensional structure. The invariant equilibrium falls close to the centre. Let P be the vertical axis. The third diagram shows that three of the univariant equilibria end on the top or bottom side. And the second diagram shows that it is 1 and 4 that end on the top and 2 that ends on the bottom. 3 ends on the mu(C);P side at high T.

The fourth diagram is from another complete potential phase diagram obtained by using mu(Fe) instead of mu(C).

8.5. Sections of potential phase diagrams

Compute the μ_O, μ_S phase diagram for the Cu-O-S system at 1 atm. Then make a section at 1000 K, using P_{O_2} to express μ_O and P_{S_2} to express μ_S.

Hint

You are invited to try to interpret the resulting potential diagram before sectioning. It may then be helpful to consult the long list of print-outs from the computations of equilibria.

Instructions for using T-C

1) In order to reject the many minor kinds of molecules in the gas and not affect the description of the condensed phases, there is a special command for that purpose.

2) You like to use activities as axis variables during mapping and should thus start with an initial equilibrium using them as conditions. However, it is sometimes difficult for POLY to find the equilibrium under such conditions. It may thus be wise as the very first action to compute an equilibrium under a given composition.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PSUB
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el Cu O S
 CU                     O                        S
   DEFINED
TDB_PSUB:
```

*) You like to reject all the many species in the gas without affecting the solid phases. Then you can **rej**ect **co**nstituents in the **gas**, in this case all *****.

```
TDB_PSUB: rej co gas *

 *** ERROR  1000 IN TDBMPE
 *** NO SUCH CONSTITUENT IN SUBLATTICE
TDB_PSUB:
```

*) This error message is a mistake. Just ignore it and restore O2 and S2. However, in this particular case you can restore only one at a time.

```
TDB_PSUB: rest co gas O2
 O2 IN GAS:G SUBLATTICE   1 RESET
CONSTITUENT: S2
 S2 IN GAS:G SUBLATTICE   1 RESET
CONSTITUENT:
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Reference REF2       missing
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
```

```
POLY_3:
```

*) You are only interested in equilibria between condensed phases. The gas was included just to allow you to use it for references.

```
POLY_3: ch-st p gas=sus
POLY_3:
```

*) For the first, single equilibrium before stepping, you may choose any composition with enough Cu to form the pure Cu phase.

```
POLY_3: s-c P=101325 T=1000 N=1 x(O)=.2 x(S)=.2
POLY_3: c-e
 Using global minimization procedure
 Calculated           16  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) You like to map with mu(O) and mu(S) as axes and must start by introducing them as conditions for the single equilibrium.

```
POLY_3: s-c x(O)=none mu(O)=
Value /-186710.6771/:
POLY_3: s-c x(S)=none mu(S)=
Value /-138765.8325/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Using already calculated grid
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) With P constant at 1 atm you still have three axes.

```
POLY_3: s-a-v 1
Condition /NONE/:  mu(S)
Min value /0/:
```

*) Chemical potentials have negative values when SER is used as reference. Since you are not familiar with the system, you should use wide ranges of the chemical potentials.

```
Min value /0/:  -400000
Max value /1/:  0
Increment /10000/:
POLY_3: s-a-v 2
Condition /NONE/:  mu(O)
Min value /0/:  -400000
Max value /1/:  0
Increment /10000/:
POLY_3: s-a-v 3
Condition /NONE/:  T
Min value /0/:  500
Max value /1/:  1500
Increment /25/:
POLY_3: map

 Organizing start points

Using ADDED start equilibria

 Calculated    10 equilibria

 Phase region boundary   1 at:  -1.388E+05 -1.867E+05  7.170E+02
  ** CU2O
  ** CU2S_S2
     CU2S_S3
 Calculated     4 equilibria
```

```
Phase region boundary   2 at:  -1.303E+05 -1.954E+05  7.170E+02
    CU
 ** CU2O
 ** CU2S_S2
    CU2S_S3

Phase region boundary   3 at:  -1.303E+05 -1.954E+05  7.170E+02
 ** CU
 ** CU2O
    CU2S_S2
Calculated    14 equilibria

Phase region boundary   4 at:  -1.303E+05 -1.954E+05  7.170E+02
 ** CU
 ** CU2O
    CU2S_S3
Calculated    29 equilibria

Phase region boundary   5 at:  -2.017E+05 -2.275E+05  1.358E+03
 ** CU
 ** CU2O
    CU2S_S3
    CU_L

Phase region boundary   6 at:  -2.017E+05 -2.275E+05  1.358E+03
 ** CU
 ** CU2O
    CU_L
*** Sorry cannot continue ***    9


Phase region boundary   7 at:  -2.017E+05 -2.275E+05  1.358E+03
 ** CU
    CU2S_S3
 ** CU_L
Calculated    21 equilibria

Phase region boundary   8 at:  -2.017E+05 -2.275E+05  1.358E+03
 ** CU2O
    CU2S_S3
 ** CU_L
Calculated     5 equilibria

Phase region boundary   9 at:  -2.061E+05 -2.292E+05  1.402E+03
 ** CU2O
    CU2S_L
    CU2S_S3
 ** CU_L

Phase region boundary  10 at:  -2.061E+05 -2.292E+05  1.402E+03
 ** CU2O
 ** CU2S_L
    CU_L
Calculated    10 equilibria

Phase region boundary  11 at:  -2.061E+05 -2.292E+05  1.402E+03
 ** CU2O
 ** CU2S_L
    CU2S_S3
Calculated     9 equilibria
```

```
Phase region boundary  12 at:  -1.764E+05 -1.995E+05  1.402E+03
 ** CU2O
    CU2SO4
 ** CU2S_L
    CU2S_S3

Phase region boundary  13 at:  -1.764E+05 -1.995E+05  1.402E+03
 ** CU2O
 ** CU2SO4
    CU2S_L
Calculated    10 equilibria

Phase region boundary  14 at:  -1.764E+05 -1.995E+05  1.402E+03
 ** CU2O
 ** CU2SO4
    CU2S_S3
Calculated    24 equilibria

Phase region boundary  15 at:  -1.272E+05 -1.833E+05  8.681E+02
 ** CU2O
 ** CU2SO4
    CU2S_S3
    CUSO4

Phase region boundary  16 at:  -1.272E+05 -1.833E+05  8.681E+02
 ** CU2O
 ** CU2SO4
    CUSO4
Calculated    30 equilibria

Phase region boundary  17 at:  -1.272E+05 -1.833E+05  8.681E+02
 ** CU2O
    CU2S_S3
 ** CUSO4
*** Buffer saved on file: USERPROFILE\RESULT.POLY3
Calculated     9 equilibria

Phase region boundary  18 at:  -1.151E+05 -1.802E+05  7.170E+02
 ** CU2O
    CU2S_S2
    CU2S_S3
 ** CUSO4

Phase region boundary  19 at:  -1.151E+05 -1.802E+05  7.170E+02
 ** CU2O
 ** CU2S_S2
    CUSO4
Calculated    14 equilibria

Phase region boundary  20 at:  -1.151E+05 -1.802E+05  7.170E+02
 ** CU2O
 ** CU2S_S2
    CU2S_S3
Terminating at known equilibrium
Calculated     3 equilibria

Phase region boundary  21 at:  -1.151E+05 -1.802E+05  7.170E+02
 ** CU2S_S2
    CU2S_S3
 ** CUSO4
Calculated    10 equilibria
```

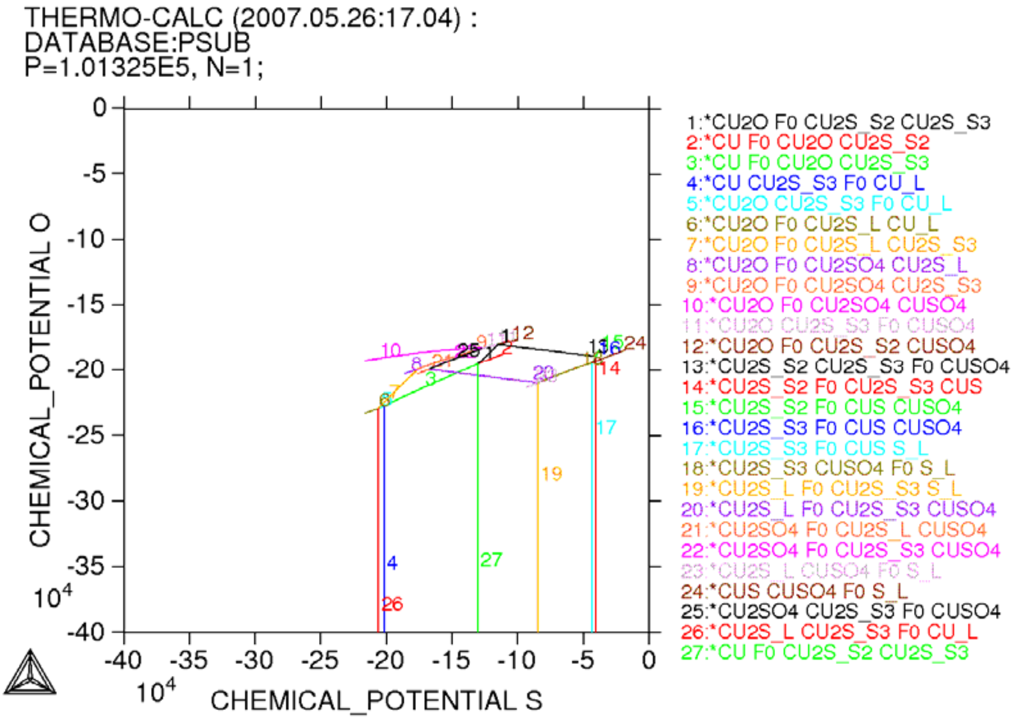
```
Phase region boundary  22 at:  -4.047E+04 -1.896E+05  7.170E+02
 ** CU2S_S2
 ** CU2S_S3
    CUS
    CUSO4

Phase region boundary  23 at:  -4.047E+04 -1.896E+05  7.170E+02
 ** CU2S_S2
 ** CU2S_S3
    CUS
Calculated    26 equilibria

Phase region boundary  24 at:  -4.047E+04 -1.896E+05  7.170E+02
 ** CU2S_S2
 ** CUS
    CUSO4
Calculated    14 equilibria

Phase region boundary  25 at:  -4.047E+04 -1.896E+05  7.170E+02
 ** CU2S_S3
 ** CUS
    CUSO4
Calculated    10 equilibria

Phase region boundary  26 at:  -4.319E+04 -1.944E+05  8.880E+02
 ** CU2S_S3
 ** CUS
    CUSO4
    S_L

Phase region boundary  27 at:  -4.319E+04 -1.944E+05  8.880E+02
 ** CU2S_S3
 ** CUS
    S_L
Calculated    24 equilibria

Phase region boundary  28 at:  -4.319E+04 -1.944E+05  8.880E+02
 ** CU2S_S3
    CUSO4
 ** S_L
Calculated    23 equilibria

Phase region boundary  29 at:  -8.469E+04 -2.098E+05  1.402E+03
    CU2S_L
 ** CU2S_S3
    CUSO4
 ** S_L

Phase region boundary  30 at:  -8.469E+04 -2.098E+05  1.402E+03
 ** CU2S_L
 ** CU2S_S3
    S_L
Calculated    24 equilibria

Phase region boundary  31 at:  -8.469E+04 -2.098E+05  1.402E+03
 ** CU2S_L
 ** CU2S_S3
    CUSO4
Calculated    12 equilibria
```

```
Phase region boundary  32 at:  -1.675E+05 -1.995E+05  1.402E+03
    CU2SO4
 ** CU2S_L
 ** CU2S_S3
    CUSO4
*** Buffer saved on file: USERPROFILE\RESULT.POLY3

Phase region boundary  33 at:  -1.675E+05 -1.995E+05  1.402E+03
 ** CU2SO4
 ** CU2S_L
    CU2S_S3
*** Sorry cannot continue ***    9


Phase region boundary  34 at:  -1.675E+05 -1.995E+05  1.402E+03
 ** CU2SO4
 ** CU2S_L
    CUSO4
Calculated    10 equilibria

Phase region boundary  35 at:  -1.675E+05 -1.995E+05  1.402E+03
 ** CU2SO4
 ** CU2S_S3
    CUSO4
Terminating at known equilibrium
Calculated    24 equilibria

Phase region boundary  36 at:  -8.469E+04 -2.098E+05  1.402E+03
 ** CU2S_L
    CUSO4
 ** S_L
Calculated    10 equilibria

Phase region boundary  37 at:  -4.319E+04 -1.944E+05  8.880E+02
 ** CUS
    CUSO4
 ** S_L
Calculated    20 equilibria

Phase region boundary  38 at:  -1.272E+05 -1.833E+05  8.681E+02
 ** CU2SO4
    CU2S_S3
 ** CUSO4
Terminating at known equilibrium
Calculated    24 equilibria

Phase region boundary  39 at:  -1.764E+05 -1.995E+05  1.402E+03
 ** CU2SO4
 ** CU2S_L
    CU2S_S3
*** Sorry cannot continue ***    9


Phase region boundary  40 at:  -2.061E+05 -2.292E+05  1.402E+03
 ** CU2S_L
    CU2S_S3
 ** CU_L
Calculated    22 equilibria

Phase region boundary  41 at:  -1.303E+05 -1.954E+05  7.170E+02
 ** CU
```

```
  ** CU2S_S2
     CU2S_S3
 Calculated    24 equilibria

 Phase region boundary  42 at:  -1.388E+05 -1.867E+05  7.170E+02
  ** CU2O
  ** CU2S_S2
     CU2S_S3
 Terminating at known equilibrium
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) From the list of results you note that the mapping follows three-phase fields, which will thus appear as lines in the diagram. Four-phase fields appear only at unique temperatures and will thus appear as points.

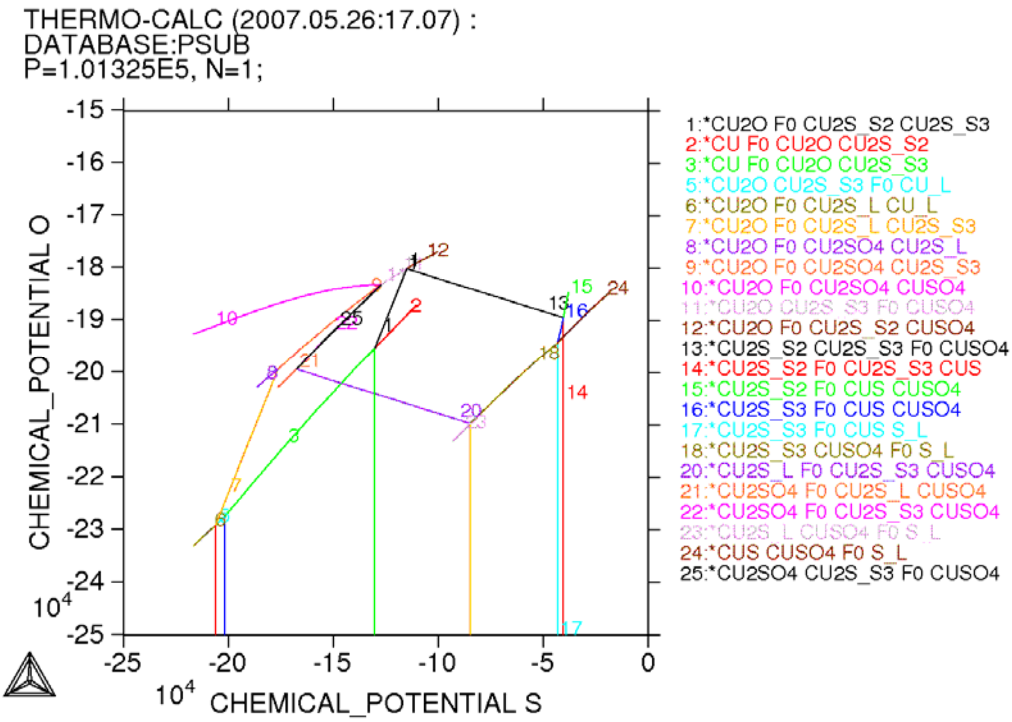
```
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Magnify the region with most details.

```
POST: s-s-s x n -250000 0
POST: s-s-s y n -250000 -150000
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) This is a very confusing diagram. One reason is that there is a third axis, T, perpendicular to the paper. It is thus a two-dimensional projection of a three-dimensional phase diagram. You would get a much simpler diagram by sectioning at a constant T instead of projecting.

In the three-dimensional phase diagram the lines represent three-phase equilibria. The lines in the section would represent two-phase equilibria. It is thus evident that a new mapping is necessary in order to trace the two-phase equilibria and produce the section. Start by going back to POLY and **rein**itiate in order to erase what was done so far.

```
POST: b
POLY_3: rein
POLY_3: ch-st p gas=sus
POLY_3: s-c P=101325 T=1000 N=1 x(O)=.2 x(S)=.2
POLY_3: c-e
 Using global minimization procedure
 Calculated           16  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: s-c x(O)=none mu(O)=
Value /-186710.6771/:
POLY_3: s-c x(S)=none mu(S)=
Value /-138765.8325/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Using already calculated grid
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: s-a-v 1 mu(S)
Min value /0/:
```

*) Chemical potentials have negative values when SER is used as reference.

```
Min value /0/:  -250000
Max value /1/:  0
Increment /6250/:
POLY_3: s-a-v 2 mu(O)
Min value /0/:  -250000
```

```
Max value /1/:  -150000
Increment /2500/:
POLY_3:
```

*) The mapping procedure starts from the current equilibrium, i.e., the single equilibrium that precedes the definition of axes. Sometimes additional starting equilibria are needed in order to catch all features of a system. The command **add**-initial-equilibrium allows you to add such. You could also indicate in what direction from the added equilibrium there may be a feature that could be followed by mapping.

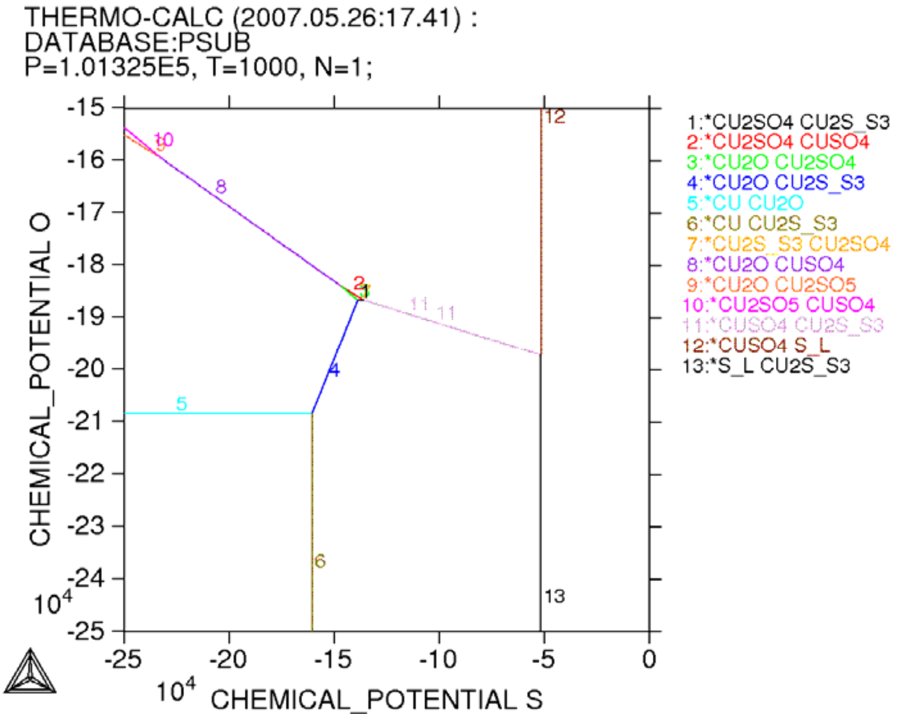
+1 or +2 for positive direction of axis 1 or 2, respectively.
-1 or -2 for negative direction of axis 1 or 2, respectively.

POLY will normally start in the positive direction of axis 1. If mapping is not successful, you can make POLY go in the positive direction of axis 2 by simply typing **add +2.**

```
POLY_3: add +2
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

Using ADDED start equilibria

 Calculated     4 equilibria

 Phase region boundary   1 at:  -1.388E+05 -1.867E+05
  ** CU2SO4
     CU2S_S3
 Calculated     3 equilibria

 Phase region boundary   2 at:  -1.360E+05 -1.867E+05
  ** CU2SO4
     CU2S_S3
     CUSO4

 Phase region boundary   3 at:  -1.360E+05 -1.867E+05
  ** CU2SO4
     CUSO4
 Calculated     8 equilibria

 Phase region boundary   4 at:  -1.470E+05 -1.840E+05
     CU2O
  ** CU2SO4
     CUSO4

 Phase region boundary   5 at:  -1.470E+05 -1.840E+05
  ** CU2O
     CU2SO4
 Calculated     8 equilibria

 Phase region boundary   6 at:  -1.388E+05 -1.867E+05
  ** CU2O
     CU2SO4
     CU2S_S3

 Phase region boundary   7 at:  -1.388E+05 -1.867E+05
  ** CU2O
     CU2S_S3
 Calculated    18 equilibria

 Phase region boundary   8 at:  -1.604E+05 -2.084E+05
```

```
    CU
 ** CU2O
    CU2S_S3

Phase region boundary   9 at:  -1.604E+05 -2.084E+05
 ** CU
    CU2O
Calculated    23 equilibria

Phase region boundary  10 at:  -1.604E+05 -2.084E+05
 ** CU
    CU2S_S3
Calculated    27 equilibria

Phase region boundary  11 at:  -1.388E+05 -1.867E+05
    CU2SO4
 ** CU2S_S3
Terminating at known equilibrium
Calculated     4 equilibria

Phase region boundary  12 at:  -1.470E+05 -1.840E+05
 ** CU2O
    CUSO4
Calculated    39 equilibria

Phase region boundary  13 at:  -2.327E+05 -1.595E+05
 ** CU2O
    CU2SO5
    CUSO4

Phase region boundary  14 at:  -2.327E+05 -1.595E+05
 ** CU2O
    CU2SO5
Calculated    12 equilibria

Phase region boundary  15 at:  -2.327E+05 -1.595E+05
 ** CU2SO5
    CUSO4
Calculated    12 equilibria

Phase region boundary  16 at:  -1.360E+05 -1.867E+05
    CU2S_S3
 ** CUSO4
*** Buffer saved on file: USERPROFILE\RESULT.POLY3
Calculated    23 equilibria

Phase region boundary  17 at:  -5.157E+04 -1.973E+05
    CU2S_S3
 ** CUSO4
    S_L

Phase region boundary  18 at:  -5.157E+04 -1.973E+05
 ** CUSO4
    S_L
Calculated    30 equilibria

Phase region boundary  19 at:  -5.157E+04 -1.973E+05
    CU2S_S3
 ** S_L
Calculated    33 equilibria
```

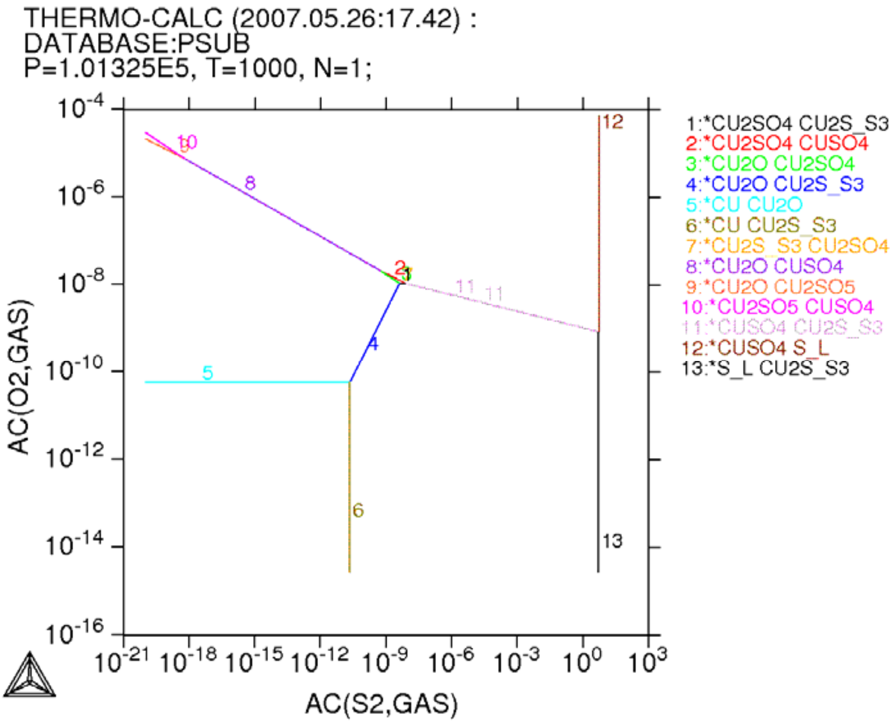
```
 Phase region boundary  20 at:  -1.388E+05 -1.867E+05
  ** CU2SO4
     CU2S_S3
 Terminating at known equilibrium
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) This time you may like to express the chemical potentials through the partial pressures in a gas, had there been such a gas present. The present database works with an ideal gas model, for which the partial pressure in units of atm of a species is equal to the activity if the reference is the pure species at 1 atm and the same temperature. That quantity can be obtained directly with the notation **ac(S2,gas)**. This is a special notation for two reasons. Usually, one should give the name of the phase first and then the component. Furthermore, **S2** is not defined as a component but is used in this special case.

```
POST: s-d-a x ac(S2,gas)
POST: s-d-a y ac(O2,gas)
POST: s-ax-ty x log
POST: s-ax-ty y log
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3: exit
 CPU time              1  seconds
```

Comments

1) The sections are much easier to interpret but give less information. It may be a good idea to make a stereographic pair of the three-dimensional potential diagram before sectioning but maybe after omitting some lines.

2) It is not evident how to relate a section to the full potential diagram. A line in the section is not at all seen in the full potential diagram. A point of intersection of lines in the section falls somewhere on a line in the full potential diagram.

8.7. Ternary systems

Consider the possible oxidation of Cu in water without any extra oxygen present. There are two possible oxides, Cu_2O and CuO, in addition to H_2O.

Hint

Cu would first oxidize to Cu_2O and O would have to come from H_2O. Free hydrogen would thus form and dissolve in the water or form gas bubbles if the H potential is high enough, i.e. if the partial pressure of H_2 would be high enough compared to the external pressure. It would thus be interesting to compute the equilibria and express the result as partial pressure of H_2 in a hypothetical gas phase. Do that from 0 to 100°C.

It is conceivable that oxidation continues and results in CuO. First you should thus consider the equilibrium $H_2O/Cu_2O/Cu$ and then $H_2O/CuO/Cu_2O$.

When you have completed this problem you have obtained a diagram which may be regarded as a potential phase diagram for the Cu-O system with the H potential in water as an expression of the O potential. The diagram has three phase fields, one each for Cu, Cu_2O and CuO. In Section 8.7 there is already a diagram showing the equilibrium between CuO and Cu_2O although it is more complicated but does not show Cu. Furthermore, it uses the O potential instead of the H potential.

Instructions for using T-C

In POLY you can introduce H in an ideal gas at current T and P as a reference and thus get the H_2 partial pressure directly. It is then identical to the activity of H_2.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PSUB
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el Cu O H
 CU                       O                        H
   DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
 GAS:G       :H H2 O O2 O3 H1O1 H1O2 H2O1 H2O2 CU CU2 CU1H1 CU1O1 CU1H1O1:
  > Gaseous Mixture, using the ideal gas model
 CU          :CU:
  > This is pure Cu_FCC(A1)
 CU_L        :CU:
 H2O_L       :H2O1:
 H2O2_L      :H2O2:
 CUO         :CU1O1:
 CU2O        :CU2O1:
 CU2O_L      :CU2O1:
TDB_PSUB: rej p H2O2_L CU2O_L CU_L
 H2O2_L                   CU2O_L                   CU_L
   REJECTED
TDB_PSUB:
```

*) You like to reject all the many constituents in the gas. If you had instead rejected all the species, they would have been rejected in all the phases.

```
TDB_PSUB: rej const gas *
 H IN GAS:G SUBLATTICE   1 REJECTED
 H2 IN GAS:G SUBLATTICE   1 REJECTED
 O IN GAS:G SUBLATTICE   1 REJECTED
 O2 IN GAS:G SUBLATTICE   1 REJECTED
 O3 IN GAS:G SUBLATTICE   1 REJECTED
 H1O1 IN GAS:G SUBLATTICE   1 REJECTED
 H1O2 IN GAS:G SUBLATTICE   1 REJECTED
 H2O1 IN GAS:G SUBLATTICE   1 REJECTED
 H2O2 IN GAS:G SUBLATTICE   1 REJECTED
 CU IN GAS:G SUBLATTICE   1 REJECTED
 CU2 IN GAS:G SUBLATTICE   1 REJECTED
 CU1H1 IN GAS:G SUBLATTICE   1 REJECTED
 CU1O1 IN GAS:G SUBLATTICE   1 REJECTED
```

```
 CU1H1O1 IN GAS:G SUBLATTICE   1 REJECTED

 *** ERROR  1000 IN TDBMPE
 *** NO SUCH CONSTITUENT IN SUBLATTICE
TDB_PSUB:
```

*) This error message has no meaning in this case. Just continue.

```
TDB_PSUB: rest const gas H2
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENTS/:
 GAS:G       :H2:
  > Gaseous Mixture, using the ideal gas model
 CU          :CU:
  > This is pure Cu_FCC(A1)
 H2O_L       :H2O1:
 CUO         :CU1O1:
 CU2O        :CU2O1:
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You like to fix the three phases that should take part in the equilibrium and suspend the other two.

```
POLY_3: ch-st p CU CU2O H2O_L=fix 1
POLY_3: ch-st p gas CUO=sus
POLY_3: s-c T=300 P=101325
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            3  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Now you should step in temperature and could just as well use a larger range than required. It will be adjusted when plotting.

```
POLY_3: s-a-v 1 T 250 400
Increment /3.75/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    300.000     for:
     CU
     CU2O
     H2O_L
```

```
 Calculated    30 equilibria

 Phase Region from    300.000     for:
     CU
     CU2O
     H2O_L
 Calculated    17 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:
```

*) Now consider the equilibrium of H_2O with CuO and Cu_2O.

```
POLY_3: ch-st p CUO=fix 1
POLY_3: ch-st p CU=sus
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            3  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) The T axis with its limits is already given.

```
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    300.000     for:
     CU
     CUO
     H2O_L
 Calculated    30 equilibria

 Phase Region from    300.000     for:
     CU
     CUO
     H2O_L
 Calculated    17 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) Use a T axis in ^{o}C.

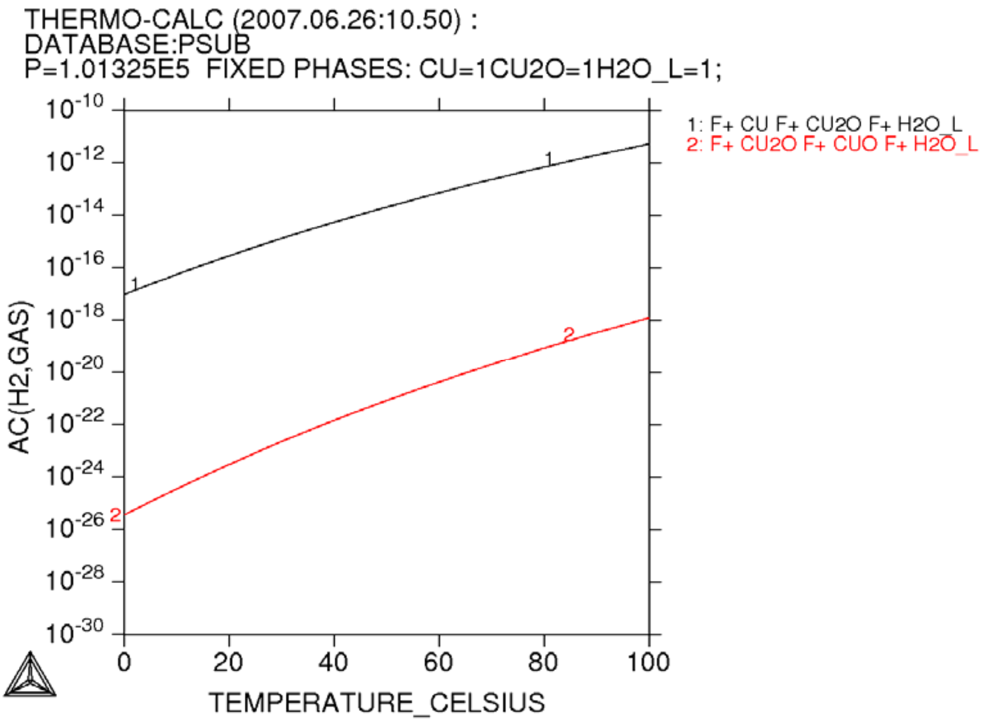
```
POST: s-d-a x T-C
POST: s-s-s x n 0 100
POST:
```

*) Express the H potential through the partial pressure of H_2.

```
POST: s-d-a y ac(H2,gas)
POST:
```

*) It is the logarithm of the partial pressure of H_2 that is proportional to the chemical potential. It is thus convenient to use a logarithmic scale.

```
POST: s-ax-ty y log
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



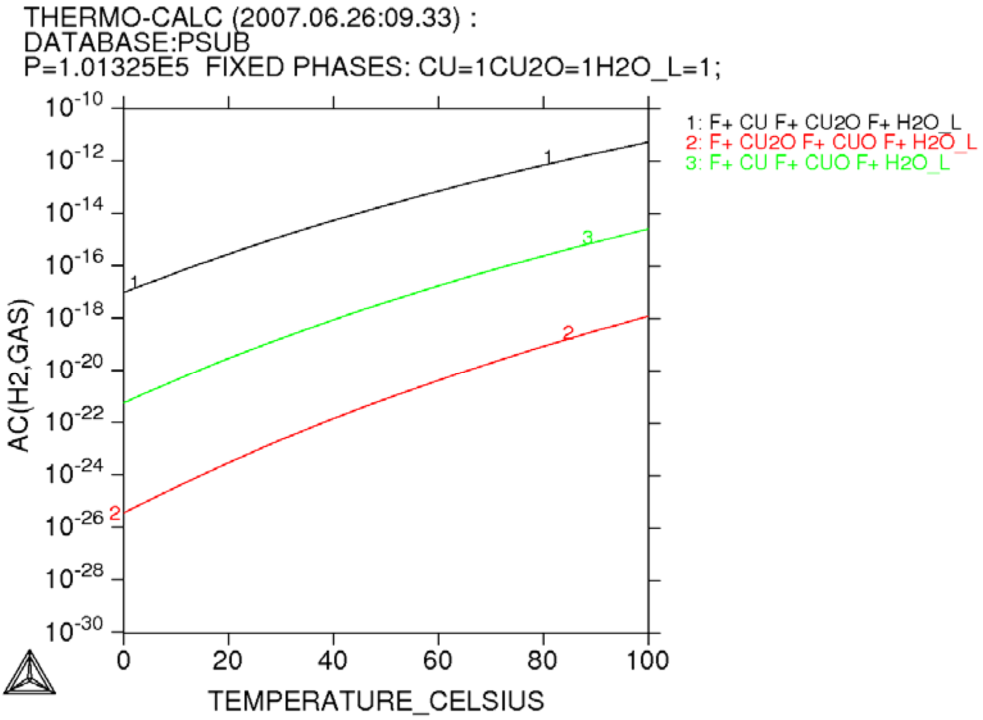
```
POLY_3: b
```

*) Now consider the metastable equilibrium of H_2O with CuO and Cu.

```
POLY_3: ch-st p CU=fix 1
POLY_3: ch-st p CU2O=sus
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            3  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) The T axis with its limits is already given.

```
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    300.000     for:
     CU
     CUO
     H2O_L
 Calculated    30 equilibria

 Phase Region from    300.000     for:
     CU
     CUO
     H2O_L
 Calculated    17 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time               0  seconds
```

Comments

The first diagram shows that Cu immersed in water will not oxidize to Cu_2O if the H_2 content of the water corresponds to a partial pressure higher than indicated by the line for Cu_2O/Cu (1). In order for CuO to form from Cu_2O, the H_2 pressure must be below the line for CuO/Cu_2O (2), which represents H_2 pressures about eight orders of magnitude lower.

The second diagram also shows the metastable equilibrium for CuO/Cu. It is natural that it falls in the middle of the potentials for the two stable equilibria.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

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Chapter 9. Molar phase diagrams

9.1. Molar axes

Compute and plot the phase diagram for Fe-C at 1 atm and between 1650 and 1850 K and 0 and 0.03 mol% C. Then, try to use enthalpy and C content as axes in the diagram.

Hint

You should realize that you may have to declare that you are not interested in the values for two-phase mixtures but for the individual phases present in the mixtures.

Instructions for T-C

POLY may have difficulties of identifying which one of the phases taking part in an equilibrium that is required when a certain feature is to be plotted. It may help to give a more specific command.

Prompts, commands and responses

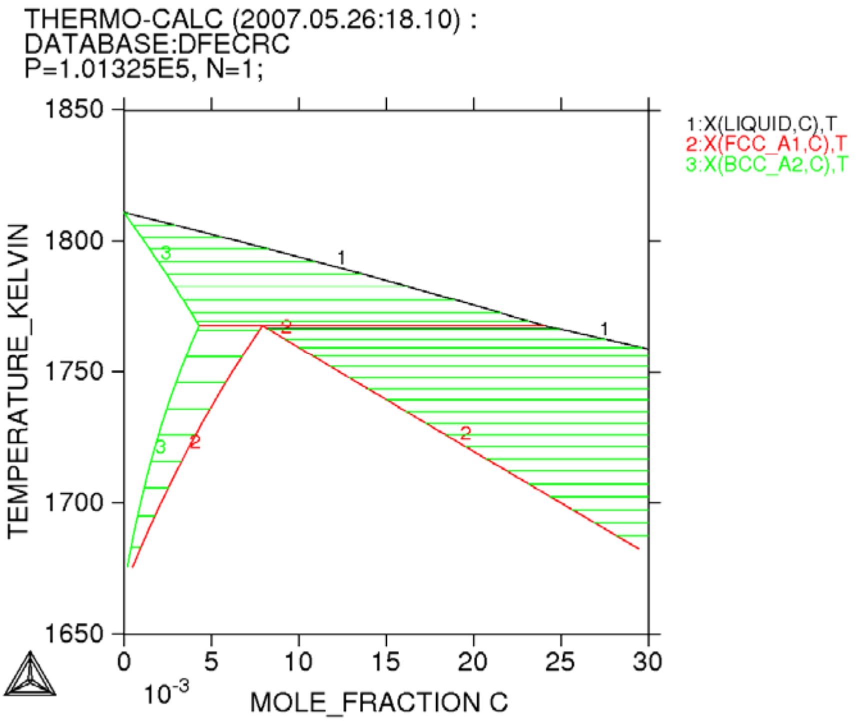
```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                       C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   CEMENTITE                M7C3
 M23C6                    GRAPHITE  REJECTED
TDB_DFECRC: rest p fcc bcc liq
FCC_A1                   BCC_A2                   LIQUID:L
 GRAPHITE  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
```

```
 PARAMETERS ...
 Rewind to read functions          58
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c T=1700 P=101325 x(C)=.01 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated          412  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: s-a-v 1 x(C)
Min value /0/:
Max value /1/:  .03
Increment /7.5E-04/:
POLY_3: s-a-v 2 T
Min value /0/:  1650
Max value /1/:  1850
Increment /5/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   1.000E-02  1.759E+03
  ** LIQUID
     FCC_A1
 Calculated    15 equilibria

 Phase region boundary   2 at:   2.407E-02  1.768E+03
     LIQUID
     BCC_A2
  ** FCC_A1

 Phase region boundary   3 at:   7.935E-03  1.768E+03
  ** BCC_A2
     FCC_A1
 Mapping terminated 2
 Calculated    49 equilibria

 Phase region boundary   4 at:   2.407E-02  1.768E+03
```

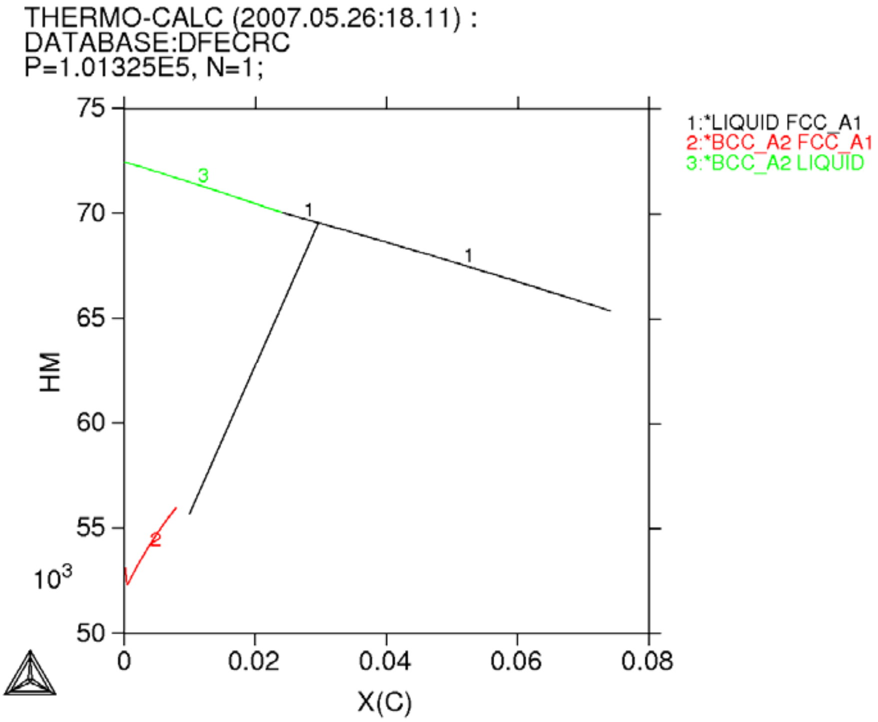
```
     LIQUID
   ** BCC_A2
 Calculated    50 equilibria

 Phase region boundary   5 at:   1.000E-02  1.759E+03
   ** LIQUID
      FCC_A1
 Mapping terminated 1
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis
POST:
```

*) You like to include tie-lines but it may be sufficient to show every fifth one. Then, start with the ordinary T-x phase diagram. You may obtain it automatically but may use option **e** for “setting labels”, i.e., setting digits for identifying univariant phase fields.

```
POST: s-t-s 5
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



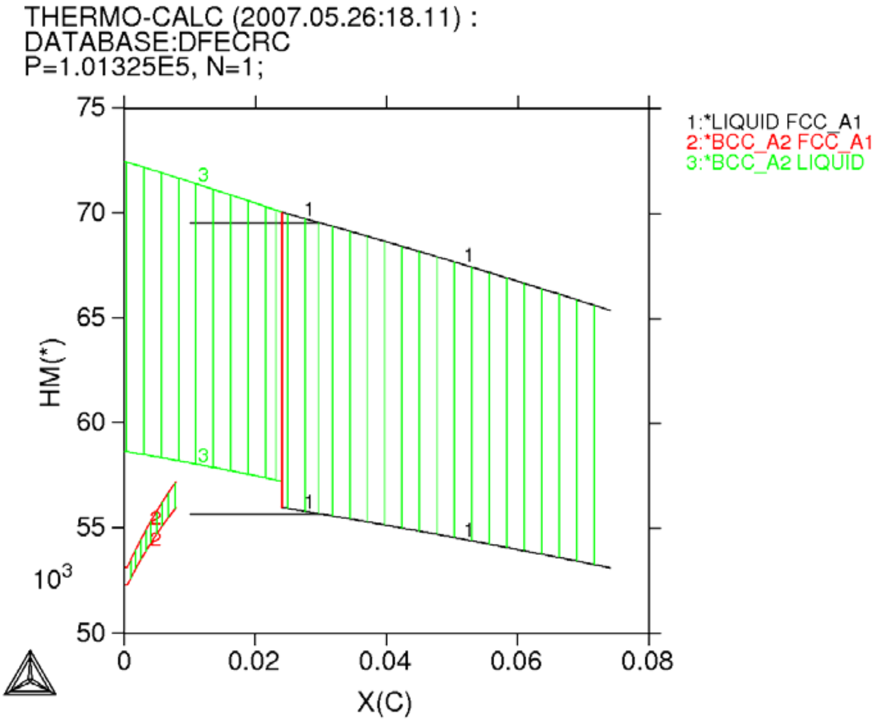
```
POST: s-d-a x x(C)
   Warning: maybe you should use MOLE_FRACTION C instead of X(C)
POST: s-d-a y Hm
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) This diagram looks strange because lines are missing. You better be more specific and require that information from all **(*)** the individual phase should be used for Hm.

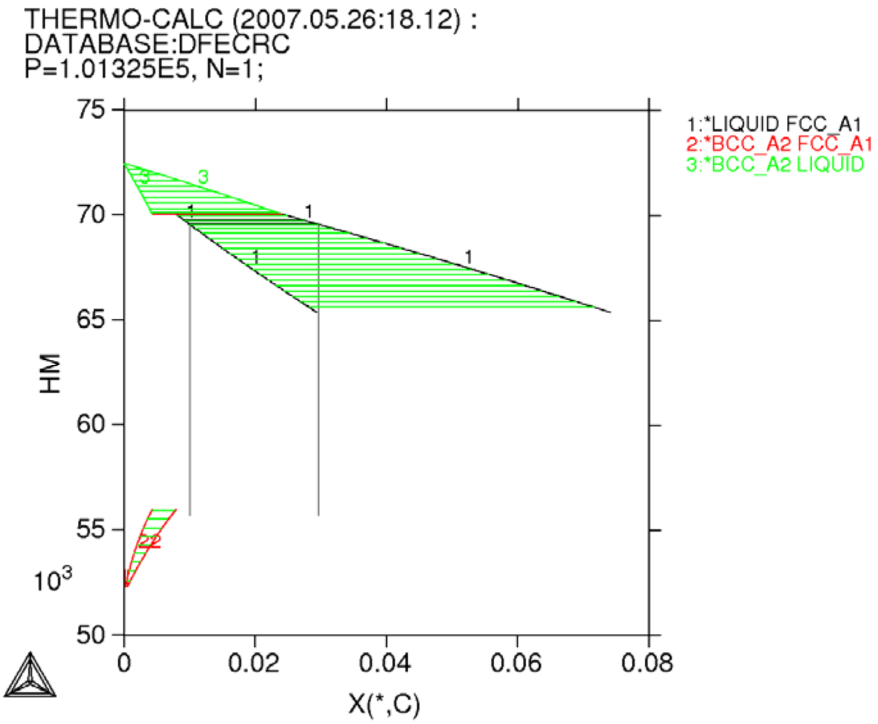
```
POST: s-d-a y Hm(*)
COLUMN NUMBER /*/:
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) It did not help completely. Test if it was x(C) that needs this same help.

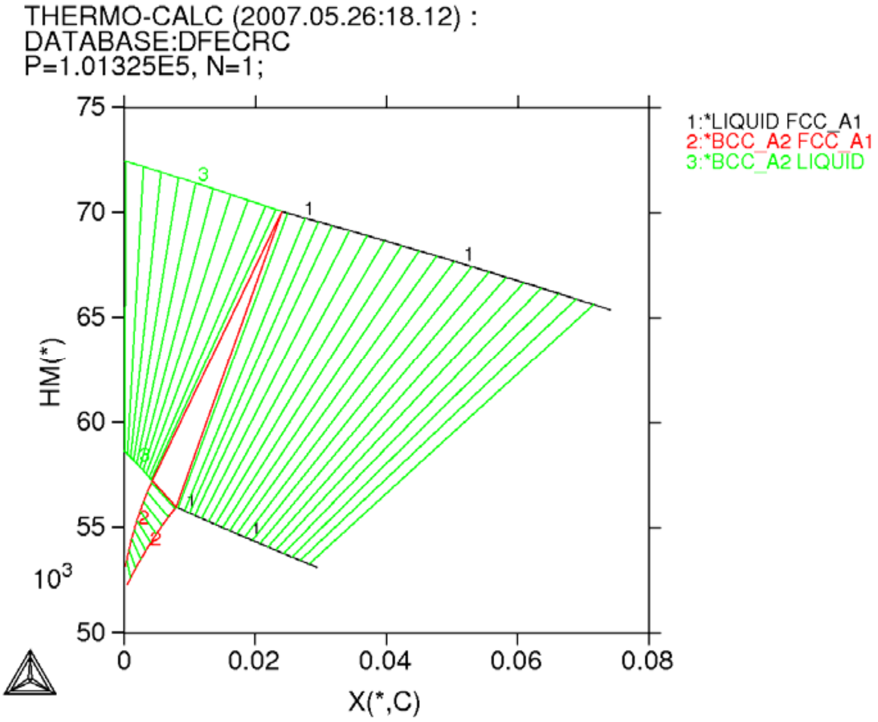
```
POST: s-d-a x x(*,C)
COLUMN NUMBER /*/:
POST: s-d-a y Hm
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Before giving up, try to “help” both variables.

```
POST: s-d-a y Hm(*)
COLUMN NUMBER /*/:
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



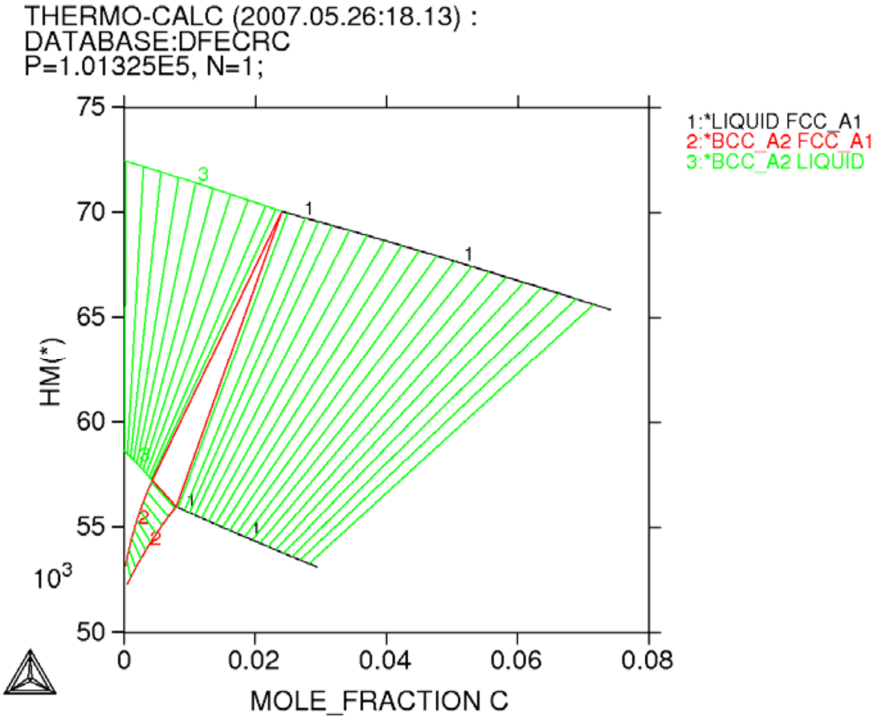
```
POST:
```

*) Success! This looks like a true phase diagram.

```
OUTPUT TO SCREEN OR FILE /SCREEN/:
POST:
```

*) Finally, try to use the advice to use “m-f C” given in the warning you got from the post-processor when you first gave the command x(C).

```
POST: s-d-a x m-f C
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

) Evidently, it works as x(,C) and may thus be convenient to use more generally.

```
POST: b
POST: exit
 CPU time            2  seconds
```

Comments

When plotting molar diagrams it is important that the plotting procedure identifies the values for the individual phases correctly. Hm and x(C) actually represent the values for the whole system and could give the value of a phase if the plotting procedure is able to pick the composition of the correct phase. This does not always happen. It is much safer to plot the values of a given phase, Hm(phase) or x(phase,C), or of all phases as they appear, H(*) or x(*,C). The command “mole-fraction C" (**m-f C**) has the same meaning as x(*,C) and is thus convenient to use.

9.2. Sets of conjugate variables containing molar variables

Compute the phase equilibria for pure Fe between 500 and 1000 K and between 8E9 to 14E9 bar. Plot the results as phase diagrams with various pairs of axes. In particular combine H_m with other quantities.

Hint

As shown in Table 9.1, all combinations of axes don't give true phase diagrams.

Instructions for using T-C

In order to use a function as an axis variable, when the function is not one of those defined basically, it is necessary to enter a symbol for the function. When this function must be evaluated for more than one phase, it should be defined for each phase.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe
 FE  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L               FCC_A1                 BCC_A2
 HCP_A3  REJECTED
TDB_DFECRC: rest p fcc bcc hcp
 FCC_A1                 BCC_A2                 HCP_A3
   RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
```

```
 PARAMETERS ...
 Rewind to read functions          32
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

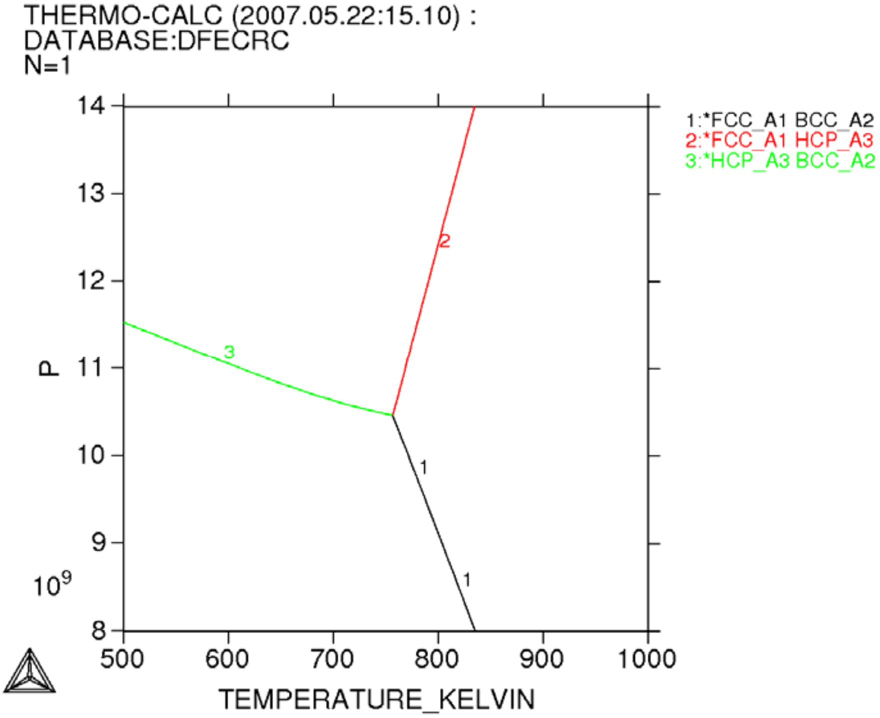
*) Before starting the mapping you must begin with an initial equilibrium but you should then use as conditions those variables you like to use as variables on the axes.

```
POLY_3: s-c P=9E9 T=700 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated            3  grid points in            0  s
POLY_3: s-a-v 1 T 500 1000
Increment /12.5/:
POLY_3: s-a-v 2 P 8E9 14E9
Increment /150000000/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   8.036E+02  9.000E+09
     BCC_A2
  ** FCC_A1
 Calculated    15 equilibria

 Phase region boundary   2 at:   8.036E+02  9.000E+09
     BCC_A2
  ** FCC_A1
 Calculated    20 equilibria

 Phase region boundary   3 at:   7.566E+02  1.046E+10
     BCC_A2
  ** FCC_A1
     HCP_A3

 Phase region boundary   4 at:   7.566E+02  1.046E+10
  ** FCC_A1
     HCP_A3
 Calculated    37 equilibria

 Phase region boundary   5 at:   7.566E+02  1.046E+10
     BCC_A2
  ** HCP_A3
 Calculated    36 equilibria
```

```
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

Setting automatic diagram axis

POST:
```

*) The automatic plotting procedure will produce a T,P phase diagram because those axes were used in the mapping. Use **set-lab e** in order to identify the phase fields.

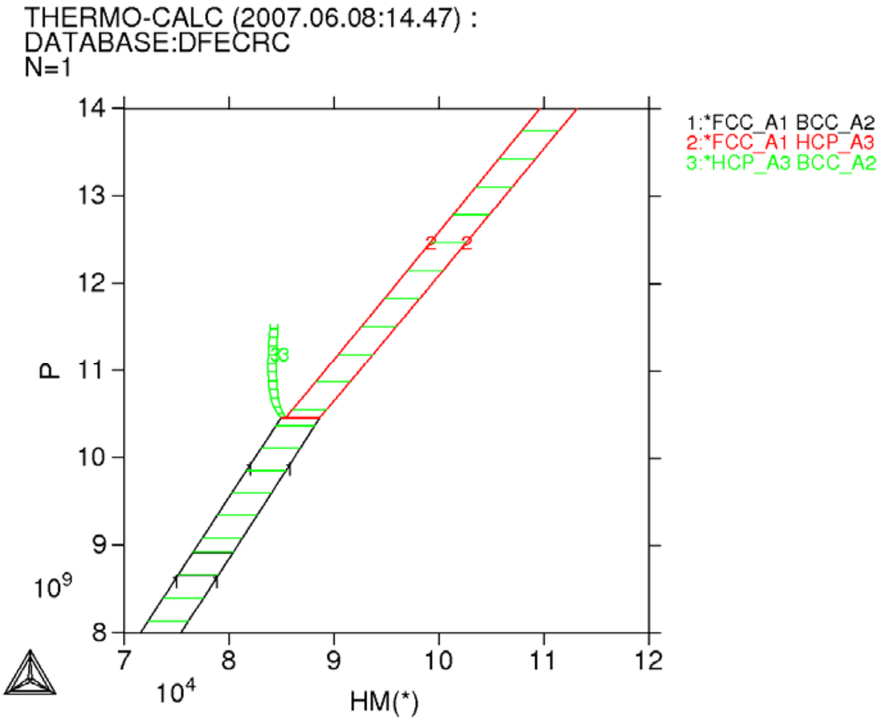
```
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Introduce Hm instead of T on the x axis. Include tie-lines and accept every third one from the computed equilibria. In order for POST to plot Hm for all the phases you better write Hm(*).

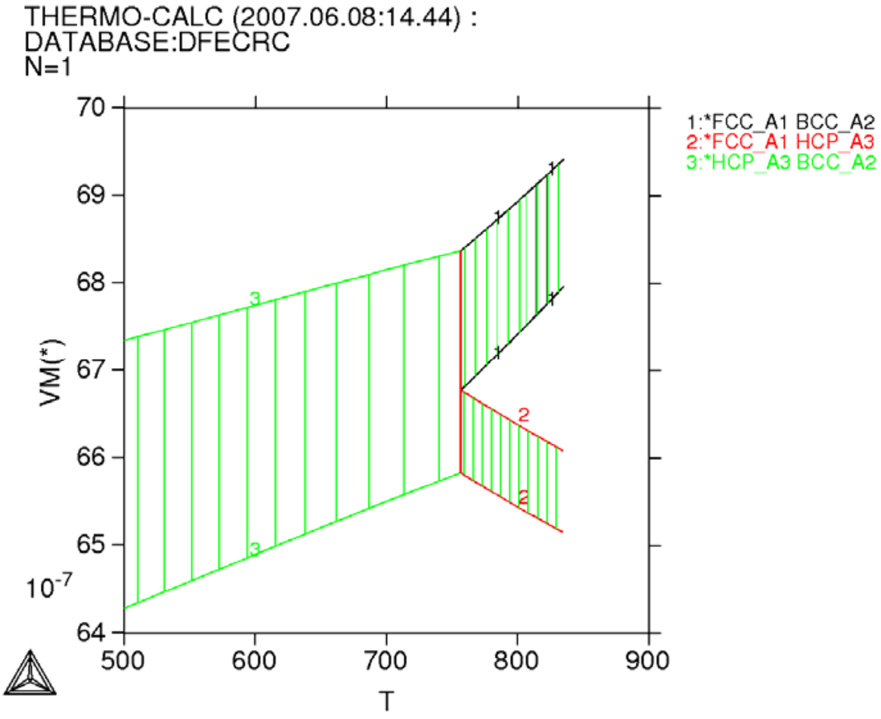
```
POST: s-d-a x Hm(*)
COLUMN NUMBER /*/:
POST: s-t-s 3
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Restore the T axis and introduce Vm instead of P on the y axis.

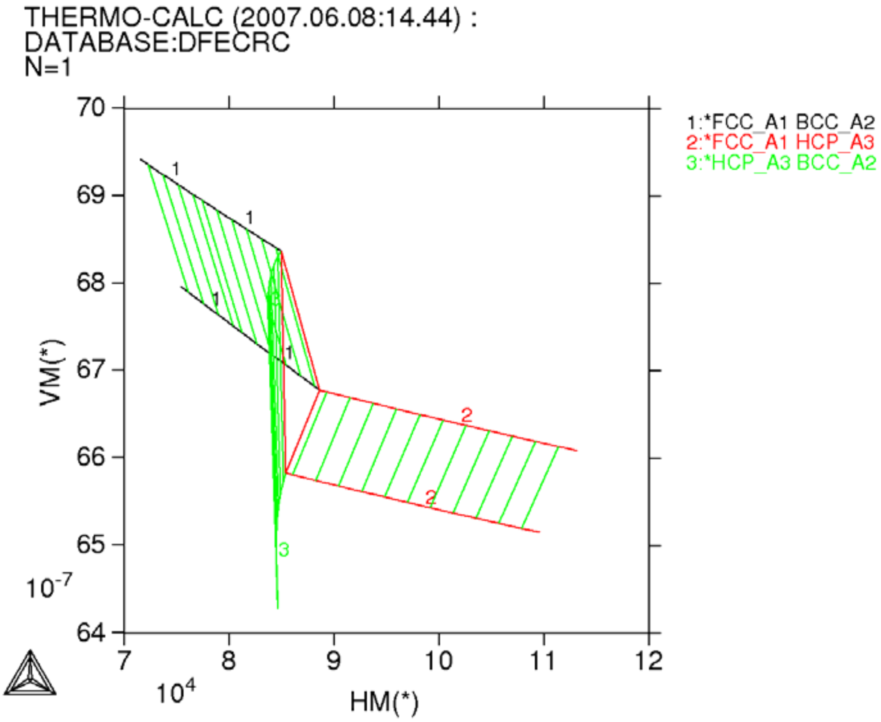
```
POST: s-d-a x T
COLUMN NUMBER /*/:
POST: s-d-a y Vm(*)
COLUMN NUMBER /*/:
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Use both Hm and Vm axes.

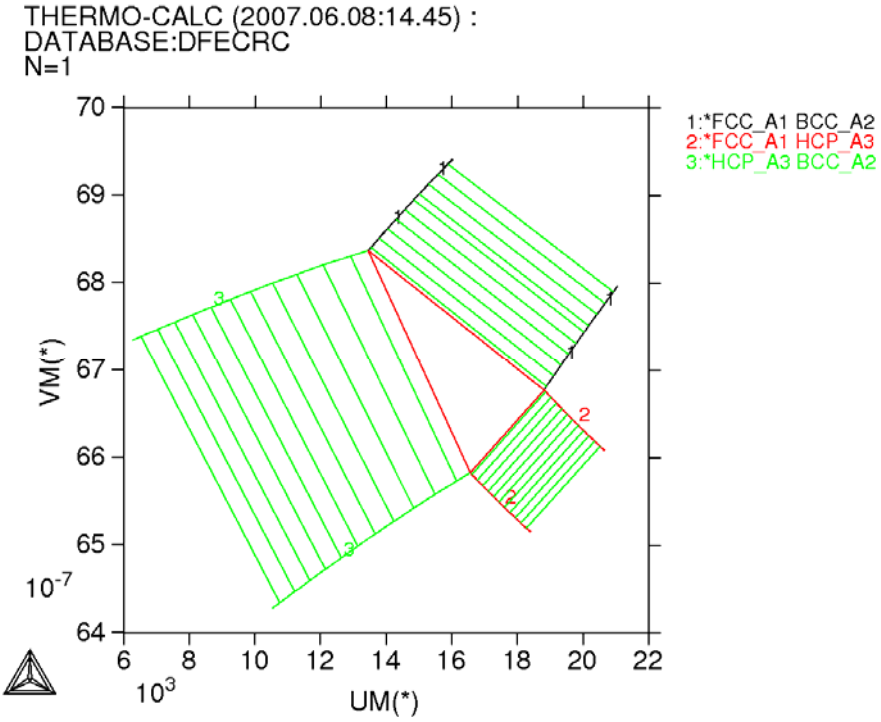
```
POST: s-d-a x Hm(*)
COLUMN NUMBER /*/:
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Two two-phase fields now overlap and the diagram is not a true phase diagram. According to the fourth row in Table 9.1 you may combine Vm with Um to get a true phase diagram.

```
POST: s-d-a x Um(*)
COLUMN NUMBER /*/:
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3: exit
 CPU time             1  seconds
```

Comments

Starting from the T,P phase diagram, you will obtain true phase diagrams by introducing Hm(*) instead of T and by introducing Vm(*) instead of P but not by using both Hm(*) and Vm(*). In order to obtain a true phase diagram with Vm(*) and another molar variable you may use Um(*), as indicated by Table 9.1.

9.4. Sections of molar phase diagrams

Consider a carbon free Fe-6 mass% Cr alloy being carburised. Demonstrate with a diagram how the alloy would move from phase field to phase field as the C content is increasing. Construct the diagram for temperatures between 650 and 1550^{o}C. Then, try to figure out the number of phases in the various phase fields. Finally, compute diagrams showing how the amounts of the phases change with the C content during carburisation and with temperature during cooling.

Hint

Evidently, you are asked to compute a so-called isopleth with a constant ratio of Fe to Cr. It will give the same result whether you define this ratio with mass fractions or mole fractions.

Instructions for using T-C

With POLY you can give the condition for an isopleth by constructing a linear expression that is zero.

Prompts, commands and responses

```
Evidently, you should calculate an isoplethal section by just adding C.
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                      CR                      C
   DEFINED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You don't like graphite to take part in the equilibria but could use it as reference if you keep it suspended.

```
POLY_3: ch-st p gra=sus
POLY_3:
```

*) You will soon step in C content and would then like the ratio between Fe and Cr to stay constant. Already when computing the single equilibrium you should prepare for this condition.

```
POLY_3: s-c P=101325 T=1800 N=1 w(C)=.01
POLY_3: s-c 94*w(Cr)-6*w(Fe)=0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        87413  grid points in            1  s
```

```
  20 ITS,  CPU TIME USED   1 SECONDS
POLY_3: s-a-v 1 w(C) 0 .1
Increment /.0025/:
POLY_3: s-a-v 2 T 923 1823
Increment /22.5/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Tie-lines not in the plane of calculation

 Phase region boundary   1 at:   1.000E-02  1.724E+03
     LIQUID
  ** FCC_A1
 Calculated     5 equilibria

 Phase region boundary   2 at:   5.684E-03  1.750E+03
     LIQUID
     BCC_A2
  ** FCC_A1
 Calculated     7 equilibria

 Phase region boundary   3 at:   9.984E-04  1.745E+03
  ** LIQUID
     BCC_A2
     FCC_A1
 Calculated     3 equilibria

 Phase region boundary   4 at:   2.379E-03  1.743E+03
     LIQUID
  ** BCC_A2
     FCC_A1
 Terminating at known equilibrium
 Calculated     4 equilibria

 Phase region boundary   5 at:   2.379E-03  1.743E+03
  ** BCC_A2
     FCC_A1
 Calculated    11 equilibria

 Phase region boundary   6 at:   2.379E-03  1.743E+03
  ** LIQUID
     FCC_A1
 Calculated    14 equilibria

 Phase region boundary   7 at:   1.825E-02  1.483E+03
  ** LIQUID
     FCC_A1
     M7C3
 Calculated     5 equilibria

 Phase region boundary   8 at:   2.417E-02  1.451E+03
  ** LIQUID
     CEMENTITE
     FCC_A1
```

```
    M7C3

Phase region boundary   9 at:   3.065E-02  1.451E+03
    LIQUID
 ** CEMENTITE
    FCC_A1
Calculated     8 equilibria

Phase region boundary  10 at:   4.373E-02  1.445E+03
    LIQUID
    CEMENTITE
 ** FCC_A1
Calculated    12 equilibria

Phase region boundary  11 at:   6.717E-02  1.434E+03
 ** LIQUID
    CEMENTITE
    FCC_A1
Terminating at known equilibrium
Calculated    19 equilibria

Phase region boundary  12 at:   6.717E-02  1.434E+03
 ** LIQUID
    CEMENTITE
Calculated     6 equilibria

Phase region boundary  13 at:   6.717E-02  1.503E+03
 ** LIQUID
    CEMENTITE
    M7C3
Calculated    10 equilibria

Phase region boundary  14 at:   8.474E-02  1.489E+03
    LIQUID
 ** CEMENTITE
    M7C3
Calculated    12 equilibria

Phase region boundary  15 at:   6.181E-02  1.502E+03
    LIQUID
    CEMENTITE
 ** M7C3
Convergence problems, increasing smallest sitefraction from 1.00E-30
to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
Terminating at known equilibrium
Calculated     5 equilibria

Phase region boundary  16 at:   6.181E-02  1.502E+03
    LIQUID
 ** M7C3
Calculated    20 equilibria

Phase region boundary  17 at:   6.181E-02  1.502E+03
    LIQUID
 ** CEMENTITE
Terminating at known equilibrium
Calculated    10 equilibria

Phase region boundary  18 at:   8.474E-02  1.489E+03
 ** CEMENTITE
    M7C3
```

```
Calculated    30 equilibria

Phase region boundary  19 at:   8.474E-02  1.489E+03
 ** LIQUID
    M7C3
*** Sorry cannot continue ***    4

Calculated     8 equilibria

Phase region boundary  20 at:   6.717E-02  1.503E+03
    LIQUID
    CEMENTITE
 ** M7C3
Terminating at known equilibrium
Calculated     5 equilibria

Phase region boundary  21 at:   6.717E-02  1.503E+03
    CEMENTITE
 ** M7C3
*** Buffer saved on file: USERPROFILE\RESULT.POLY3
Calculated    32 equilibria

Phase region boundary  22 at:   6.717E-02  1.434E+03
    CEMENTITE
 ** FCC_A1
Calculated    22 equilibria

Phase region boundary  23 at:   6.717E-02  1.007E+03
    BCC_A2
    CEMENTITE
 ** FCC_A1
Calculated    21 equilibria

Phase region boundary  24 at:   2.184E-02  1.022E+03
    BCC_A2
    CEMENTITE
 ** FCC_A1
    M7C3

Phase region boundary  25 at:   1.107E-02  1.022E+03
    BCC_A2
 ** CEMENTITE
    M7C3
Calculated     9 equilibria

Phase region boundary  26 at:   1.107E-02  1.022E+03
    BCC_A2
 ** FCC_A1
    M7C3
Calculated     8 equilibria

Phase region boundary  27 at:   5.874E-05  1.084E+03
    BCC_A2
    FCC_A1
 ** M7C3
Calculated     3 equilibria

Phase region boundary  28 at:   1.373E-03  1.082E+03
 ** BCC_A2
    FCC_A1
    M7C3
```

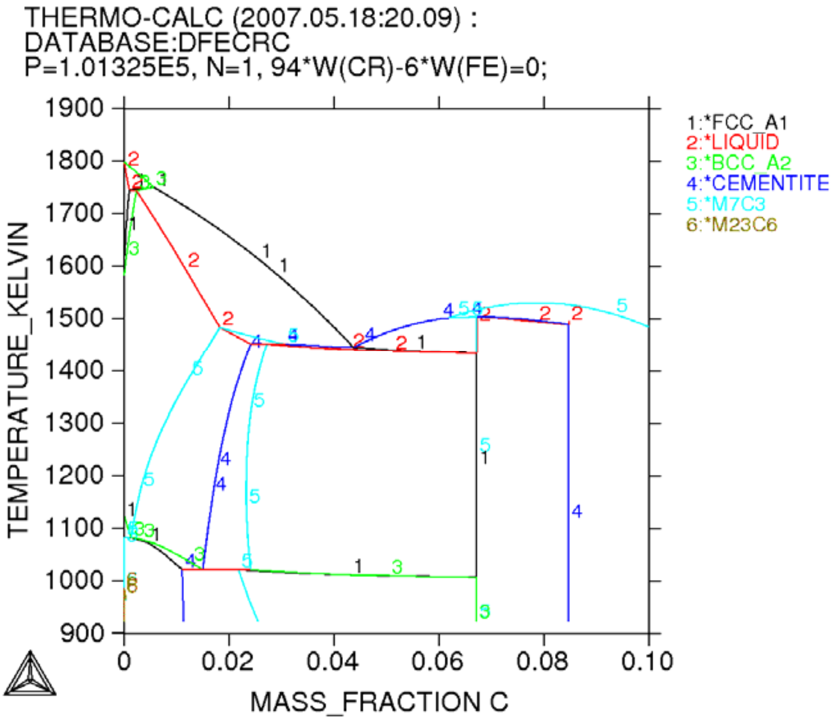
```
Terminating at known equilibrium
Calculated     8 equilibria

Phase region boundary  29 at:   1.373E-03  1.082E+03
 ** BCC_A2
    FCC_A1
Calculated     7 equilibria

Phase region boundary  30 at:   1.373E-03  1.082E+03
    FCC_A1
 ** M7C3
Terminating at known equilibrium
Calculated    21 equilibria

Phase region boundary  31 at:   5.874E-05  1.084E+03
    BCC_A2
 ** M7C3
Calculated     7 equilibria

Phase region boundary  32 at:   1.020E-05  9.865E+02
    BCC_A2
    M23C6
 ** M7C3
Mapping terminated 2
Calculated     5 equilibria

Phase region boundary  33 at:   1.020E-05  9.865E+02
    BCC_A2
 ** M23C6
    M7C3
Mapping terminated 2
Calculated     5 equilibria

Phase region boundary  34 at:   1.020E-05  9.865E+02
    BCC_A2
 ** M23C6
Calculated     9 equilibria

Phase region boundary  35 at:   5.874E-05  1.084E+03
    BCC_A2
 ** FCC_A1
Calculated     6 equilibria

Phase region boundary  36 at:   2.407E-02  1.022E+03
 ** BCC_A2
    CEMENTITE
    FCC_A1
Terminating at known equilibrium
Calculated    20 equilibria

Phase region boundary  37 at:   2.407E-02  1.022E+03
    CEMENTITE
    FCC_A1
 ** M7C3
Terminating at known equilibrium
Calculated    22 equilibria

Phase region boundary  38 at:   1.500E-02  1.022E+03
 ** BCC_A2
    FCC_A1
    M7C3
```

```
Terminating at known equilibrium
Calculated     9 equilibria

Phase region boundary  39 at:   1.500E-02  1.022E+03
 ** CEMENTITE
    FCC_A1
    M7C3
*** Buffer saved on file: USERPROFILE\RESULT.POLY3
Terminating at known equilibrium
Calculated    22 equilibria

Phase region boundary  40 at:   2.184E-02  1.022E+03
    BCC_A2
    CEMENTITE
 ** M7C3
Calculated     9 equilibria

Phase region boundary  41 at:   6.717E-02  1.007E+03
 ** BCC_A2
    CEMENTITE
Calculated    10 equilibria

Phase region boundary  42 at:   4.373E-02  1.445E+03
    LIQUID
 ** FCC_A1
Terminating at known equilibrium
Calculated    18 equilibria

Phase region boundary  43 at:   4.373E-02  1.445E+03
    LIQUID
 ** CEMENTITE
Terminating at known equilibrium
Calculated    10 equilibria

Phase region boundary  44 at:   3.065E-02  1.451E+03
    LIQUID
    FCC_A1
 ** M7C3
Terminating at known equilibrium
Calculated     8 equilibria

Phase region boundary  45 at:   2.724E-02  1.451E+03
 ** LIQUID
    CEMENTITE
    FCC_A1
Terminating at known equilibrium
Calculated    19 equilibria

Phase region boundary  46 at:   2.724E-02  1.451E+03
    CEMENTITE
    FCC_A1
 ** M7C3
Terminating at known equilibrium
Calculated    22 equilibria

Phase region boundary  47 at:   2.417E-02  1.451E+03
 ** CEMENTITE
    FCC_A1
    M7C3
Terminating at known equilibrium
Calculated    22 equilibria
```

```
 Phase region boundary  48 at:   1.825E-02  1.483E+03
     FCC_A1
  ** M7C3
 Terminating at known equilibrium
 Calculated    21 equilibria

 Phase region boundary  49 at:   9.984E-04  1.745E+03
  ** LIQUID
     BCC_A2
 Calculated     7 equilibria

 Phase region boundary  50 at:   9.984E-04  1.745E+03
     BCC_A2
  ** FCC_A1
 Calculated    10 equilibria

 Phase region boundary  51 at:   5.684E-03  1.750E+03
     LIQUID
  ** BCC_A2
 Calculated     7 equilibria

 Phase region boundary  52 at:   1.000E-02  1.724E+03
     LIQUID
  ** FCC_A1
 Terminating at known equilibrium
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) Instead of defining the two axes of your choice, you can accept the automatic procedure. Identify the phase boundaries with labels.

```
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

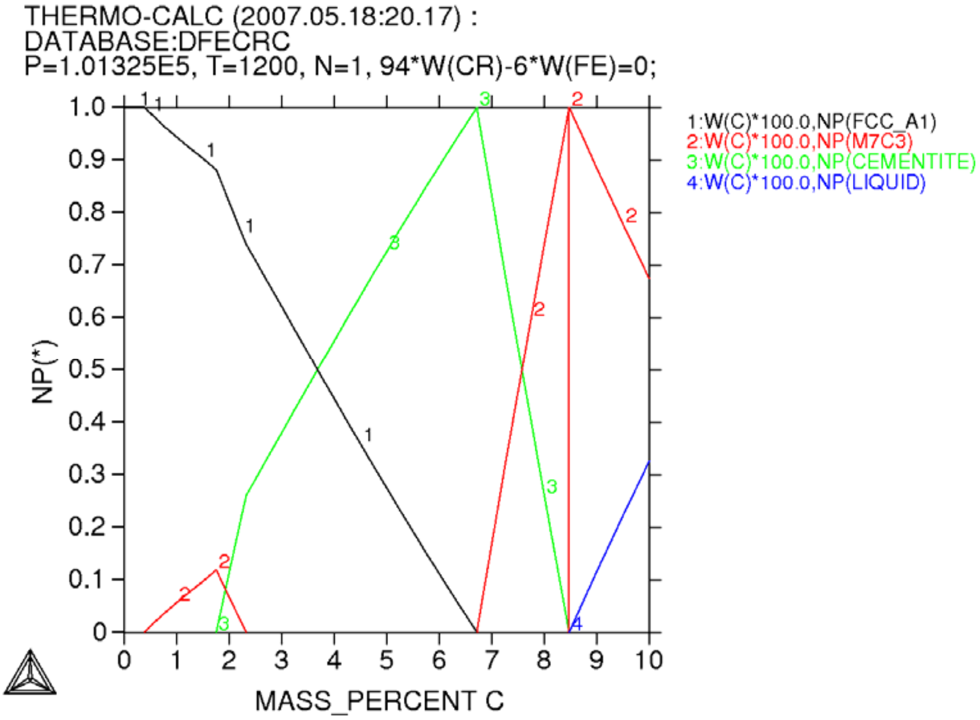
*) The numbers representing the equilibria in the diagram help you to interpret the diagram. You may also consult the list of results from the mapping. It may be interesting to try to find the invariant four-phase equilibria. Of course, you could also magnify the T axis just around them.

```
POST: b
POLY_3:
```

*) Before producing diagrams with new kinds of axes you should empty POLY from memories of the first diagram. Use **rein**itiate and prepare for stepping in C content at a fixed temperature, e.g. 1200 K.

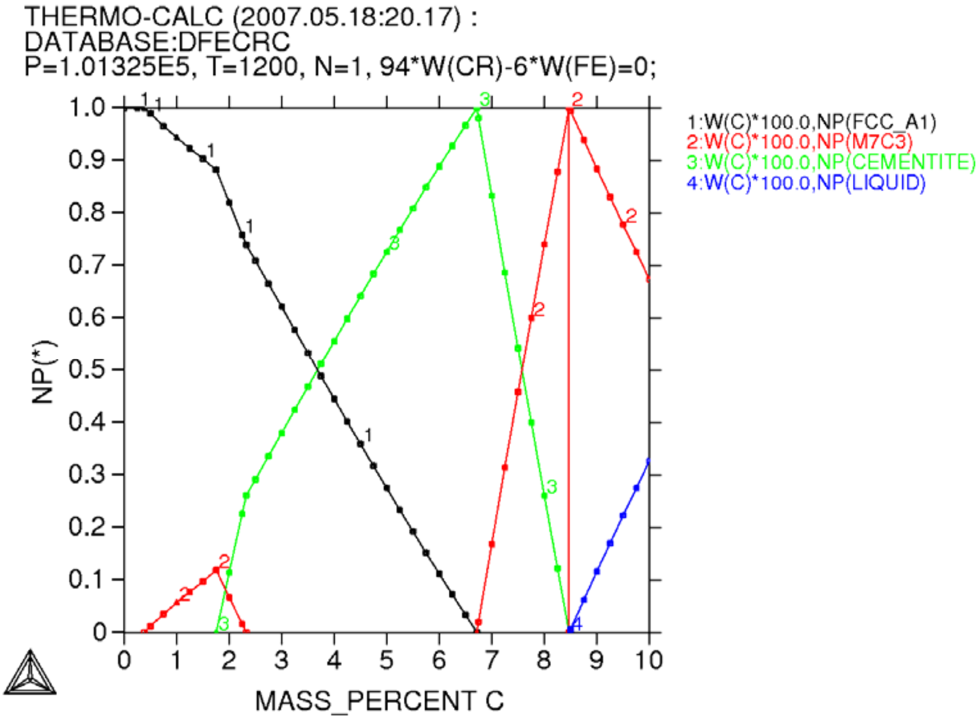
```
POLY_3: rein
POLY_3: ch-st p gra=sus
POLY_3: s-c P=101325 T=1200 N=1 w(C)=.01
POLY_3: s-c 94*w(Cr)-6*w(Fe)=0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        87413  grid points in            1  s
  33 ITS,  CPU TIME USED   1 SECONDS
POLY_3: s-a-v 1 w(C) 0 .1
Increment /.0025/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one          0

 Phase Region from   0.100000E-01 for:
     FCC_A1
     M7C3
 Calculated     6 equilibria

 Phase Region from   0.175228E-01 for:
     CEMENTITE
     FCC_A1
```

```
     M7C3
 Calculated     5 equilibria

 Phase Region from   0.232792E-01 for:
     CEMENTITE
     FCC_A1
 Calculated    20 equilibria

 Phase Region from   0.671716E-01 for:
     CEMENTITE
 Error at first increment  6.719659241194829E-002
 Calculated     2 equilibria

 Phase Region from   0.671716E-01 for:
     CEMENTITE
     M7C3
 Calculated    10 equilibria

 Phase Region from   0.847372E-01 for:
     M7C3
 Error at first increment  8.476220336147465E-002
 Calculated     2 equilibria

 Phase Region from   0.847372E-01 for:
     LIQUID
     M7C3
 Calculated    10 equilibria

 Phase Region from   0.100000E-01 for:
     FCC_A1
     M7C3
 Calculated     5 equilibria

 Phase Region from   0.387947E-02 for:
     FCC_A1
 Calculated     5 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a x w-p C
POST: s-d-a y Np(*)
COLUMN NUMBER /*/:
POST: set-lab f
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



`POST:`

*) Sometimes POST will draw extra lines. In this case there is a vertical line without any number for identification. You can examine this further by including points representing the individual equilibria that were computed. Tick the box showing a curve with some points on it. You can find it in the toolbar at the upper left side of the Thermo-Calc area. There will be no points on such an extra line.

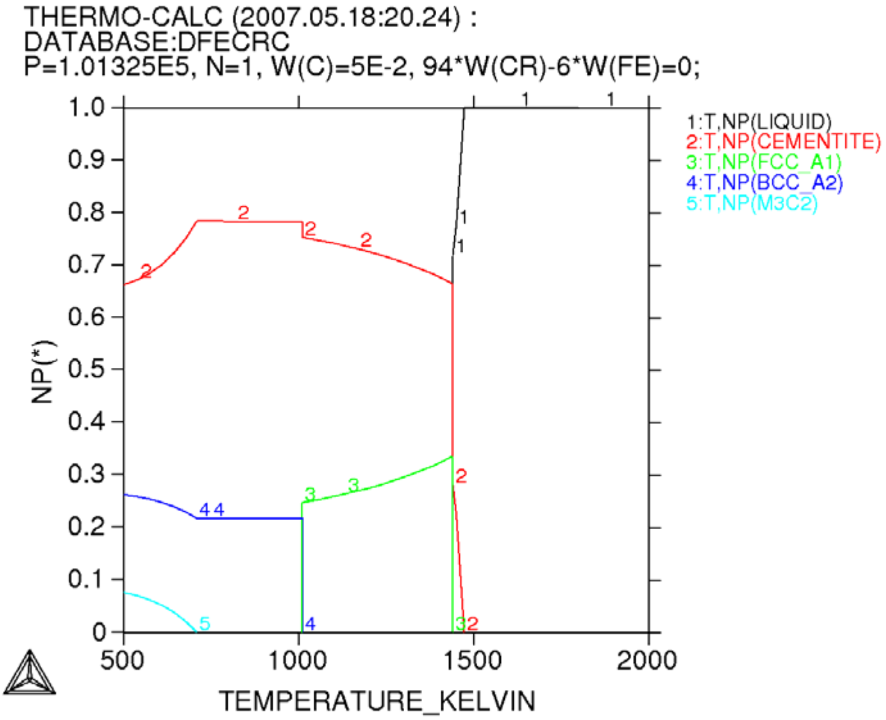


```
POST:
```

*) Now, make a diagram for cooling.

```
POST: b
POLY_3: rein
POLY_3: ch-st p gra=sus
POLY_3: s-c P=101325 T=1800 N=1 w(C)=.05
POLY_3: s-c 94*w(Cr)-6*w(Fe)=0
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        87413  grid points in            1  s
  16 ITS,  CPU TIME USED   1 SECONDS
POLY_3: s-a-v 1 T 500 1900
Increment /35/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    1800.00     for:
     LIQUID
 Calculated     6 equilibria

 Phase Region from    1800.00     for:
     LIQUID
 Calculated    12 equilibria

 Phase Region from    1473.37     for:
     LIQUID
     CEMENTITE
 Calculated     4 equilibria

 Phase Region from    1440.67     for:
     LIQUID
     CEMENTITE
     FCC_A1
 Calculated     3 equilibria

 Phase Region from    1438.25     for:
     CEMENTITE
     FCC_A1
 Calculated    15 equilibria

 Phase Region from    1010.08     for:
     BCC_A2
     CEMENTITE
     FCC_A1
 Calculated     3 equilibria

 Phase Region from    1009.86     for:
     BCC_A2
     CEMENTITE
 Calculated    12 equilibria

 Phase Region from    709.399     for:
     BCC_A2
     CEMENTITE
     M3C2
 Calculated    10 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post
```

```
  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST: set-lab f
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3: exit
 CPU time                 7   seconds
```

Comments

Here it is easy to see the invariant equilibria as revealed by vertical changes. Only the amounts of phases vary.

9.6. Topology of sectioned molar diagrams

Compute a zero-phase-fraction line of your own choice through the isopleth obtained in the first part of Problem 9.4. Plot this line in a diagram with the same axes as the isopleth.

Hint

Your data bank system should offer some method of requiring that a selected phase should take part in all the equilibria that are computed, but with zero amount.

Instructions for using T-C

In POLY this is done by defining the status of a phase.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C Cr
 FE                      C                       CR
   DEFINED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) All phases offered by the database were accepted but you would not like graphite to take part in equilibria. You should thus suspend graphite.

```
POLY_3: ch-st p gra=sus
POLY_3:
```

*) You will soon step in C content and would then like the ratio between Fe and Cr to stay constant. Already when computing the single equilibrium you should prepare for this condition.

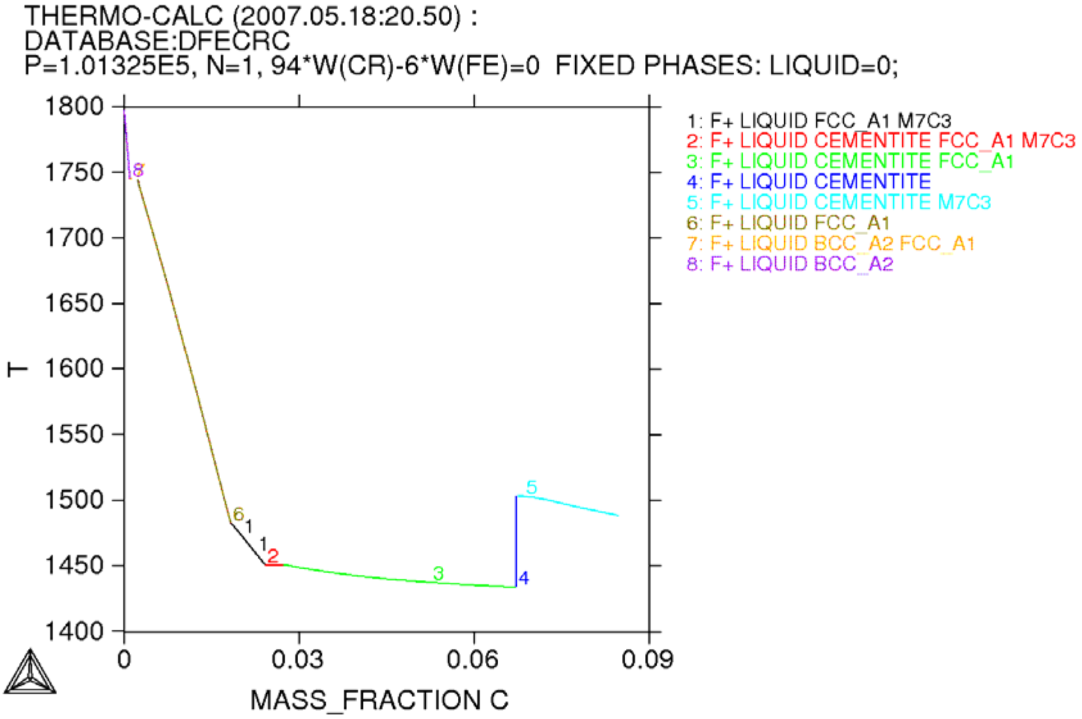
```
POLY_3: s-c P=101325 N=1 w(C)=.02 94*w(Cr)-6*w(Fe)=0
POLY_3:
```

*) You like liquid to take part in all the equilibria that will be computed, but with the amount zero.

```
POLY_3: ch-st p liq=fix 0
```

```
POLY_3: c-e
 Normal POLY minimization, not global
 Convergence problems, increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
 Testing POLY result by global minimization procedure
 Calculated        87413  grid points in            1  s
 260 ITS,  CPU TIME USED   1 SECONDS
POLY_3: s-a-v 1 w(C)
Min value /0/:  0
Max value /1/:  .1
Increment /.0025/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from   0.200000E-01 for:
     LIQUID
     FCC_A1
     M7C3
 Calculated     4 equilibria

 Phase Region from   0.241703E-01 for:
     LIQUID
     CEMENTITE
     FCC_A1
     M7C3
 Calculated     4 equilibria

 Phase Region from   0.272434E-01 for:
     LIQUID
     CEMENTITE
     FCC_A1
 Calculated    19 equilibria

 Phase Region from   0.671716E-01 for:
     LIQUID
     CEMENTITE
 jump 10
 Emergency fix  6.717159241194832E-002  6.842159241194833E-002
 Calculated     2 equilibria

 Phase Region from   0.684216E-01 for:
     LIQUID
     CEMENTITE
     M7C3
 Calculated    10 equilibria

 Phase Region from   0.847372E-01 for:
     LIQUID
     M7C3
 jump 2:         1611
  *** Sorry cannot continue

 Phase Region from   0.200000E-01 for:
     LIQUID
     FCC_A1
     M7C3
 Calculated     3 equilibria

 Phase Region from   0.182539E-01 for:
     LIQUID
```

```
     FCC_A1
 jump 13
 Emergency fix  2.49999999999989E-003  1.24999999999989E-003
 Calculated    10 equilibria

 Phase Region from   0.125000E-02 for:
     LIQUID
     BCC_A2
     FCC_A1
 Calculated     3 equilibria

 Phase Region from   0.998406E-03 for:
     LIQUID
     BCC_A2
 Calculated     4 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a x w-f C
POST: s-d-a y T
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            2  seconds
```

Comments

You can find all the pieces of the computed zero-phase-fraction line in the isopleth of Problem 9.4.

All the phase boundaries, in phase diagrams represent zero fraction of some phase. The concept of "zero-phase-fraction line" does not make sense until one combines those pieces into one line.

The zero-phase-fraction line for liquid was obtained here simply because of the condition "ch-st p liq = fix 0" for the single equilibrium in the beginning.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

---

Chapter 10. Projected and mixed phase diagrams

10.1A. Schreinemakers' projection of potential phase diagrams.

Consider the ternary Al-Mg-Si system at 1 atm and in the region 400 to 700^{o}C. It should obey the same topological rules as a binary system with a variable *P*, as Fig. 10.1(a). Calculate the three-dimensional phase diagram. Plot the result with the axes a_{Mg}, a_{Si}, which should yield a projection in the T direction with the same topology as Fig. 10.1(b). Produce a stereographic pair of pictures by using $a_{Si} \pm \varepsilon \cdot T$ instead of a_{Si} as an axis. You have to find a conveniently small value of the ε constant. That pair should give an impression of the three-dimensional structure. Another method was used in Fig. 10.1(a).

Hint

Your data bank system certainly has a standard procedure for mapping phase diagrams with axes for two components. Hopefully, it is then possible to plot the results with the activity axes. It may be most convenient to use activities based on the pure elements in their stable solid states and at the current temperature as references.

Instructions for using T-C

It may be convenient to use two mole fractions as axis variables for mapping. Activity axes can then be introduced for plotting.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DAlMgSi
TDB_DALMGSI: def-el Al Mg Si
 AL                       MG                       SI
   DEFINED
TDB_DALMGSI: get
```

```
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            3
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'N Saunders, COST project (1994); MG-SI'
  'H L Lukas, COST project (1994); AL-SI'
  'H L Lukas, COST project (1994); MG-SI'
  'H L Lukas, COST project (1994); AL-MG-SI'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DALMGSI: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You may like to use the mole fractions of Mg and Si and temperature as axis variables for mapping and should thus use them as conditions for the single equilibrium.

```
POLY_3: s-c P=101325 T=700 x(Mg)=.01 x(Si)=.01 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated        45016  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

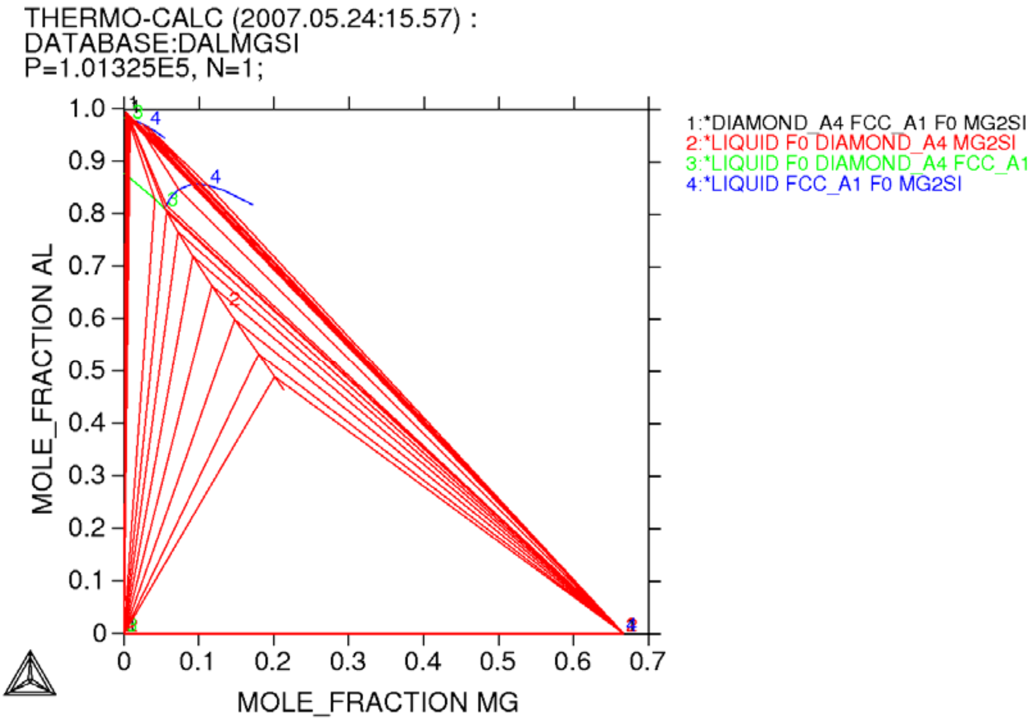
*) Before starting mapping you could just as well introduce the activities for later use as axes in plotting.

```
POLY_3: set-ref Mg hcp
Temperature /*/:
Pressure /1E5/:
POLY_3: set-ref Al fcc
Temperature /*/:
Pressure /1E5/:
POLY_3: s-a-v 1 x(Mg)
Min value /0/:
Max value /1/:
Increment /.025/:
POLY_3: s-a-v 2 x(Si)
Min value /0/:
Max value /1/:
Increment /.025/:
POLY_3: s-a-v 3 T
Min value /0/:  673
Max value /1/:  973
Increment /7.5/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points
```

```
 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   2.513E-03  3.912E-03  7.000E+02
  ** DIAMOND_A4
     FCC_A1
  ** MG2SI
 Calculated     8 equilibria

 Phase region boundary   2 at:   2.513E-03  3.912E-03  7.000E+02
  ** DIAMOND_A4
     FCC_A1
  ** MG2SI
 Calculated    20 equilibria

 Phase region boundary   3 at:   8.049E-03  1.409E-02  8.310E+02
     LIQUID
  ** DIAMOND_A4
     FCC_A1
  ** MG2SI

 Phase region boundary   4 at:   6.667E-01  3.333E-01  8.310E+02
  ** LIQUID
  ** DIAMOND_A4
     MG2SI
 Calculated    25 equilibria

 Phase region boundary   5 at:   8.049E-03  1.409E-02  8.310E+02
  ** LIQUID
  ** DIAMOND_A4
     FCC_A1
 Calculated     7 equilibria

 Phase region boundary   6 at:   8.049E-03  1.409E-02  8.310E+02
  ** LIQUID
     FCC_A1
  ** MG2SI
 Convergence problems, increasing smallest sitefraction from 1.00E-30
 to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
 Calculated    16 equilibria
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) Insert labels and every third of the computed tie-lines in a diagram with mole fractions as axes.

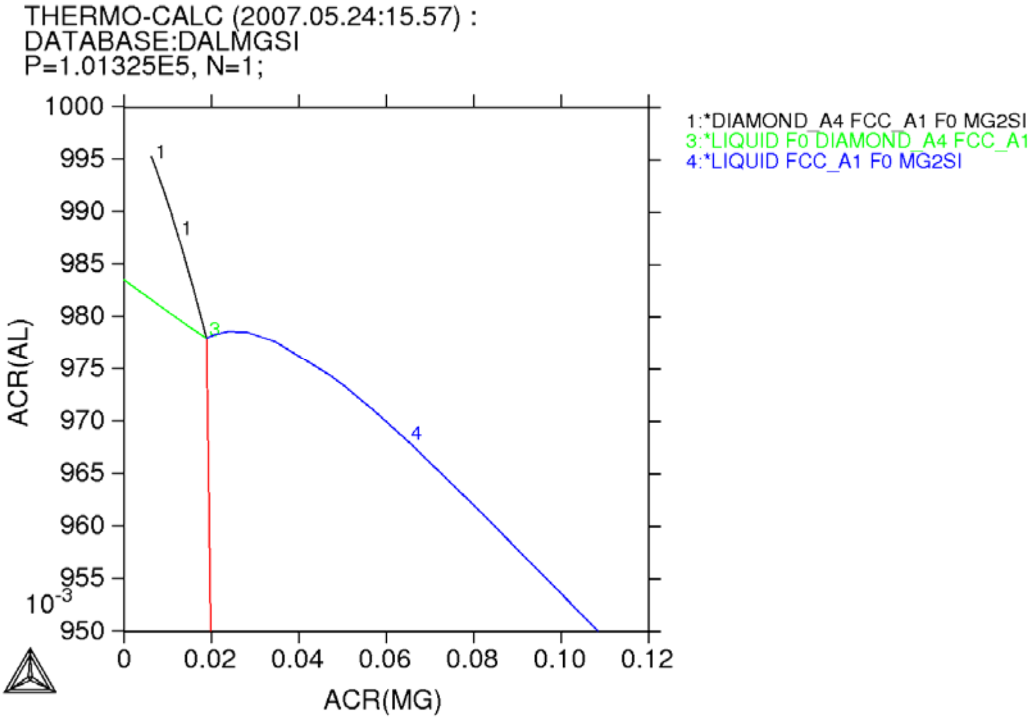
```
POST: set-lab e
POST: s-t-s 3
POST: s-d-a x m-f Mg
POST: s-d-a y m-f Al
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Introduce activity axes and define the scale for the Al axis using the command **s**et-**s**caling **s**tatus. It is the y axis and you say **N**o to automatic scaling because you may be aware of the fact that the interesting things are concentrated towards the Al corner.

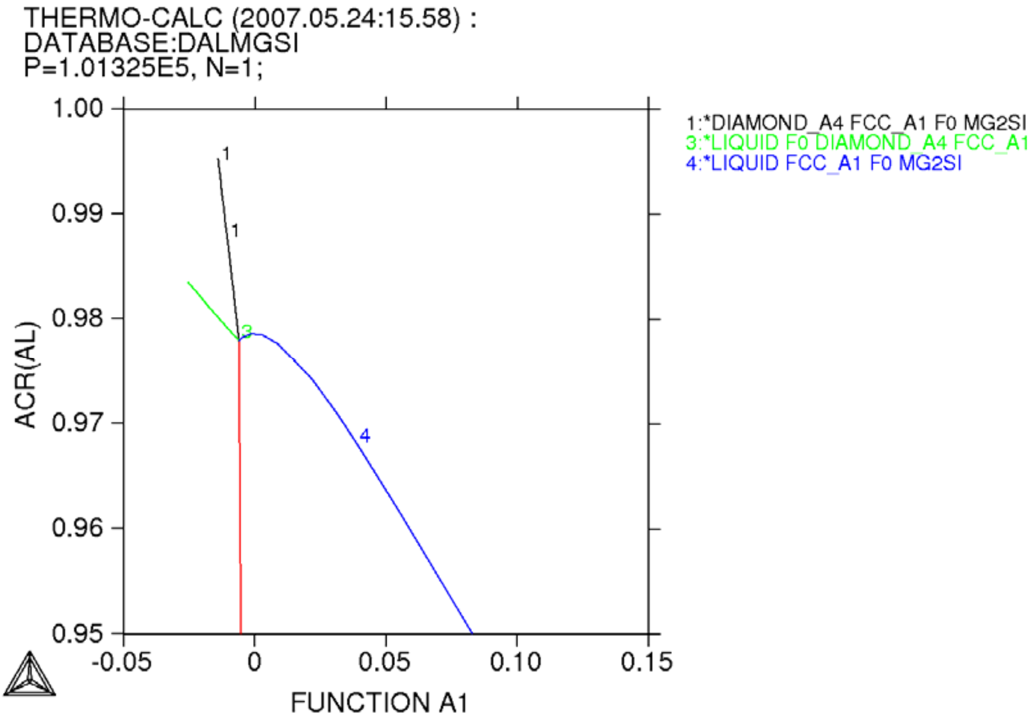
```
POST: s-d-a x acr(Mg)
POST: s-d-a y acr(Al)
POST: s-s-s y N .95 1
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POLY_3:
```

*) Finally, you try to look not quite in the direction of T .

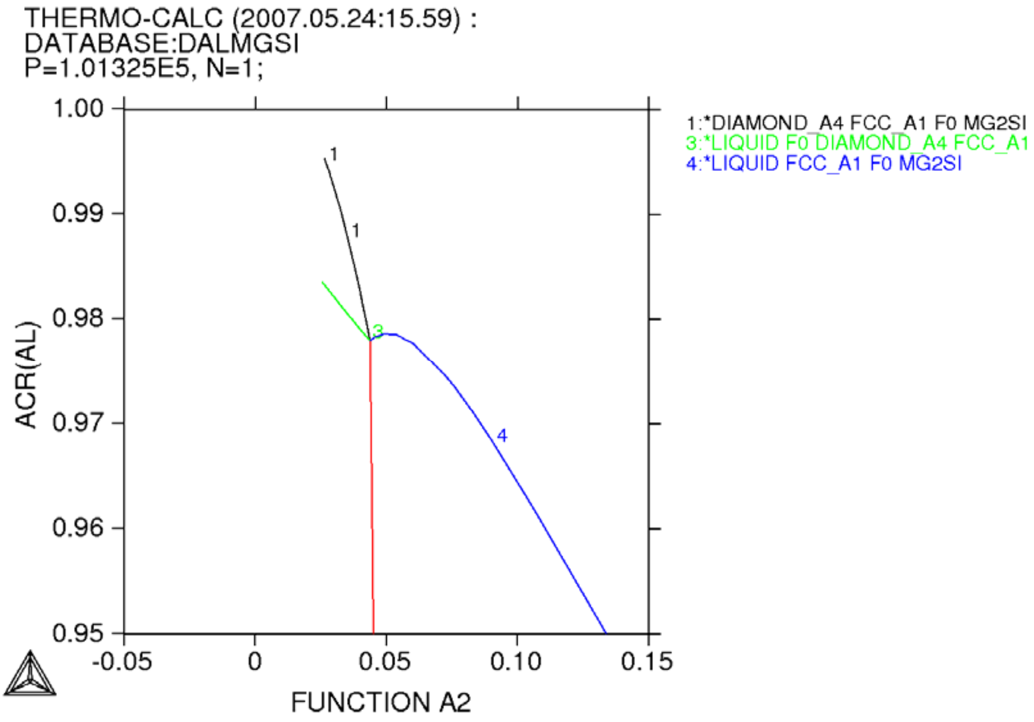
```
POST: ent-sym var k=3E-5;
POST: ent-sym fun a1=acr(Mg)-k*T;
POST: s-d-a x a1
POST: s-s-s x n -.05 .15
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POLY_3:
```

*) And from the other side.

```
POST: ent-sym fun a2=acr(Mg)+k*T;
POST: s-d-a x a2
POST: s-s-s x n -.05 .15
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



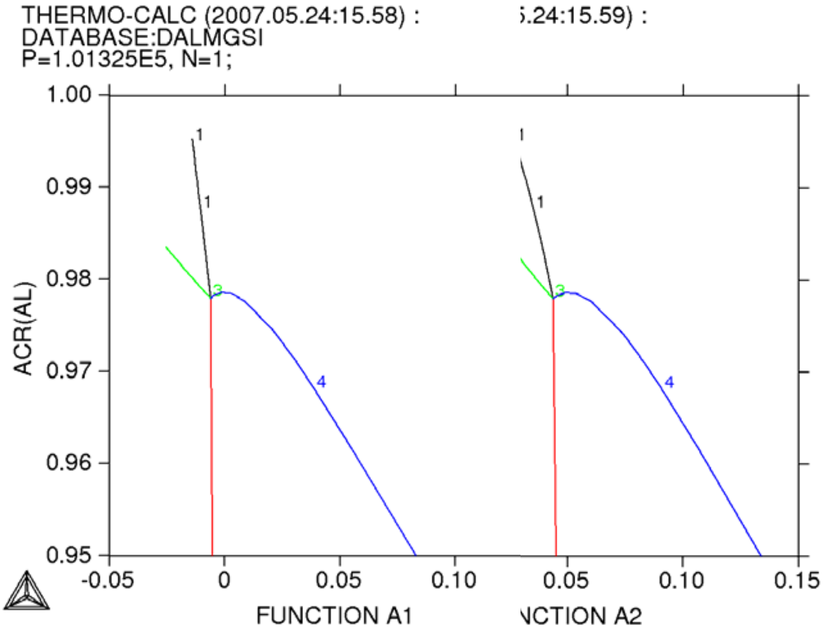
```
POST: b
POLY_3: exit
 CPU time              1  seconds
```

Comments

1) The first diagram is plotted with the mole fractions as axes. Tie-lines are included which means that the three-phase equilibria are shown as tie-triangles. Three lines representing liquid in equilibrium with two solid phases are identified with the numbers 2, 3 and 4 and they meet in a point representing an invariant equilibrium. Corresponding lines are seen in the second diagram with activity axes and a fourth line, Nr. 1, representing a univariant equilibrium between the three solids can also be seen there. It is to be expected that this line extends in the negative direction of the projected temperature axis and one may expect that the other three lines are sloping to the invariant equilibrium. The diagram would then be similar to Fig. 10.1.

2) The stereographic pair of pictures must be mounted side by side to be useful. As mounted below and looked at with parallel eyes the pair would show the positive T direction away from you and line 1 is directed towards you. Lines 3 and 4 are definitely away from you but the fourth line is difficult to judge.

3) The mounting of the stereographic pair side by side is a little tricky and will not be described here.



10.1B. Schreinemakers' projection of potential phase diagrams

Compute and plot all the liquidus surfaces for the Fe-Cr-C system at 1 atm. Then, add isotherms on the liquidus surfaces.

Hint

In principle, the first part of this problem is solved by mapping the complete potential phase diagram after sectioning at the constant pressure. However, the condition liq=fix must be used in order to avoid all other univariant equilibria (also called monovariant). To add isotherms actually means to map isothermal sections, which might require a new mapping operation for each section.

Instructions for using T-C

T-C has a special module for this purpose, **tern**ary diagram. It uses the ptern database as default. It is very robust in order to make sure that no features will be missed. The disadvantage is that it takes a very long time to execute and your screen will be filled over and over again. In the following records of a session, much of the print-out has been deleted by necessity. However, all the **prompts, commands and responses** are kept.

Prompts, commands and responses

```
SYS: go tern
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
 Current database: TCS Public Ternary Alloys TDB v1

 VA  DEFINED

 Simple ternary phase diagram calculation module
```

```
Database: /PTERN/:
First element: Fe
Second element: Cr
Third element: C
Phase Diagram, Monovariants, or Liquidus Surface: /Phase_Diagram/:  Mono
Global minimization on: /N/:
 VA  DEFINED
 REINITIATING GES5 .....
 C                       CR                       FE
   DEFINED
 *** GAS INPUT IGNORED
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
 Forcing automatic start values
 Automatic start values will be set
 Forcing automatic start values
 Automatic start values will be set
 Forcing automatic start values
 Automatic start values will be set
 Forcing automatic start values
 Forcing automatic start values
```

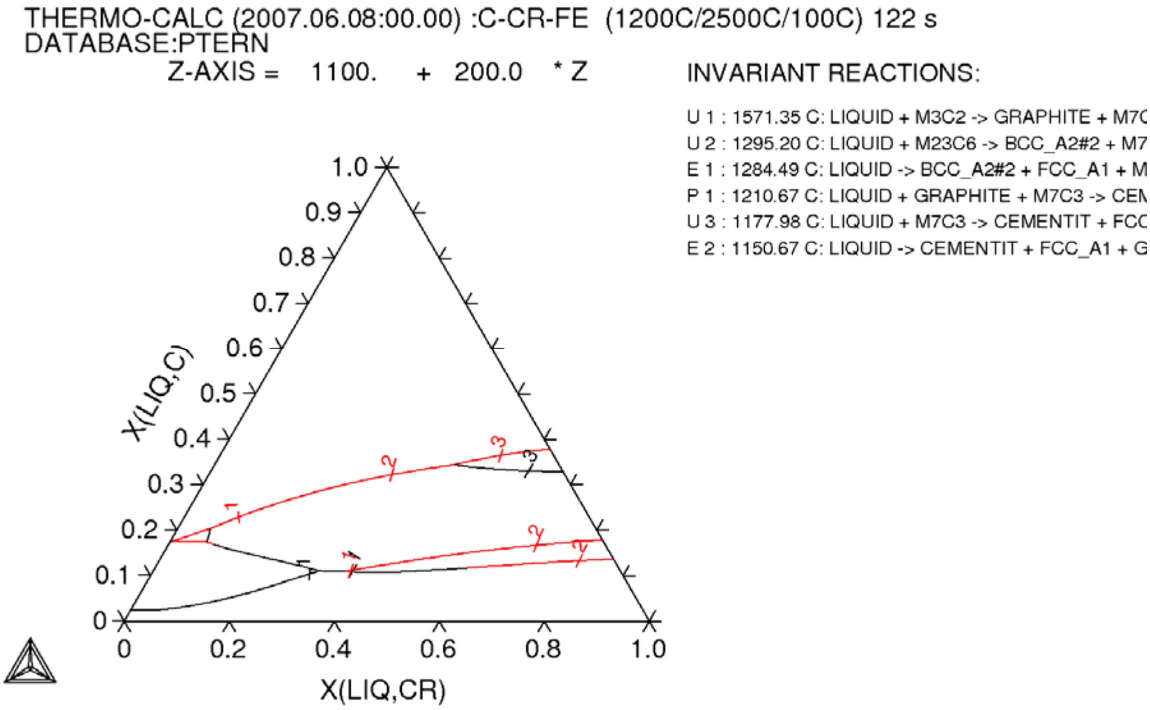
Much has been deleted here

```
 Phase region boundary  18 at:   3.669E-01  5.232E-01  1.568E+03
     LIQUID
  ** BCC_A2#2
     M23C6
  ** M7C3
 Skipping line without LIQUID#1

 Phase region boundary  19 at:   3.669E-01  5.232E-01  1.568E+03
     LIQUID
  ** BCC_A2#2
  ** M23C6
 *** Buffer saved on file: C:\DOCUME~1\Malin\MONOVAR.POLY3
 Calculated    60 equilibria

 Phase region boundary  20 at:   3.669E-01  5.232E-01  1.568E+03
     LIQUID
  ** M23C6
  ** M7C3
 Calculated    62 equilibria
 *** Last buffer saved on file: C:\DOCUME~1\Malin\MONOVAR.POLY3

 INVARIANT REACTIONS:
```

```
U 1: 1571.35 C: LIQUID + M3C2 -> GRAPHITE + M7C3
U 2: 1295.20 C: LIQUID + M23C6 -> BCC_A2#2 + M7C3
E 1: 1284.49 C: LIQUID -> BCC_A2#2 + FCC_A1 + M7C3
P 1: 1210.67 C: LIQUID + GRAPHITE + M7C3 -> CEMENTIT
U 3: 1177.98 C: LIQUID + M7C3 -> CEMENTIT + FCC_A1
E 2: 1150.67 C: LIQUID -> CEMENTIT + FCC_A1 + GRAPHITE


  POSTPROCESSOR VERSION 3.2 , last update 2002-12-01


 Setting automatic diagram axis

POST:
```

*) A list of the invariant equilibria was printed automatically and their temperatures are given in degree Celsius. The classification used here can be compared to the one in Section 12.5 as follows: E is class I, U is class II and P is Class III.

```
POST: PLOT,,,,,;
```



```
POST:
```

*) The tic marks give some temperatures on the univariant lines. You can add labels in order to identify the lines.

```
POST: set-lab e
POST:
```

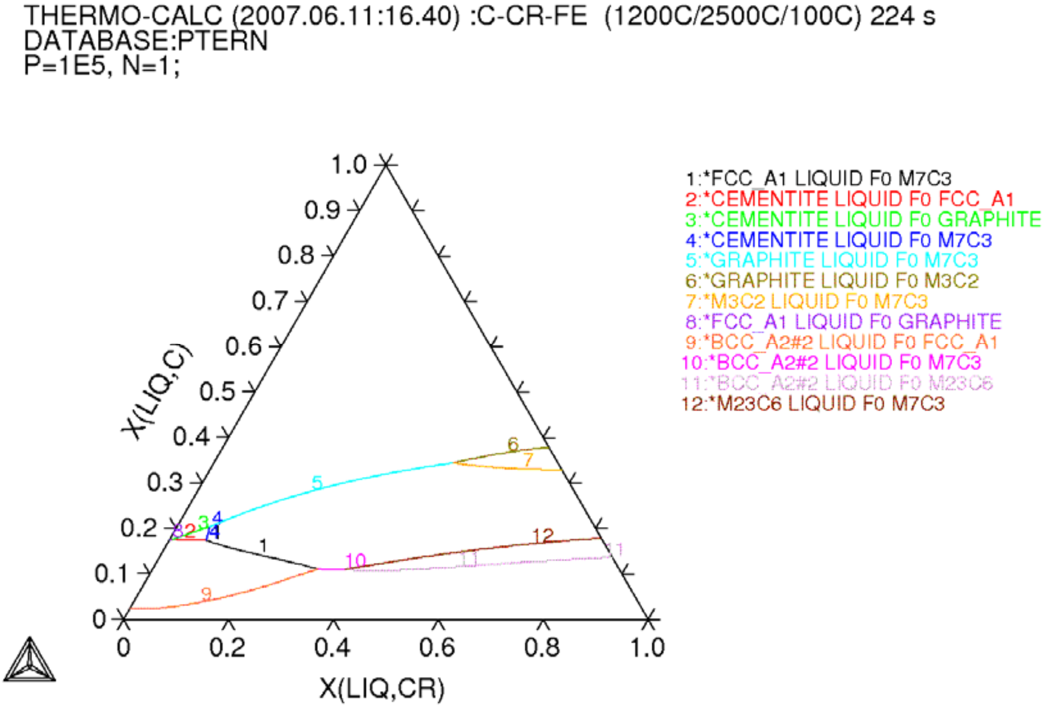
*) In order not to mix the labels with the tic marks showing the temperatures, you should remove the latter ones. They represent the third axis, the z axis.

```
POST: s-d-a z none
POST:
```

*) When labels are introduced, a list explaining them will be presented on the right where the invariant reactions are already listed in the first diagram. It would thus be convenient to remove the latter list by responding with **N**o to the question following the command **app**end.

```
POST: app
```

```
USE EXPERIMENTAL DATA (Y OR N) /N/: N
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POLY_3:
```

*) With some trouble you may identify the liquidus surfaces. It may help to consult the binary diagrams, which can be quickly obtained using another module. However, if you have computed your own diagram, you can place the pointer in any field and read the phase in the bar below the screen.

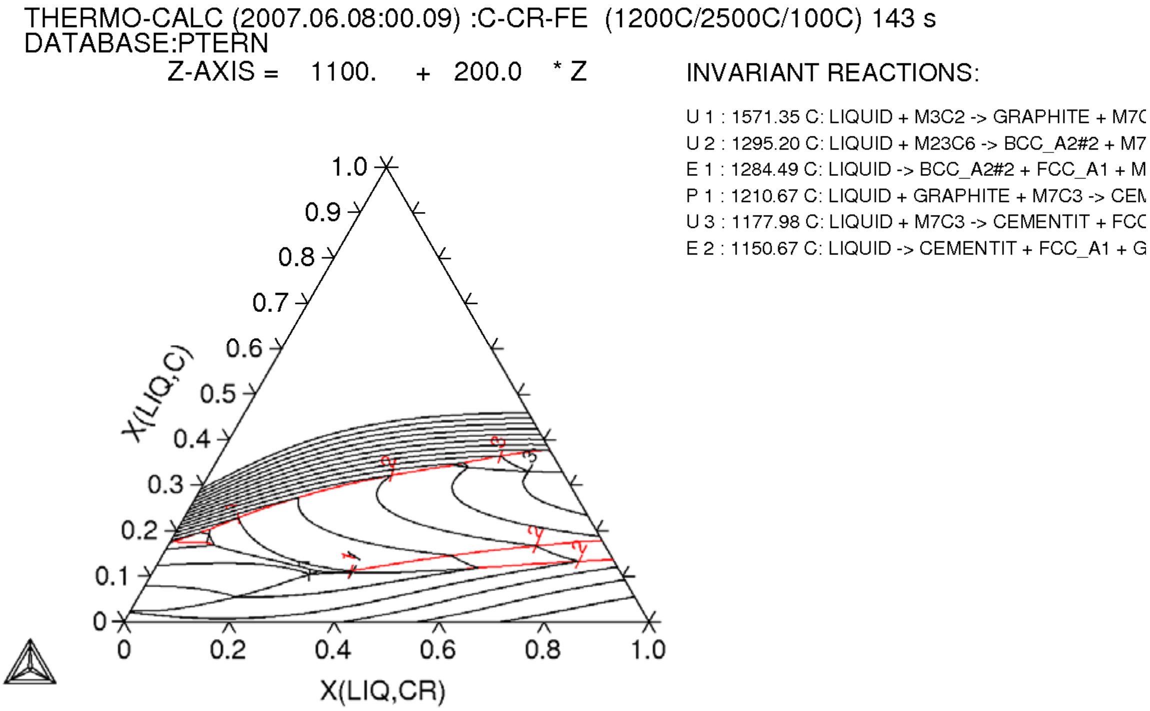
In order to plot isotherms you should go back to the TERN module.

```
POST: b
SYS: go tern
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA   DEFINED
 Current database: TCS Public Ternary Alloys TDB v1

 VA   DEFINED

 Simple ternary phase diagram calculation module

Database: /PTERN/:
First element: Fe
Second element: Cr
Third element: C
Phase Diagram, Monovariants, or Liquidus Surface: /Phase_Diagram/:  Liq
Min temperature, C /25/:
Max temperature, C /2500/:
Temperature interval /100/:
Global minimization on: /N/:
 VA   DEFINED
 REINITIATING GES5 .....
 C                        CR                       FE
   DEFINED
```

```
 *** GAS INPUT IGNORED
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data


 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
 Forcing automatic start values
 Automatic start values will be set
 Forcing automatic start values
 Automatic start values will be set
 Forcing automatic start values
 Automatic start values will be set
 Forcing automatic start values
```

Much has been deleted here

```
 Phase region boundary  80 at:   5.380E-02  8.644E-01
  ** LIQUID
     FCC_A1
 Calculated    32 equilibria
 Skipping line without LIQUID#1
 Skipping line without LIQUID#1

 Phase region boundary  81 at:   1.219E-02  8.048E-01
     LIQUID
  ** GRAPHITE
 *** Sorry cannot continue ***    4

 *** Last buffer saved on file: C:\DOCUME~1\Malin\MONOVAR.POLY3

 INVARIANT REACTIONS:

 U 1: 1571.35 C: LIQUID + M3C2 -> GRAPHITE + M7C3
 U 2: 1295.20 C: LIQUID + M23C6 -> BCC_A2#2 + M7C3
 E 1: 1284.49 C: LIQUID -> BCC_A2#2 + FCC_A1 + M7C3
 P 1: 1210.67 C: LIQUID + GRAPHITE + M7C3 -> CEMENTIT
 U 3: 1177.98 C: LIQUID + M7C3 -> CEMENTIT + FCC_A1
 E 2: 1150.67 C: LIQUID -> CEMENTIT + FCC_A1 + GRAPHITE


  POSTPROCESSOR VERSION 3.2 , last update 2002-12-01


 Setting automatic diagram axis

POST: PLOT,,,,,;
```



```
POST:
```

*) You could have obtained this directly but the labels would then have been even more difficult to interpret. The numbers give the temperatures as defined by the expression above the diagram. Z is the T axis.

```
POST: b
SYS: exit
 CPU time          303  seconds
```

Comments

Starting from a fundamental potential phase diagram, the last diagram obtained here has been sectioned twice, first at a constant pressure and then at a series at constant temperatures. Then the remaining chemical potentials have been replaced by mole fractions. The first diagram was sectioned once and projected once.

10.2. The phase field rule and projected diagrams

The fundamental property diagram of a ternary system has 3+2=5 axes, e.g. μ_A, μ_B, μ_C, T and P. By projecting in one direction one obtains a four-dimensional potential phase diagram and those four potentials then make a set of independent state variables. In order to obtain a two-dimensional phase diagram, which can be plotted on paper, one can project in the directions of three potentials and could thus obtain 5x4x3=60 different projections. An alternative would be to project in one direction and section at constant values of two potentials. That would give another 60 alternatives. Finally, one could project in two directions and section at a constant value of one. That would add yet another 60 alternatives. You are asked to make two two-dimensional phase diagrams of the Fe-Cr-C system.

Hint

1) Each time you decide to make a section, you must make a new mapping of the phase equilibria at the chosen value of the sectioned potential. On the other hand, once you have mapped the equilibria for variable conditions for all the potentials, you can directly plot any projection you like. For convenience, you should thus choose to make two projections.

2) Since only four of the potentials are independent due to the Gibbs-Duhem relation, you should choose one to be dependent, say μ_A.

3) After mapping all the univariant equilibria you should choose two pairs of potentials to be used as axes in the two diagrams. It may be most illustrative to choose T and P as one pair and μ_B and μ_C as the other.

Instructions for using T-C

Since you are going to map a potential diagram, it may be convenient to start with an initial equilibrium based on chemical potentials as conditions rather than composition. However, it is difficult to guess reasonable values for chemical potentials and you may instead use activities with the pure elements at the current temperatures as references.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                      CR                       C
   DEFINED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
```

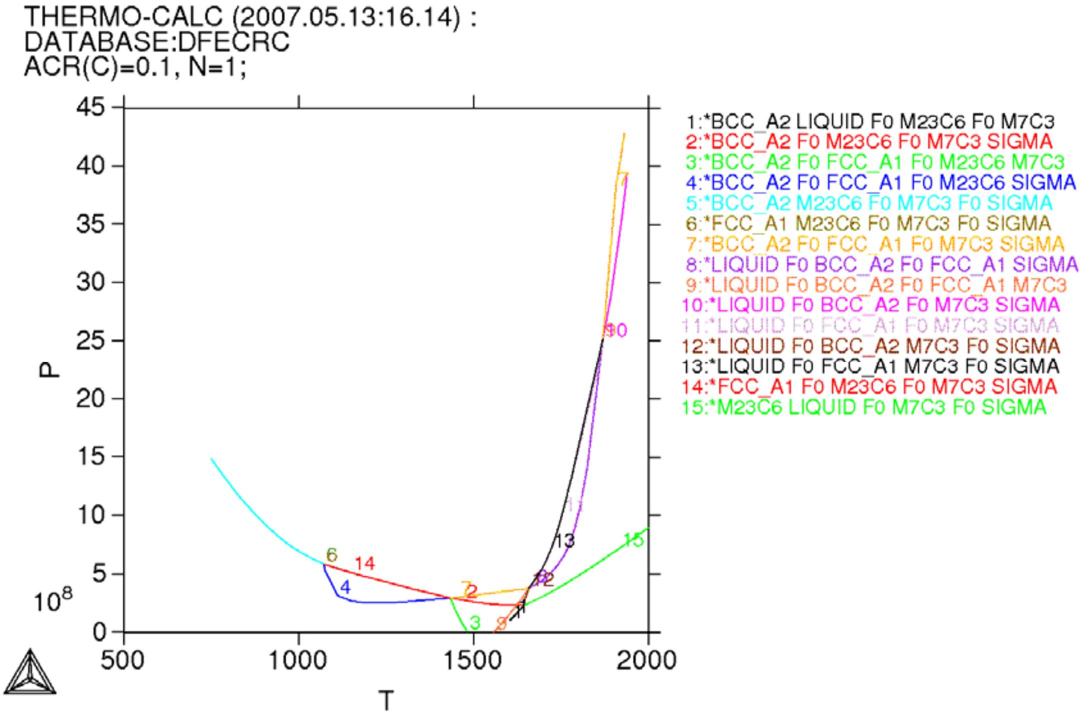
```
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
POLY_3: set-ref C gra
Temperature /*/:
Pressure /1E5/:
POLY_3: set-ref Cr bcc
Temperature /*/:
Pressure /1E5/:
POLY_3: set-ref Fe fcc
Temperature /*/:
Pressure /1E5/:
POLY_3: s-c P=1E8 T=1700 acr(C)=.1 acr(Cr)=.1 N=1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated        87414  grid points in            1  s
  15 ITS,  CPU TIME USED   1 SECONDS
POLY_3: s-a-v 1 acr(Cr) 0  1
Increment /.025/:
POLY_3: s-a-v 2 P 1E5 1E10
Increment /249997500/:  2*
 Logarithmic step set
POLY_3: s-a-v 3 T 500 2000
Increment /37.5/:
POLY_3: s-a-v 4 acr(C) 0  1
Increment /.025/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   1.900E-01  1.000E+08  1.603E+03  1.897E-02
     LIQUID
  ** BCC_A2
  ** M23C6
  ** M7C3
 Calculated     3 equilibria

 Phase region boundary   2 at:   3.915E-01  2.283E+08  1.644E+03  2.170E-02
     LIQUID
  ** BCC_A2
  ** M23C6
```

```
 ** M7C3
    SIGMA

Phase region boundary   3 at:   3.915E-01  2.283E+08  1.644E+03  2.170E-02
 ** BCC_A2
 ** M23C6
 ** M7C3
    SIGMA
Calculated     9 equilibria

Phase region boundary   4 at:   2.831E-01  2.918E+08  1.434E+03  2.308E-02
 ** BCC_A2
    FCC_A1
 ** M23C6
 ** M7C3
    SIGMA

Phase region boundary   5 at:   2.831E-01  2.918E+08  1.434E+03  2.308E-02
 ** BCC_A2
 ** FCC_A1
 ** M23C6
    M7C3
Calculated    25 equilibria

Phase region boundary   6 at:   2.831E-01  2.918E+08  1.434E+03  2.308E-02
 ** BCC_A2
 ** FCC_A1
 ** M23C6
    SIGMA
Calculated    12 equilibria

Phase region boundary   7 at:   1.919E-01  5.834E+08  1.072E+03  8.404E-03
 ** BCC_A2
 ** FCC_A1
    M23C6
    M7C3
 ** SIGMA

Phase region boundary   8 at:   1.919E-01  5.834E+08  1.072E+03  8.404E-03
 ** BCC_A2
 ** FCC_A1
 ** M7C3
    SIGMA
Convergence problems, increasing smallest sitefraction from 1.00E-30
to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
*** Sorry cannot continue ***    9

Calculated     3 equilibria

Phase region boundary   9 at:   1.919E-01  5.834E+08  1.072E+03  8.404E-03
 ** BCC_A2
 ** FCC_A1
    M23C6
 ** M7C3
*** Sorry cannot continue ***    9


Phase region boundary  10 at:   1.919E-01  5.834E+08  1.072E+03  8.404E-03
 ** BCC_A2
    M23C6
 ** M7C3
```

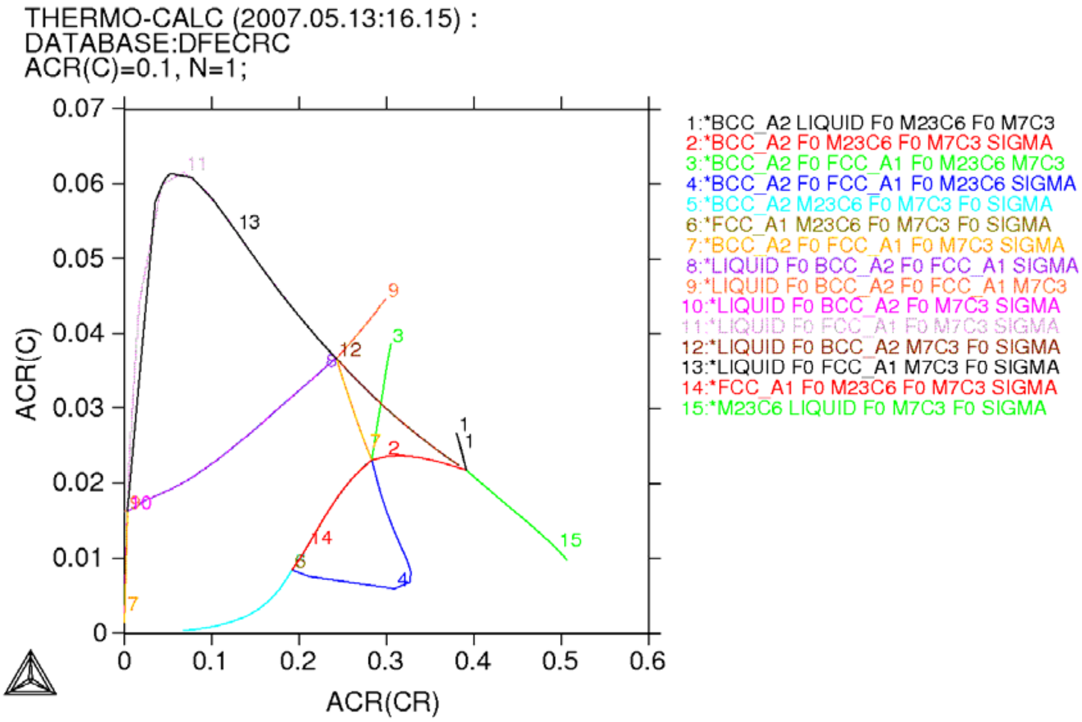
```
 ** SIGMA
*** Sorry cannot continue ***    9

Calculated    12 equilibria

Phase region boundary  11 at:   1.919E-01  5.834E+08  1.072E+03  8.404E-03
 ** FCC_A1
    M23C6
 ** M7C3
 ** SIGMA
Terminating at known equilibrium
Calculated    13 equilibria

Phase region boundary  12 at:   2.831E-01  2.918E+08  1.434E+03  2.308E-02
 ** BCC_A2
 ** FCC_A1
 ** M7C3
    SIGMA
Calculated    11 equilibria

Phase region boundary  13 at:   2.426E-01  3.768E+08  1.658E+03  3.667E-02
    LIQUID
 ** BCC_A2
 ** FCC_A1
    M7C3
 ** SIGMA

Phase region boundary  14 at:   2.426E-01  3.768E+08  1.658E+03  3.667E-02
 ** LIQUID
 ** BCC_A2
 ** FCC_A1
    SIGMA
Calculated    13 equilibria

Phase region boundary  15 at:   3.384E-03  2.516E+09  1.870E+03  1.622E-02
 ** LIQUID
 ** BCC_A2
 ** FCC_A1
    M7C3
    SIGMA

Phase region boundary  16 at:   3.384E-03  2.516E+09  1.870E+03  1.622E-02
 ** LIQUID
 ** BCC_A2
 ** FCC_A1
    M7C3
Calculated     4 equilibria

Phase region boundary  17 at:   3.384E-03  2.516E+09  1.870E+03  1.622E-02
 ** LIQUID
 ** BCC_A2
 ** M7C3
    SIGMA
Calculated     6 equilibria

Phase region boundary  18 at:   3.384E-03  2.516E+09  1.870E+03  1.622E-02
 ** LIQUID
 ** FCC_A1
 ** M7C3
    SIGMA
Terminating at known equilibrium
```

```
Calculated    13 equilibria

Phase region boundary  19 at:   3.384E-03  2.516E+09  1.870E+03  1.622E-02
 ** BCC_A2
 ** FCC_A1
 ** M7C3
    SIGMA
Calculated     5 equilibria

Phase region boundary  20 at:   2.426E-01  3.768E+08  1.658E+03  3.667E-02
 ** LIQUID
 ** BCC_A2
 ** FCC_A1
    M7C3
Calculated    25 equilibria

Phase region boundary  21 at:   2.426E-01  3.768E+08  1.658E+03  3.667E-02
 ** LIQUID
 ** BCC_A2
    M7C3
 ** SIGMA
*** Sorry cannot continue ***    4

Calculated     9 equilibria

Phase region boundary  22 at:   2.426E-01  3.768E+08  1.658E+03  3.667E-02
 ** LIQUID
 ** FCC_A1
    M7C3
 ** SIGMA
Terminating at known equilibrium
Calculated    14 equilibria

Phase region boundary  23 at:   2.831E-01  2.918E+08  1.434E+03  2.308E-02
 ** FCC_A1
 ** M23C6
 ** M7C3
    SIGMA
Terminating at known equilibrium
Calculated    12 equilibria

Phase region boundary  24 at:   3.915E-01  2.283E+08  1.644E+03  2.170E-02
    LIQUID
 ** BCC_A2
 ** M23C6
 ** SIGMA
*** Sorry cannot continue ***    4

Calculated     3 equilibria

Phase region boundary  25 at:   3.915E-01  2.283E+08  1.644E+03  2.170E-02
    LIQUID
 ** BCC_A2
 ** M7C3
 ** SIGMA
*** Sorry cannot continue ***    9


Phase region boundary  26 at:   3.915E-01  2.283E+08  1.644E+03  2.170E-02
    LIQUID
 ** M23C6
```

```
  ** M7C3
  ** SIGMA
 Calculated    15 equilibria

 Phase region boundary  27 at:   1.900E-01  1.000E+08  1.603E+03  1.897E-02
    LIQUID
  ** BCC_A2
  ** M23C6
  ** M7C3
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
 Terminating at known equilibrium
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

POST: s-d-a x T
POST: s-d-a y P
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: s-d-a x acr(Cr)
POST: s-d-a y acr(C)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time                9   seconds
```

Comments

In the second diagram you can see two points where five lines emanate. Evidently, they represent invariant five-phase equilibria. There is one point where only four lines emanate. That could not be an invariant point according to the phase field rule but seems to be. There is a similar example in Fig. 10.5 and the explanation was then given in an exercise. By noting the phases for the univariant equilibria 1 and 2 you can identify the five phases of this invariant equilibrium. By further noting the phases for lines 12 and 15 you can identify the missing line as representing the bcc+liq+M23+sigma equilibrium. It would extend perpendicular to the diagram if it is not affected by projected variables, i.e T and P. That is not reasonable and you should conclude that POLY has missed that line during the mapping. If you were really interested in that line, you could go back to POLY and start with an equilibrium close to that line.

10.4. Coincidence of projected surfaces

Compute the Fe+FeO+Fe_2O_3+FeS equilibrium at 1 atm. In order to simplify the problem, include only the fcc phase as an Fe phase. Compute the connecting four three-phase equilibria in a reasonably large region around the invariant point. Plot those four-phase lines using T and $\mu_{O_2} - \mu_{O_2}^{ref}$ as axes. Use O_2 gas of 1 atm and the current temperature as reference for O_2. Then change the latter axis to $\mu_{O_2} - \mu_{O_2}^{ref} \pm \varepsilon \cdot (\mu_{S_2} - \mu_{S_2}^{ref})$ where ε is a conveniently small number.

Hint

1) The chemical potentials of O_2 and S_2 are used for convenience because they are the predominant species in the gas.

2) You may find that the modified axis made a new line appear. From where did it come?

Instructions for using T-C

Fetch data also for the gas in order to express the chemical potentials of O and S through those of O_2 and S_2 even though the gas is not present. In order to ascertain that it does not take part in the equilibria, you should suspend the gas at the beginning of the session in POLY.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw PSUB
 Current database: TCS Public Pure Substances TDB v1

 VA  DEFINED
TDB_PSUB: def-el Fe O S
 FE                       O                        S
   DEFINED
TDB_PSUB: rej p *
 GAS:G                    FE                       FE_S2
 FE_S3                    FE_L                     S
 S_S2                     S_L                      WUSTITE
 HEMATITE                 FE2O3_GAMMA              MAGNETITE
 FE3O4_L                  PYRRHOTITE               PYRRHOTITE_S2
 PYRITE                   FESO4                    FE2S3O12
   REJECTED
TDB_PSUB: rest p FE PYRRHOTITE WUSTITE MAGNETITE gas
 FE                       PYRRHOTITE               WUSTITE
 MAGNETITE                GAS:G  RESTORED
TDB_PSUB: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 FUNCTIONS ....

 List of references for assessed data

  'TCS public data set for gaseous species, stoichiometric solids and
      liquids in the Cu-Fe-H-N-O-S system.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PSUB: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Since P will be constant, it may be possible for POLY to find the four-phase equilibrium directly by using fix 1 for all the condensed phases. Then you should suspend the gas. It was included simply in order to make it possible to give the potentials of O and S as partial pressures in a gas if it coexisted with the system.

```
POLY_3: ch-st p *=fix 0
POLY_3: ch-st p gas=sus
POLY_3: s-c P=101325
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            4  grid points in           0  s
  12 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

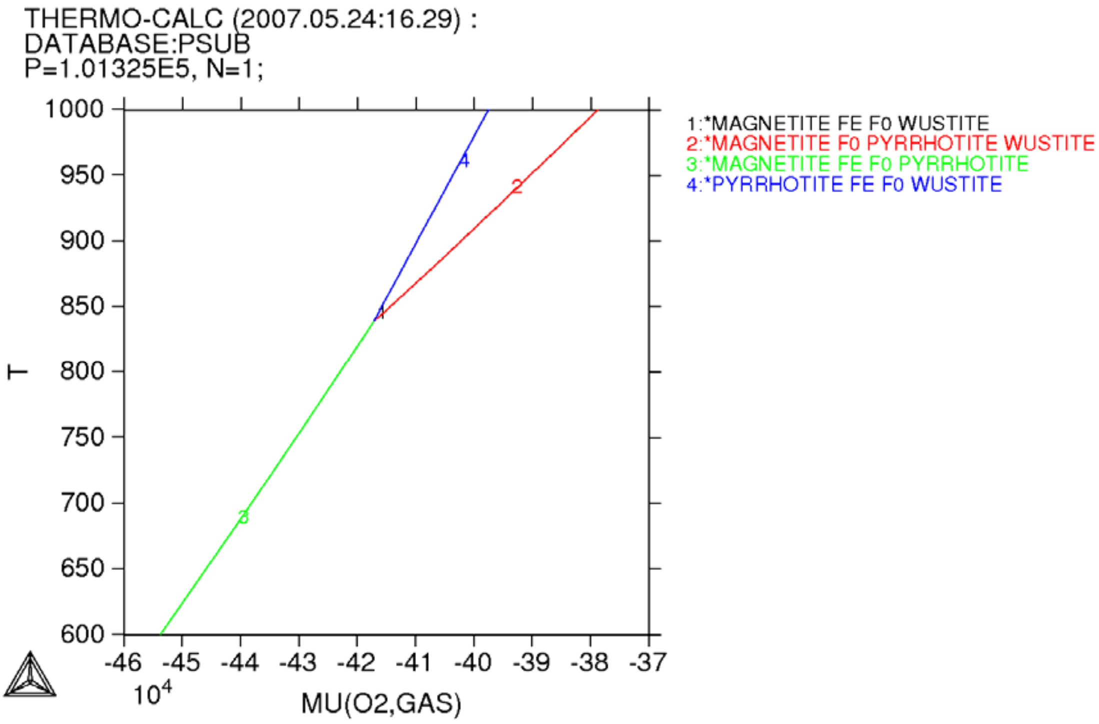
*) It is not convenient to start mapping from an invariant point. You should instead find a point on one of the univariant equilibria emanating from it. Thus, you should show the temperature and then use as condition a slightly different temperature. In this case you should make the phases entered and make sure that the gas is still suspended.

```
POLY_3: sh T
 T=838.71257
POLY_3: ch-st p *=ent 1
POLY_3: ch-st p gas=sus
POLY_3: s-c N=1 T=900
POLY_3:
```

*) You like to use the chemical potentials as axes during the mapping and reasonable values are obtained from the computed invariant equilibrium. By the use of mu(O2,gas) instead of mu(O) or mu(O2), the values will be given with pure O_2 gas as reference.

```
POLY_3: s-c mu(O2,gas)
Value /-446335.6636/:
POLY_3: s-c mu(S2,gas)
Value /-203990.0789/:
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated            4  grid points in           0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3: s-a-v 1 mu(O2,gas) -10e5 -1E5
Increment /22500/:
POLY_3: s-a-v 2 mu(S2,gas) -10e5 -1E5
Increment /22500/:
POLY_3: s-a-v 3 T 600 1000
Increment /15/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:  -4.097E+05 -2.040E+05  8.387E+02
     FE
  ** MAGNETITE
  ** WUSTITE
 Calculated    40 equilibria

 Phase region boundary   2 at:  -4.097E+05 -2.040E+05  8.387E+02
     FE
  ** MAGNETITE
  ** WUSTITE
 Calculated     3 equilibria

 Phase region boundary   3 at:  -4.172E+05 -2.002E+05  8.387E+02
```

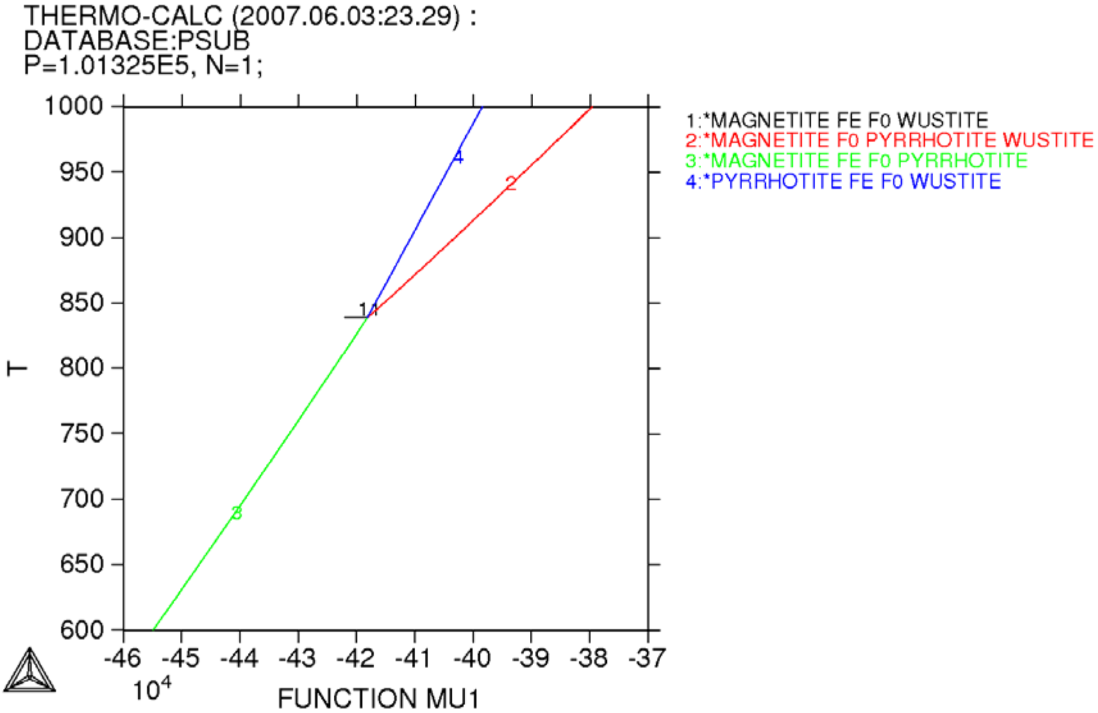
```
    FE
 ** MAGNETITE
    PYRRHOTITE
 ** WUSTITE

Phase region boundary   4 at:  -4.172E+05 -2.002E+05  8.387E+02
 ** MAGNETITE
 ** PYRRHOTITE
    WUSTITE
Calculated    21 equilibria

Phase region boundary   5 at:  -4.172E+05 -2.002E+05  8.387E+02
    FE
 ** MAGNETITE
 ** PYRRHOTITE
Calculated    30 equilibria

Phase region boundary   6 at:  -4.172E+05 -2.002E+05  8.387E+02
    FE
 ** PYRRHOTITE
 ** WUSTITE
Calculated    21 equilibria
*** Last buffer saved on file: USERPROFILE\RESULT.POLY3

POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 *** ERROR  1111 IN GSELA
 *** NO ELEMENT NAMED O2
POST: s-d-a x mu(O2,gas)
POST: s-d-a y T
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



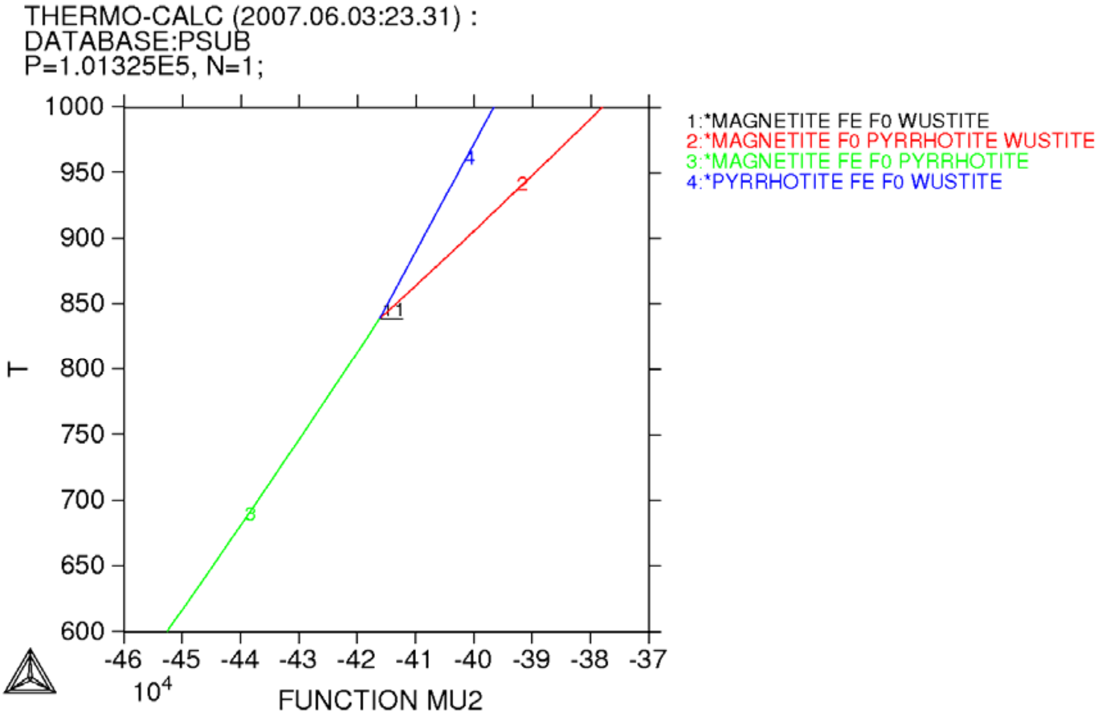
```
POST:
```

*) The lines representing three univariant equilibria meet in a point. However, the list of phases for the lines reveals that there are altogether four phases and there should thus have been a fourth univariant equilibrium. Use a stereographic pair to examine if the corresponding line is perpendicular to the diagram.

```
POST: ent-sym fun mu1=mu(O2,gas)+.005*mu(S2,gas);
POST: s-d-a x mu1
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



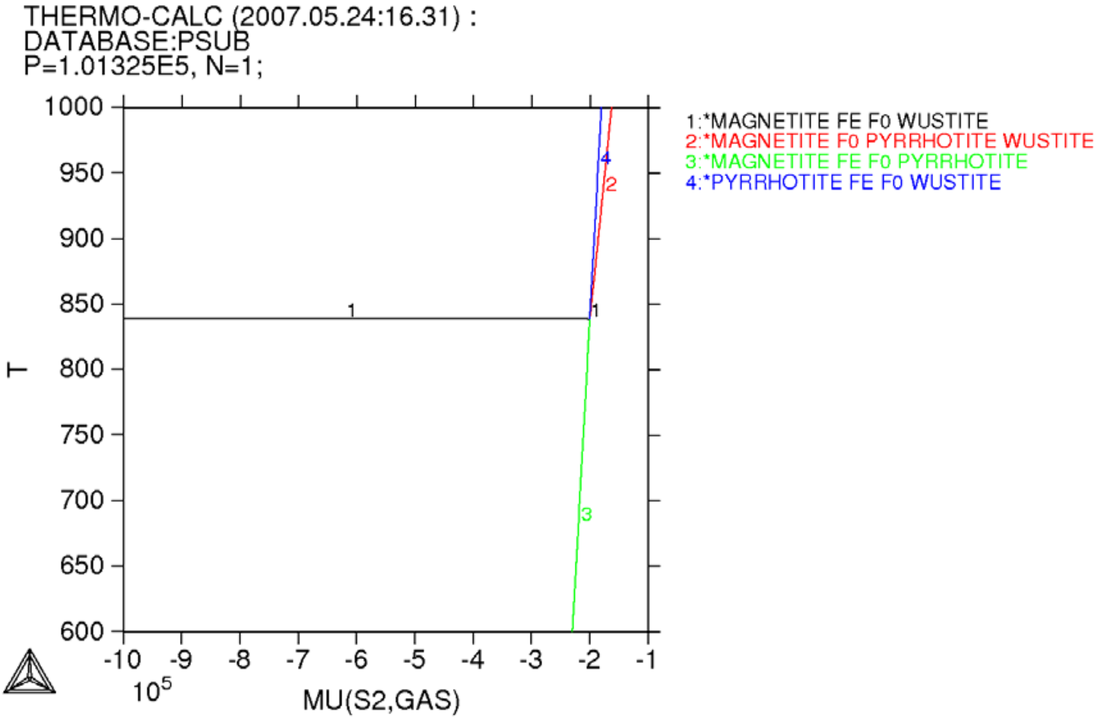
```
POST: ent-sym fun mu2=mu(O2,gas)-.005*mu(S2,gas);
POST: s-d-a x mu2
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Yes, the missing line was perpendicular. Of course, it could have been detected in a much simpler way by plotting with mu(S2) as an axis and projecting in the mu(O2) direction.

```
POST: s-d-a x mu(S2,gas)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time              0   seconds
```

Comments

1) It is not convenient to start mapping from an invariant equilibrium.

2) A stereographic pair of diagrams provides a powerful method of interpreting three-dimensional potential diagrams even though the simple question in the present case could be answered more directly.

10.7A. Selection of axes in mixed diagrams

Compute the phase diagram for Pb-Sn at 1 bar. Plot the result in a diagram with the μ_{Pb}, S_m axes. It should look as Fig. 10.18. Plot the diagram with the following pairs of axes, μ_{Pb}, S_{Pb}; μ_{Pb}, T; x_{Pb}, S_m; x_{Pb}, S_{Pb}; $(\mu_{Pb} - \mu_{Sn}), S_m$.

Hint

In order to obtain a true phase diagram you must choose a pair of axes that belong to the same set of conjugate variables.

Instructions for using T-C

With T-C you can easily try several combinations of axis variables, even functions that you define for a special purpose.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw pbin
 Current database: TCS Public Binary Alloys TDB v1

 VA                     /-  DEFINED
 IONIC_LIQ:Y            L12_FCC                 B2_BCC
 BCC_B2  REJECTED
TDB_PBIN: def-el Pb Sn
 PB                     SN  DEFINED
TDB_PBIN: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions            3
 FUNCTIONS ....

 List of references for assessed data

   91Din 'A.T. Dinsdale, SGTE Data for Pure Elements, CALPHAD, Vol.15,
       No.4, pp.317-425, (1991)'
   ANS-PBSN 'I Ansara, unpublished work, Pb-Sn'
```

```
 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_PBIN: go pol

 POLY version  3.32,  Aug 2001
POLY_3: s-c P=101325 T=500 x(Pb)=.5 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated          412  grid points in            0  s
 Found the set of lowest grid points in            0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

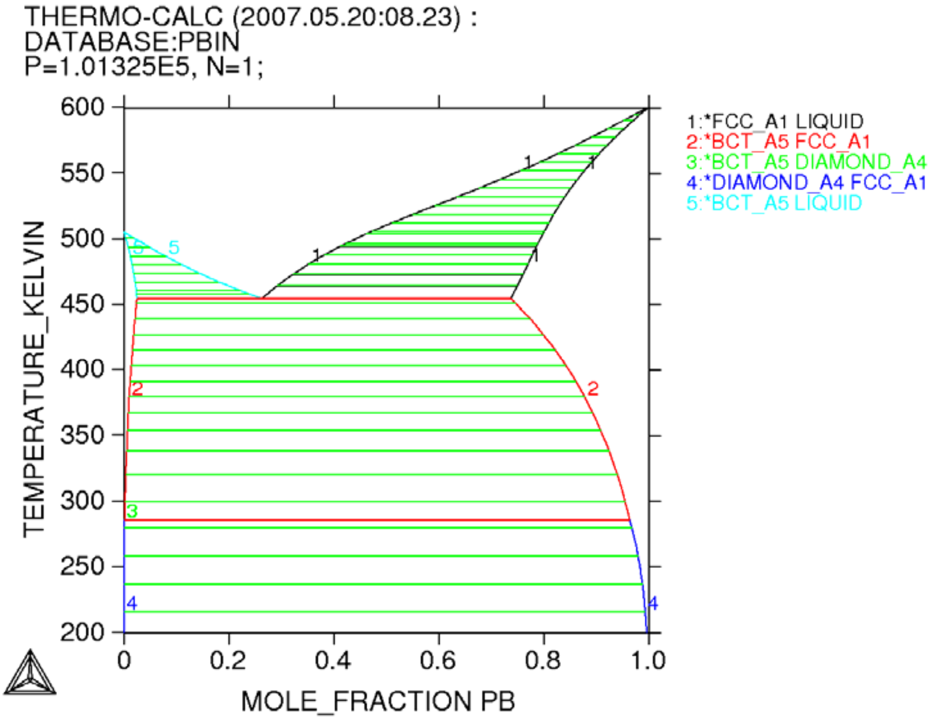
*) It may be convenient now to define a function that you will not need until you are going to plot the result.

```
POLY_3: ent-sym fun diff=mu(Pb)-mu(Sn);
POLY_3: s-a-v 1 x(Pb) 0 1
Increment /.025/:
POLY_3: s-a-v 2 T
Min value /0/:  200
Max value /1/:  650
Increment /10/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   4.410E-01  5.000E+02
     LIQUID
  ** FCC_A1
 Calculated    21 equilibria

 Phase region boundary   2 at:   2.627E-01  4.546E+02
     LIQUID
     BCT_A5
  ** FCC_A1

 Phase region boundary   3 at:   7.368E-01  4.546E+02
  ** BCT_A5
     FCC_A1
 Calculated    38 equilibria

 Phase region boundary   4 at:   9.632E-01  2.857E+02
  ** BCT_A5
     DIAMOND_A4
     FCC_A1

 Phase region boundary   5 at:   0.000E+00  2.857E+02
  ** BCT_A5
     DIAMOND_A4
 Calculated     4 equilibria

 Phase region boundary   6 at:   9.632E-01  2.857E+02
  ** DIAMOND_A4
```

```
     FCC_A1
 Calculated    16 equilibria

 Phase region boundary   7 at:   2.627E-01  4.546E+02
     LIQUID
  ** BCT_A5
 Calculated    27 equilibria

 Phase region boundary   8 at:   4.410E-01  5.000E+02
     LIQUID
  ** FCC_A1
 Calculated    52 equilibria
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) You get the ordinary kind of phase diagram automatically.

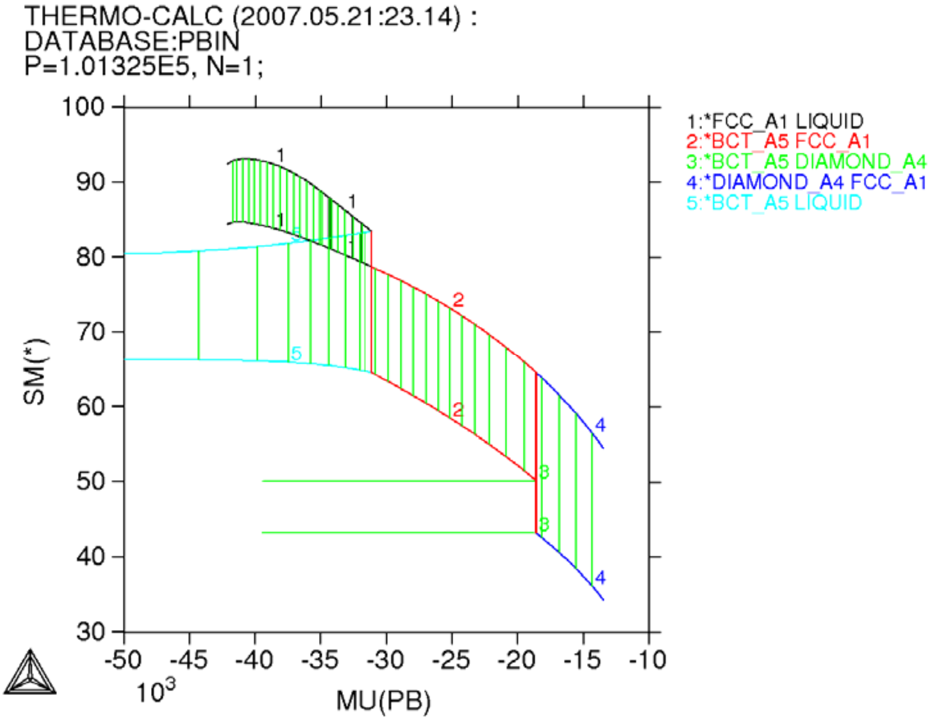
```
POST: s-t-s 3
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



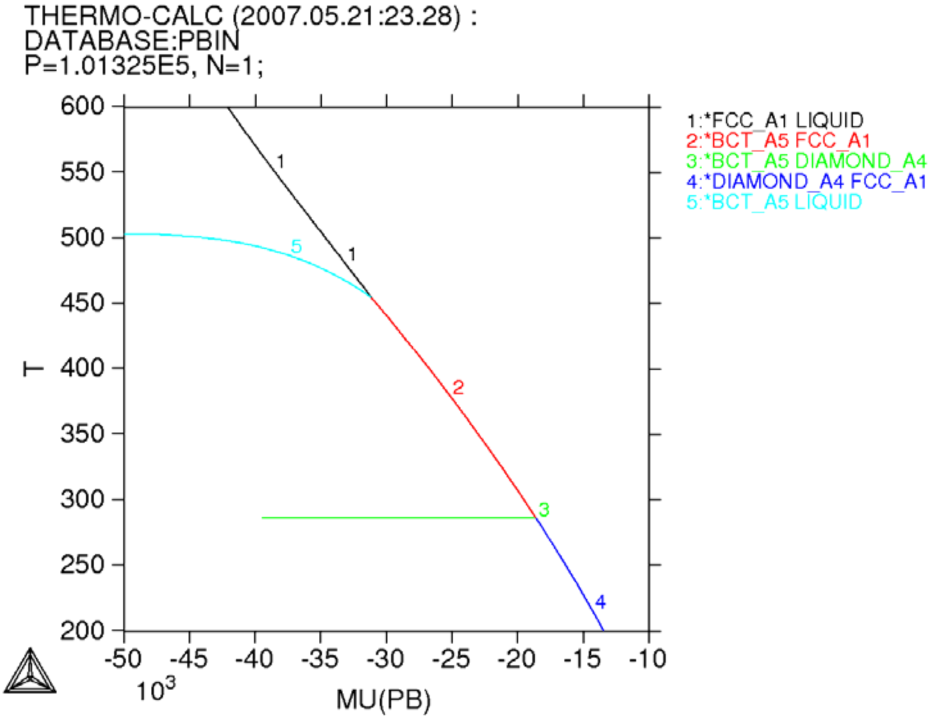
```
POST:
```

*) You get the ordinary kind of phase diagram automatically

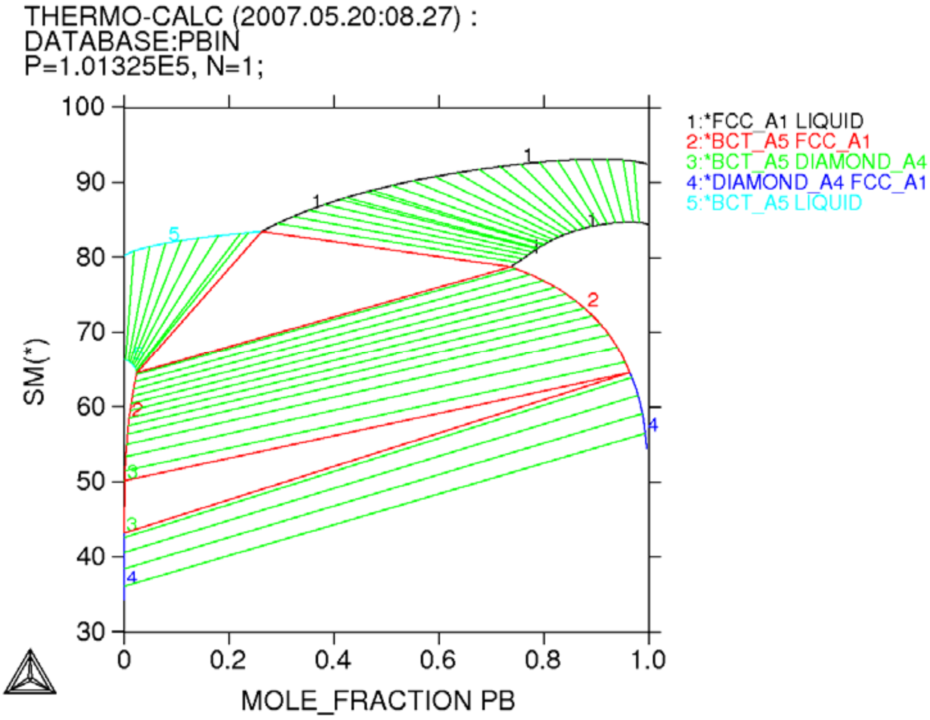
```
POST: s-d-a x mu(Pb)
POST: s-d-a y sm(*)
COLUMN NUMBER /*/:
POST: s-s-s x n -5E4 -1E4
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: s-d-a y T
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



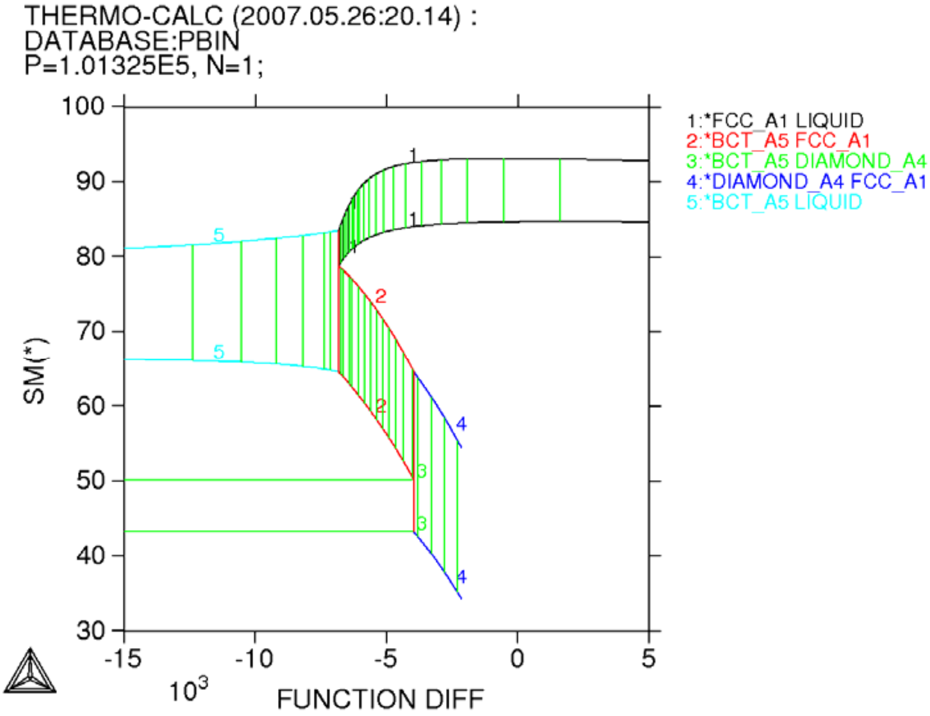
```
POST: s-d-a x m-f Pb
POST: s-d-a y Sm(*)
COLUMN NUMBER /*/:
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Now you may try the difference in chemical potentials, which was defined just before the mapping. It could just as well have been defined here.

```
POST: s-d-a x diff
POST: s-d-a y sm(*)
COLUMN NUMBER /*/:
POST: s-s-s x n -1.5E4 .5E4
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3: exit
 CPU time            1  seconds
```

Comments

The second and fifth diagrams are similar but with one important difference. In the second diagram there are two overlapping phase fields. That diagram is not a true phase diagram. The reason is that the pair of axis variables does not belong to the same set of conjugate variables in Table 9.1 or 9.3.

10.7B. Selection of axes in mixed diagrams

Compute the isothermal section of the Fe-Cr-C system at 1200^{o}C and 1 atm. Then, plot the result with the axes u_{Cr}, μ_C as in Fig. 10.19. The diagram probably shows swallow tails. Try to get rid of them by changing the axes. It may be worth trying x_{Cr}, μ_C ; u_{Cr},($\mu_C - \mu_{Fe}$); u_{Cr},($\mu_C - \mu_{Cr}$); u_{Cr},ln(a_C/a_{Fe}) and x_{Cr},a_C.

Hint

Consult Tables 9.1 and 3 regarding the ways of combining variables for the axes in a true phase diagram.

Instructions for using T-C

When using the u variable for plotting, you have to declare what elements should go into the denominator. If you for a ternary system give only one element, then the resulting variable would be what is denoted by z in Chapter 4 and you should consult Table 9.2 rather than 9.3. It is not proposed that you do that exercise but you could.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr C
 FE                      CR                      C
   DEFINED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          100
 FUNCTIONS ....

 List of references for assessed data
```

```
  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Start with an initial equilibrium before mapping. Use the variables as conditions that you like to use for mapping.

```
POLY_3: s-c P=101325 T=1473 x(Cr)=.01 x(C)=.01 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated        87414  grid points in            1  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     1  s
POLY_3: s-a-v 1 x(Cr)
Min value /0/:
Max value /1/:
Increment /.025/:
POLY_3: s-a-v 2 x(C)
Min value /0/:
Max value /1/:
Increment /.025/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   1.398E-01  1.000E-02
  ** BCC_A2
     FCC_A1
 Calculated     9 equilibria

 Phase region boundary   2 at:   1.398E-01  1.000E-02
  ** BCC_A2
     FCC_A1
 Calculated    12 equilibria

 Phase region boundary   3 at:   2.284E-01  6.870E-03
     BCC_A2
  ** FCC_A1
```

```
    M23C6

Phase region boundary   4 at:   4.977E-01  2.069E-01
 ** FCC_A1
    M23C6
Calculated     3 equilibria

Phase region boundary   5 at:   4.943E-01  2.069E-01
 ** FCC_A1
    M23C6
    M7C3

Phase region boundary   6 at:   5.503E-01  3.000E-01
 ** FCC_A1
    M7C3
Calculated    22 equilibria

Phase region boundary   7 at:   2.684E-01  3.000E-01
    LIQUID
 ** FCC_A1
    M7C3

Phase region boundary   8 at:   5.373E-02  8.181E-02
 ** LIQUID
    FCC_A1
Calculated    11 equilibria

Phase region boundary   9 at:   2.684E-01  3.000E-01
 ** LIQUID
    M7C3
Calculated     6 equilibria

Phase region boundary  10 at:   2.022E-01  3.000E-01
 ** LIQUID
    CEMENTITE
    M7C3

Phase region boundary  11 at:   1.025E-01  2.500E-01
 ** LIQUID
    CEMENTITE
Calculated     4 equilibria

Phase region boundary  12 at:   7.358E-02  2.500E-01
 ** LIQUID
    CEMENTITE
    GRAPHITE

Phase region boundary  13 at:   0.000E+00  1.000E+00
 ** LIQUID
    GRAPHITE
Convergence problems, increasing smallest sitefraction from 1.00E-30
to hardware precision 2.00E-12.  You can restore using SET-NUMERICAL-LIMITS
Calculated     7 equilibria

Phase region boundary  14 at:   7.358E-02  2.500E-01
    CEMENTITE
 ** GRAPHITE
Calculated     4 equilibria

Phase region boundary  15 at:   9.213E-02  2.500E-01
    CEMENTITE
```

```
  ** GRAPHITE
     M7C3

 Phase region boundary  16 at:   1.863E-01  3.000E-01
  ** GRAPHITE
     M7C3
 Calculated    23 equilibria

 Phase region boundary  17 at:   5.456E-01  3.000E-01
  ** GRAPHITE
     M3C2
     M7C3

 Phase region boundary  18 at:   6.000E-01  4.000E-01
  ** GRAPHITE
     M3C2
 *** Sorry cannot continue ***   17


 Phase region boundary  19 at:   5.456E-01  3.000E-01
  ** M3C2
     M7C3
 *** Sorry cannot continue ***    4

 Calculated    15 equilibria

 Phase region boundary  20 at:   9.213E-02  2.500E-01
     CEMENTITE
  ** M7C3
 Terminating at known equilibrium
 Calculated     5 equilibria

 Phase region boundary  21 at:   2.022E-01  3.000E-01
  ** CEMENTITE
     M7C3
 Terminating at known equilibrium
 Calculated     3 equilibria

 Phase region boundary  22 at:   4.943E-01  2.069E-01
     M23C6
  ** M7C3
 *** Sorry cannot continue ***    4

 Calculated    23 equilibria

 Phase region boundary  23 at:   2.284E-01  6.870E-03
     BCC_A2
  ** M23C6
 *** Sorry cannot continue ***    4

 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

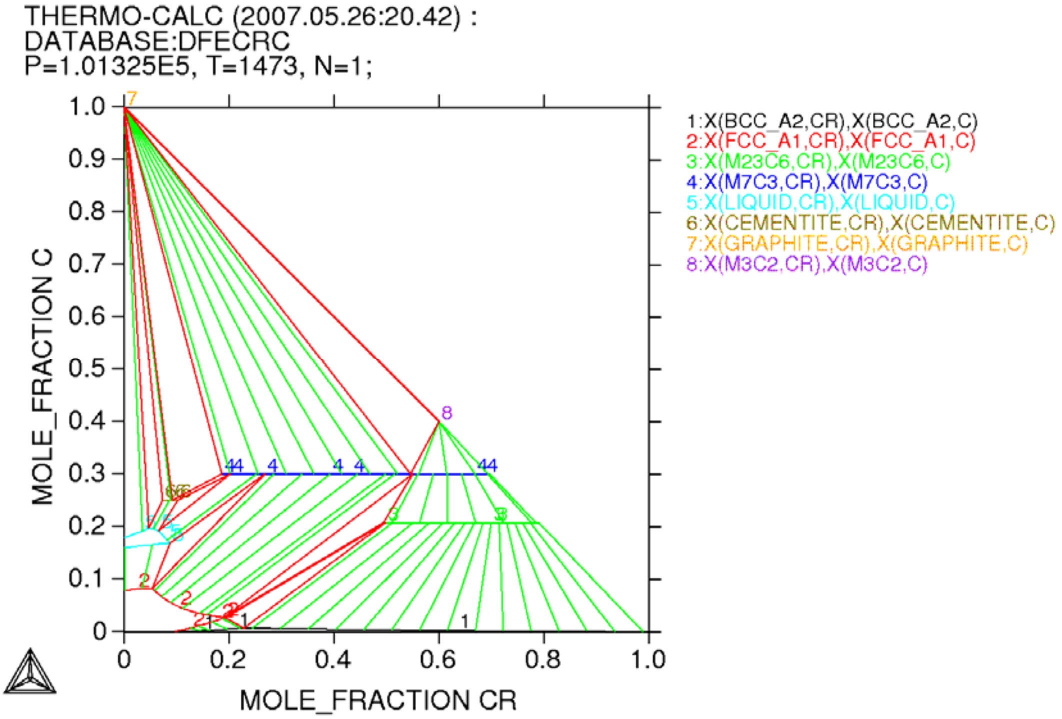
*) Ask for tie-lines to be plotted. It may be enough to show every third tie-line that is available. Each tie-line originates from a computation of an equilibrium.

```
POST: s-t-s 3
```

```
POST:
```

*) Start with an ordinary phase diagram with compositional axes. You get it automatically. Lable the curves using option **f**.

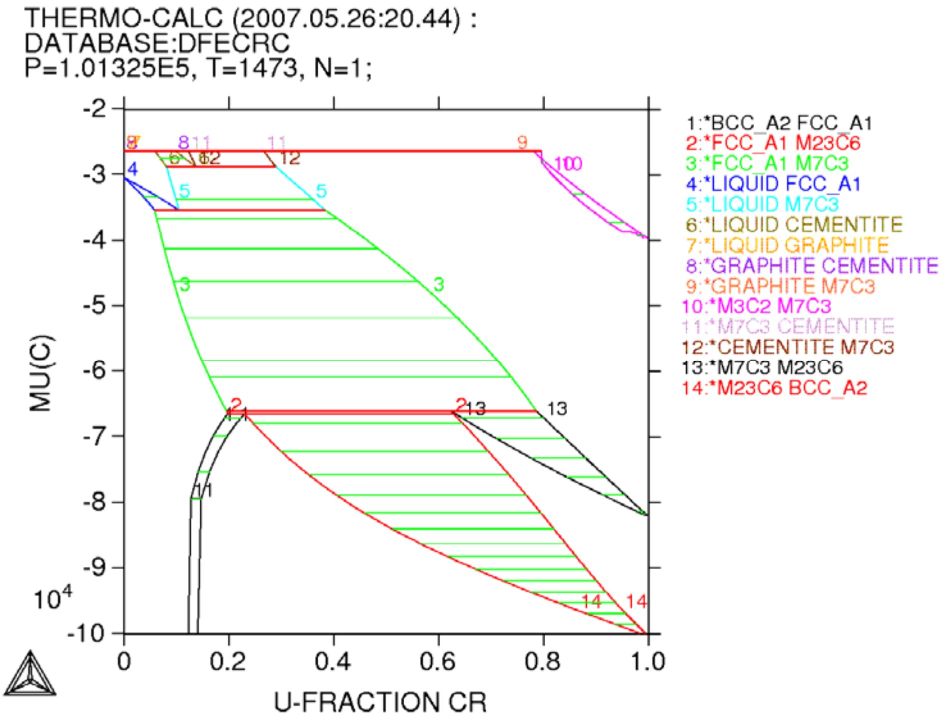
```
POST: set-lab f
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) This is really a triangular diagram. You can get a square diagram by using the u fraction on the x axis. Then you can plot a chemical potential on the y axis.

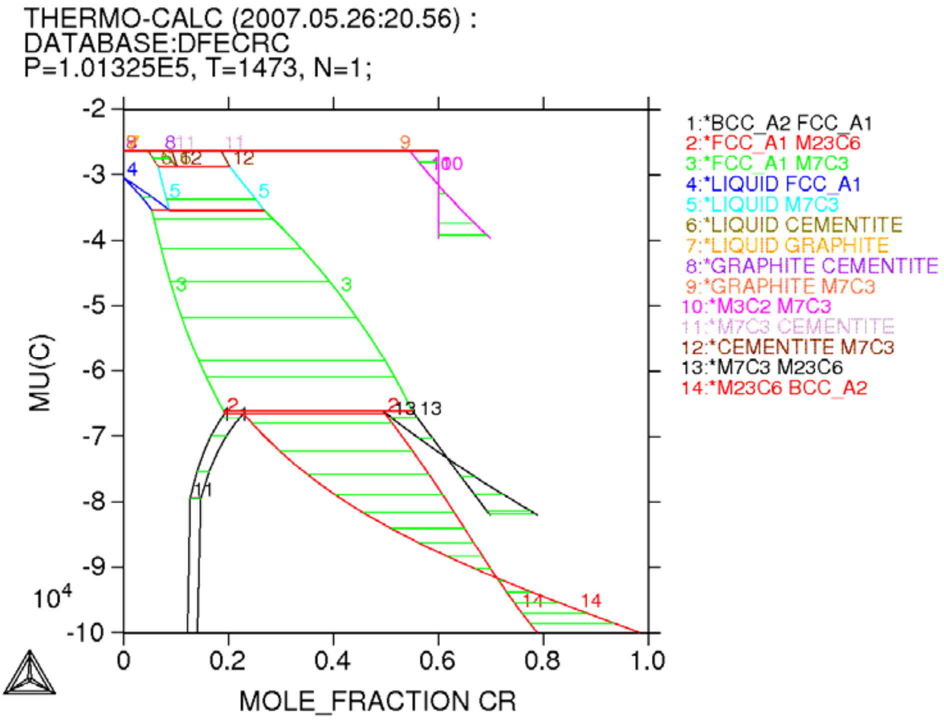
```
POST: s-d-a x u-fr Cr
COMPONENTS IN DENOMINATOR : /C CR FE/:  Cr Fe
POST: s-d-a y mu(C)
POST: s-s-s y n -10E4 -2E4
POST: set-lab e
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) It may be interesting to try to use the ordinary mole fraction in combination with the potential.

```
POST: s-d-a x m-f Cr
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```

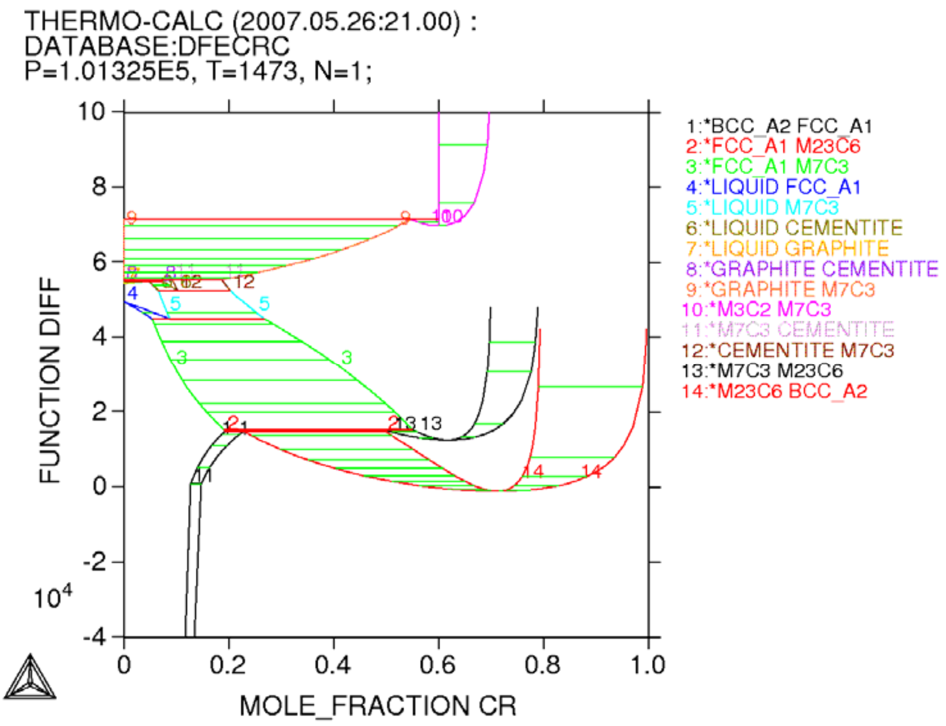


```
POST:
```

*) This did not work well. In order to get a true phase diagram with a potential axis, the ordinary mole fraction must be combined with a difference in potentials.

```
POST: ent-sym fun diff=mu(C)-mu(Fe);
```

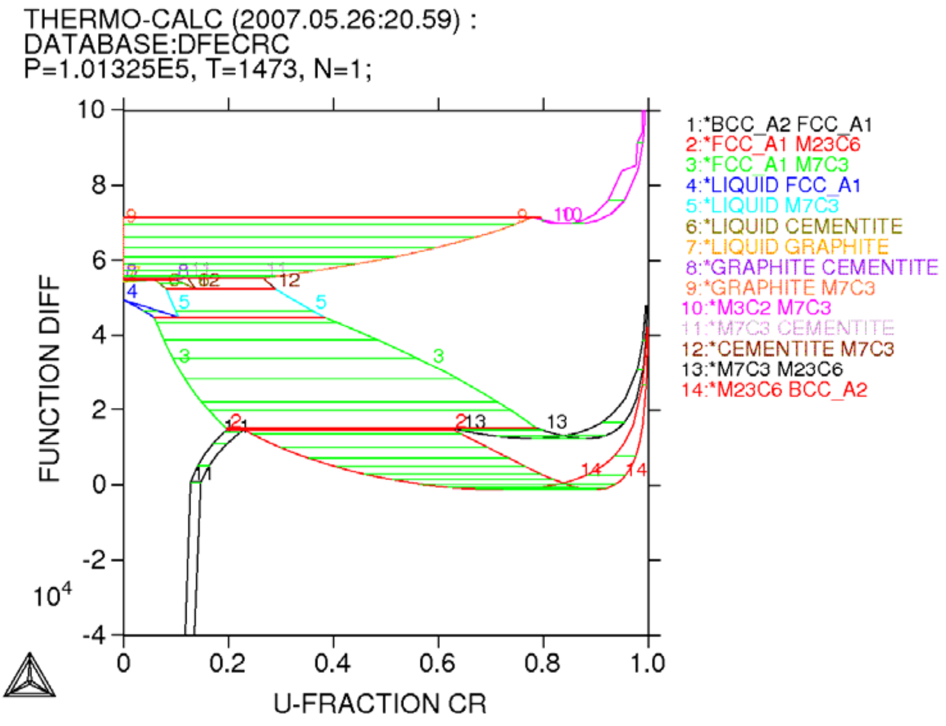
```
POST: s-d-a y diff
POST: s-s-s y n -4E4 10E4
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) On the other hand, the u fraction should not be combined with this difference in potentials.

```
POST: s-d-a x u-fr Cr
COMPONENTS IN DENOMINATOR : /CR FE/:  CR FE
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: b
POLY_3: exit
CPU time      5 seconds
```

Comments

1) The first diagram is really triangular because x(Cr)+x(C)=1-x(Fe) and can never be more than 1.

2) The first diagram shows that graphite takes part in several phase equilibria. Since graphite is pure C, it has a constant chemical potential, and activity, and all those phase equilibria fall on a horizontal line when plotted with a potential axis.

3) All the two-phase fields should have end points on the two sides of a phase diagram with a u-fraction axis because the number of components is there reduced from three to two. See the second diagram. Either x(Fe) or x(Cr) turns zero on the sides.

4) This is not so on the right-hand side of the third mu(C);x(Cr) diagram because x(Fe) turns negative sooner. Compare with the triangular shape of the first diagram. This is not a true phase diagram because those axis variables don't belong to the same set of conjugate pairs.

5) The two variables in the fourth mu(C)-mu(Fe);x(Cr) diagram belong to the same set of conjugate pairs in Table 9.1 and should result in a true phase diagram but it resembles the next diagram which is not. However, careful examination reveals that here the phase boundaries actually touch each other at the points of minimum and they don't intersect. An example of the same feature will be given in the last diagram of Problem 10.8.

6) The two-phase fields do have end points on the right-hand side in the last diagram, mu(C)-mu(Fe);u(Cr), although those variables don't belong to the same set. That diagram is not a true phase diagram and it has an incorrect feature. The two-phase fields ending on the right-hand side seem to have a congruent point of transition, which was the case in the previous diagram. Close inspection will show that the points of minimum of the two phase boundaries don't coincide in this diagram. The boundaries intersect a small distance above their points of minimum in agreement with the intersections in the third diagram.

7) You may now ask whether there is a congruent transition or not. There seems to be no indications in the second, third and fifth diagrams. However, the first diagram gives the explanation. The two-phase field 1/3, which is bcc/$M_{23}C_6$, has a vertical tie-line at about 71 mol% Cr. If the C content can be increased under constant Cr content, then there can indeed be a sharp transformation bcc$\rightarrow M_{23}C_6$. That would require that the Fe content has a corresponding decrease. The congruent transition displayed by the fourth diagram indicates that the balanced increase of C and decrease of Fe would be obtained if it were possible experimentally to increase mu(C)-mu(Fe) gradually in an alloy with 71 mol% Cr. Experimentally, it would be much easier to increase mu(C) at a constant u-fraction of Cr, relative to Fe, because C diffuses much more rapidly than Cr and Fe but the second diagram shows that this would not result in a congruent transition for any Cr content.

10.8. Konovalov's rule

In the T-x diagram for the Fe-Cr system there is a bcc+fcc two-phase field showing a congruent transformation. Use an isothermal section to examine how the phase field extends into the ternary diagram when C is added. First, choose axes for the mole fractions of Cr and C. Show what kind of diagram you should then use in order to obtain a congruent transformation point. With what experimental technique could one observe it?

There is another pair of axes that would give a similar diagram. Compare the Cr content of the congruent point in the two diagrams. Explain the difference by studying a diagram with two potential axes.

Hint

You may get some inspiration from Problem 10.7B. There you obtained two true phase diagrams with one potential axis. Only one of them seemed to indicate a congruent transformation.

Instructions for using T-C

1) It may be convenient to use activities for representing chemical potentials. Start the session with three components by setting new references for all three components.

2) Start with the Fe-Cr system and then go back to the database module and add C.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC:
```

*) Start by defining only Fe and Cr.

```
TDB_DFECRC: def-el Fe Cr
 FE                       CR  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                  BCC_A2
 HCP_A3                   SIGMA  REJECTED
TDB_DFECRC: rest p fcc bcc
 FCC_A1                   BCC_A2  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           34
 FUNCTIONS ....

 List of references for assessed data
```

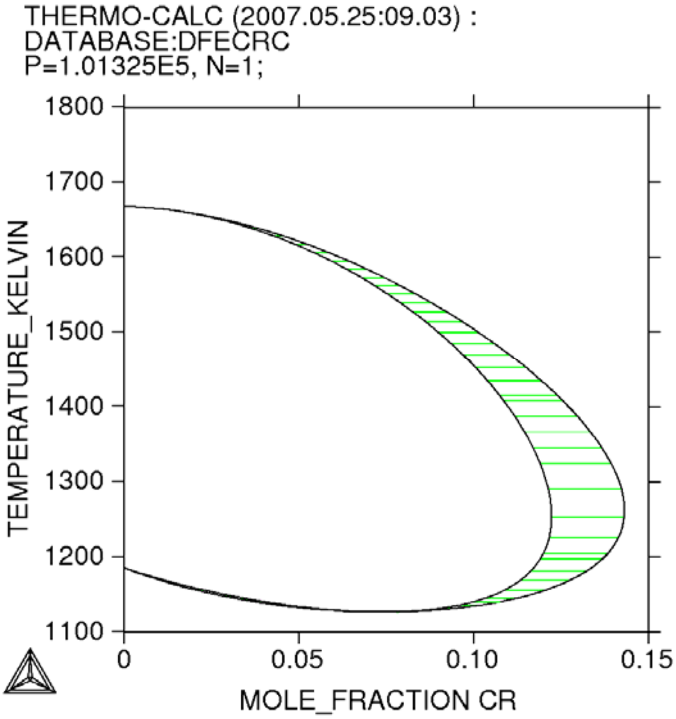
```
  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) Start with an initial equilibrium at some low Cr content because you know that the bcc/fcc equilibrium exists in pure Fe at about 1200 as well as 1700 K.

```
POLY_3: s-c P=101325 T=1200 x(Cr)=.1 N=1
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     0  s
POLY_3: s-a-v 1 x(Cr) 0 .15
Increment /.00375/:
POLY_3: s-a-v 2 T 1100 1800
Increment /17.5/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   1.000E-01  1.140E+03
  ** BCC_A2
     FCC_A1
 Calculated    53 equilibria

 Phase region boundary   2 at:   1.000E-01  1.140E+03
  ** BCC_A2
     FCC_A1
 Calculated   100 equilibra, continuing
 Calculated   115 equilibria
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) Automatic setting of axes will probably give what you want.

```
POST: s-t-s 3
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Yes you got the so-called gamma loop. Gamma is the common name of fcc and that is the phase inscribed by the two-phase field. It has a congruent transformation on its lower side. Now you go back to the database and add C.

```
POST: b
POLY_3: go da
TDB_DFECRC: def-el C
 C  DEFINED
TDB_DFECRC: rej p *
 FCC_A1                   BCC_A2                   CEMENTITE
 M3C2                     M7C3                     M23C6
 GRAPHITE  REJECTED
POLY_3:
```

*) Restore also graphite in case you like to use it as reference for the C activity.

```
TDB_DFECRC: rest p fcc bcc gra
 FCC_A1                   BCC_A2                   GRAPHITE
   RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions          49
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'
```

```
  'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
  'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
      C-CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

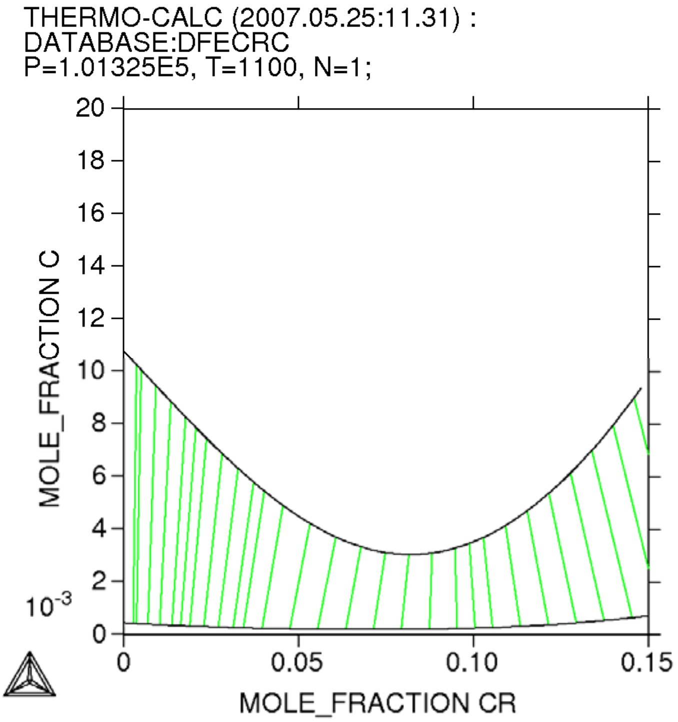
*) POLY has no memory of the first session because now you have entered POLY with a new system. You should thus repeat all the conditions necessary. Add a small amount of C. You are now going to examine how the gamma loop extends into the ternary system. You may know that C stabilizes the fcc phase and may thus expect to find the gamma loop at a temperature below the congruent point in the Fe-Cr system. Try 1100 K.

```
POLY_3: s-c P=101325 T=1100 x(Cr)=.1 N=1 x(C)=.001
POLY_3: set-ref Cr bcc
Temperature /*/:
Pressure /1E5/:
POLY_3: set-ref C gra
Temperature /*/:
Pressure /1E5/:
POLY_3: c-e
 Using global minimization procedure
 Calculated        39297  grid points in            1  s
 Found the set of lowest grid points in             0  s
 Calculated POLY solution       0 s, total time     1  s
POLY_3: s-a-v 1 x(Cr) 0 .15
Increment /.00375/:
POLY_3: s-a-v 2 x(C) 0 .02
Increment /5E-04/:
POLY_3: map
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Organizing start points

 No initial equilibrium added, trying to fix one
 Automatic saving workspaces on
 USERPROFILE\RESULT.POLY3

 Phase region boundary   1 at:   1.004E-01  2.294E-04
     BCC_A2
  ** FCC_A1
 Calculated    64 equilibria

 Phase region boundary   2 at:   1.004E-01  2.294E-04
     BCC_A2
  ** FCC_A1
 Mapping terminated 1
 *** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01
```

```
 Setting automatic diagram axis

POST:
```

*) Try automatic setting of axes again.

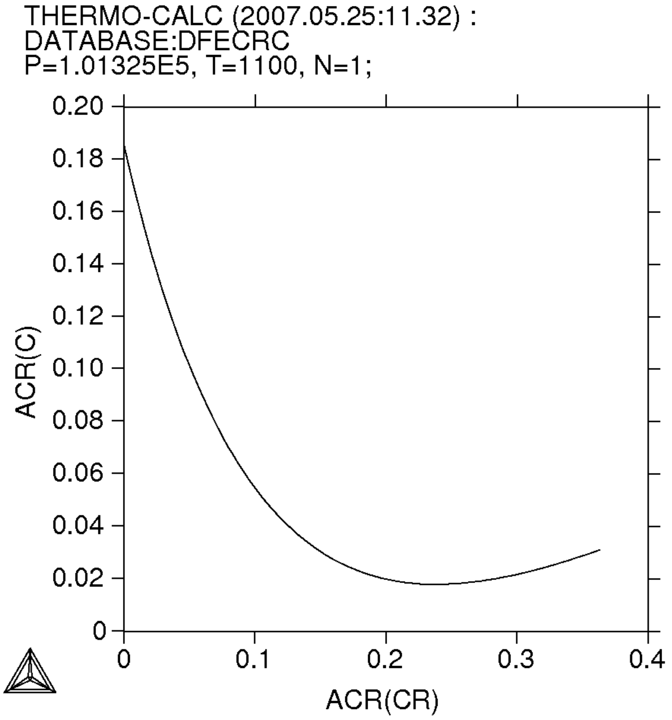
```
POST: s-t-s 3
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) Indeed you found the gamma loop at 1100 K where it does not reach the binary Fe-Cr side. Fcc is the big phase field in the diagram and bcc is the thin one at the bottom. It does not show a congruent transformation. In order to check if there is one you must have a potential axis. Change to activity axes.

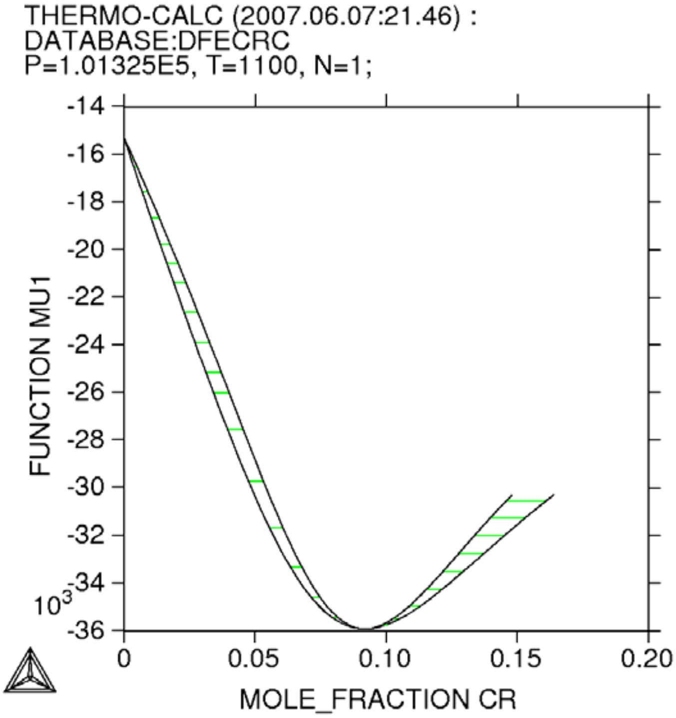
```
POST: s-d-a x acr(Cr)
POST: s-d-a y acr(C)
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) You got a diagram resembling Fig. 10.25(a). You could see a congruent transformation by taking back the molar property on the x axis. However, in order to get a true phase diagram you should make sure that the two axes make a true phase diagram together according to Tables 9.1 to 3. You cannot combine x(Cr) with acr(C) or mur(C). You should combine it with mur(C)-mur(Fe) or acr(C)/acr(Fe).

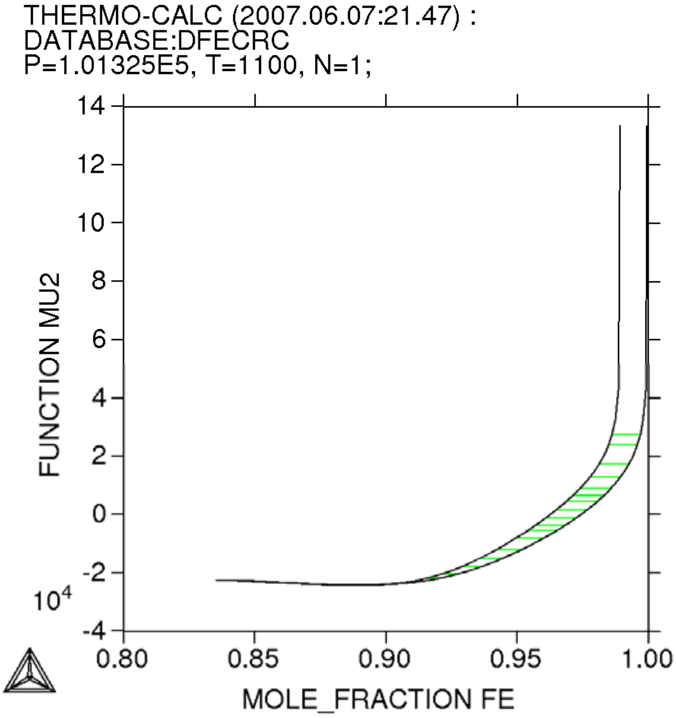
```
POST: s-d-a x m-f Cr
POST: ent-sym fun mu1=mur(C)-mur(Fe);
POST: s-d-a y mu1
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) There seems to be a congruent transformation point. However, there are other ways to combine axes. If you plot x(Fe) on the x axis it is necessary to combine it with mu(C)-mu(Cr).

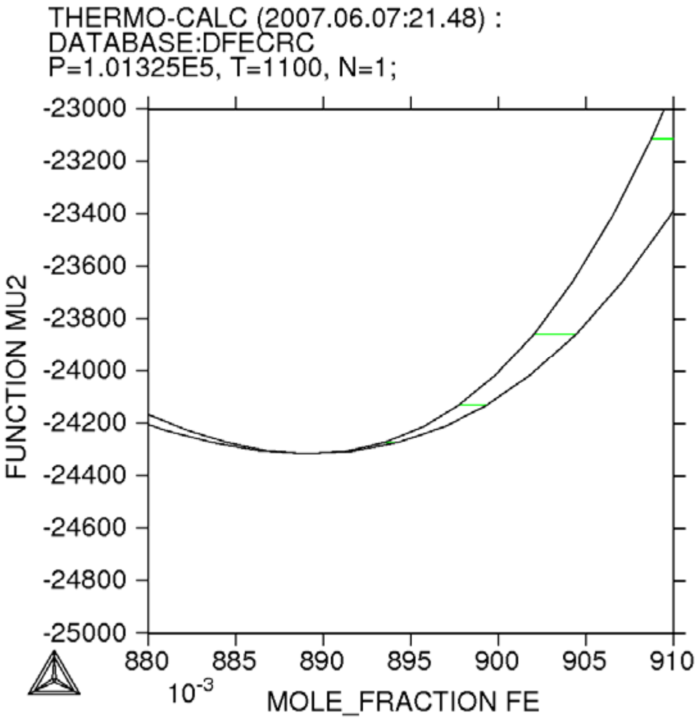
```
POST: s-d-a x m-f Fe
POST: ent-sym fun mu2=mur(C)-mur(Cr);
POST: s-d-a y mu2
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) In order to examine this case it is necessary to magnify the region around the possible congruent point.

```
POST: s-s-s x N .88 .91
POST: s-s-s y N -2.5E4 -2.3E4
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time             1  seconds
```

Comments

From the last diagram you can see that there seems to be a congruent point at about x(Fe)=0.8895. It is an interesting question whether the previous diagram would give the same congruent point if magnified enough. The answer is found by examining the second diagram, the first one for the ternary system, and applying a physical interpretation. The idea of a congruent transformation is that the transformation would be sharp although Gibbs' phase rule indicates that there should be a degree of freedom. Then one should consider what kind of change the system is exposed to. Usually one discusses a change of temperature or pressure which is well defined. In the present case there is a change in composition and there are several alternatives. From a practical point of view the important feature is that C is much more mobile that Cr or Fe. A congruent transformation under the addition of C could be described with a compositional axis showing the u fraction of Cr or Fe and the potential axis should then be μ_C according to Table 9.3 in the textbook if C is identified as component 3. One could then choose u_{Cr} or u_{Fe} from the third column and μ_C from the forth column as variables. One could also use the second diagram and examine which tie-line is directed exactly towards the C corner.

Selleby and Hillert
September 2007

Additional problems to the book Phase Equilibria, Phase Diagrams and Phase Transformation, to be solved with Thermo-Calc

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Chapter 11. Directions of phase boundaries

Problem 11.5. Congruent melting points
Problem 11.6. Vertical phase boundaries

11.5. Congruent melting points

Determine the curvatures of the two phase boundaries at the congruent transformation point for bcc/sigma in the Fe-Cr system.

Hint

You may evaluate the curvature of a curve from three points. The transformation point is one and you may compute one point on each side by requiring that T should be 0.1 K lower, for instance.

Instructions for using T-C

With POLY you can evaluate the slope at any point of a phase boundary directly. You don’t need to use the equation derived in Section 11.4. It would thus be possible to evaluate the curvature from the slopes in two points. On the other hand, it often happens that a phase changes its properties rather suddenly at a composition close to the transformation point. It may thus be interesting to study the slopes in the two points mentioned in the Hint and check if it would be necessary to make two evaluations of the curvature by using two points on each side of the congruent point.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe Cr
 FE                       CR  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                 FCC_A1                   BCC_A2
 HCP_A3                   SIGMA  REJECTED
TDB_DFECRC: rest p bcc sigma
 BCC_A2                   SIGMA  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
```

```
 PARAMETERS ...
 Rewind to read functions           25
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
      (1986); CR-FE'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) The two phases must have the same composition when they are in equilibrium at the transformation point.

```
POLY_3: s-c P=101325 w(bcc,Cr)-w(sigma,Cr)=0
POLY_3: ch-st p sigma bcc=fix 1
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in            0  s
   8 ITS,  CPU TIME USED   0 SECONDS
POLY_3: sh T
 T=1105.2128
POLY_3:
```

*) You have found the transformation temperature and may call it the congruent temperature.

```
POLY_3: ent-sym var Tcon=T;
POLY_3:
```

*) You have already shown the congruent temperature and could easily enter a slightly lower temperature as a condition for the two new points. In order to avoid the risk of making a typing error you could instead enter a symbol for it.

```
POLY_3: ent-sym var Tnew=Tcon-0.1;
POLY_3: s-c T=Tnew
POLY_3:
```

*) You must remove another condition and that should be the one that is no longer valid.

```
POLY_3: s-c w(bcc,Cr)-w(sigm,Cr)=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in            0  s
  26 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Store and show the compositions and **slo**pes of the phases at this temperature.

```
POLY_3: ent-sym var xb1=x(bcc,Cr);
POLY_3: ent-sym var xs1=x(sigm,Cr);
POLY_3: ent-sym var slob1=x(bcc,Cr).T;
POLY_3: ent-sym var slos1=x(sigm,Cr).T;
POLY_3: eval
POLY_3:
 XB1=0.44974952
 XS1=0.45332381
 SLOB1=2.3473964E-2
 SLOS1=5.6520113E-3
```

```
POLY_3:
```

*) The slopes are positive and this equilibrium is thus situated to the left of the congruent point. The other point for each curve is situated to the right and can be found by giving a start value on that side.

```
POLY_3: s-s-v y(bcc,Cr)=.6
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Using already calculated grid
  10 ITS,  CPU TIME USED   0 SECONDS
POLY_3: ent-sym var xb2=x(bcc,Cr);
POLY_3: ent-sym var xs2=x(sigm,Cr);
POLY_3: ent-sym var slob2=x(bcc,Cr).T;
POLY_3: ent-sym var slos2=x(sigm,Cr).T;
POLY_3:
```

*) You can now evaluate the curvatures defined as $d^2T/dx^2 = d(dT/dx)/dx$

```
POLY_3: ent-sym var curvb=(1/slob2-1/slob1)/(xb2-xb1);
POLY_3: ent-sym var curvs=(1/slos2-1/slos1)/(xs2-xs1);
POLY_3: eval
Name(s):
 TCON=1105.2128
 TNEW=1105.1128
 XB1=0.44974952
 XS1=0.45332381
 SLOB1=2.3473964E-2
 SLOS1=5.6520113E-3
 XB2=0.45922615
 XS2=0.45562949
 SLOB2=-2.3917906E-2
 SLOS2=-5.8721891E-3
 CURVB=-8907.1779
 CURVS=-150594.82
POLY_3: exit
 CPU time            0  seconds
```

Comments

Slob1 and slob2 have almost the same magnitude and so have slos1 and slos2. The two-phase field is thus fairly symmetric around the congruent point and there is no sign of a drastic change of properties at the congruent composition. It was not necessary to evaluate different values for the curvatures on the two sides of the congruent point.

11.6. Vertical phase boundaries

The phase boundary bcc/fcc in the Fe-C system is retrograde, i.e., the solubility of C in bcc which starts from zero at the transition point of 911^{o}C reaches a maximum value at some lower temperature and then decreases and approaches zero at low temperatures. Evaluate the temperature of maximum solubility with high accuracy.

Hint

Rather than just comparing the solubility at various temperatures it may be more accurate to evaluate the slope of the phase boundary and evaluate where it goes through zero.

Instructions for using T-C

In T-C you can evaluate the slope directly using the “.” operator. You don’t need to use the equation in Section 11.4.

Prompts, commands and responses

```
SYS: go da
 THERMODYNAMIC DATABASE module running on PC/WINDOWS NT
 Current database: TCS Demo Al-Mg-Si Alloys TDB v1

 VA  DEFINED
TDB_DALMGSI: sw DFeCrC
 Current database: TCS Demo Fe-Cr-C Alloys TDB v1

 VA  DEFINED
TDB_DFECRC: def-el Fe C
 FE                      C  DEFINED
TDB_DFECRC: rej p *
 LIQUID:L                FCC_A1                  BCC_A2
 HCP_A3                  CEMENTITE               M7C3
 M23C6                   GRAPHITE  REJECTED
TDB_DFECRC: rest p bcc fcc
 BCC_A2                  FCC_A1  RESTORED
TDB_DFECRC: get
 REINITIATING GES5 .....
 ELEMENTS .....
 SPECIES ......
 PHASES .......
 PARAMETERS ...
 Rewind to read functions           37
 FUNCTIONS ....

 List of references for assessed data

  'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
      -425, also in NPL Report DMA(A)195 Rev. August 1990'
  'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
       C-FE'
  'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
      Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

 The list of references can be obtained in the Gibbs Energy System also
 by the command LIST_DATA and option R

 -OK-
TDB_DFECRC: go pol

 POLY version  3.32,  Aug 2001
POLY_3:
```

*) You must start with an initial equilibrium. Bcc transforms to fcc at 911^{o}C and you should thus choose a somewhat lower temperature. Even though you know what phases you like to take part in the equilibrium, it is often convenient to start prescribing the composition of the system.

```
POLY_3: s-c P=101325 T=850 N=1 w(C)=.01
POLY_3: c-e
 Using global minimization procedure
 Calculated          274  grid points in            0  s
 Found the set of lowest grid points in             0  s
```

```
 Calculated POLY solution       0 s, total time     0  s
POLY_3:
```

*) Since you like to step along the bcc boundary when in equilibrium with fcc, it is convenient to use **fix 1** for bcc and **fix 0** for fcc as conditions for the single equilibrium introducing the stepping procedure. Instead you should remove the conditions for N and w(C).

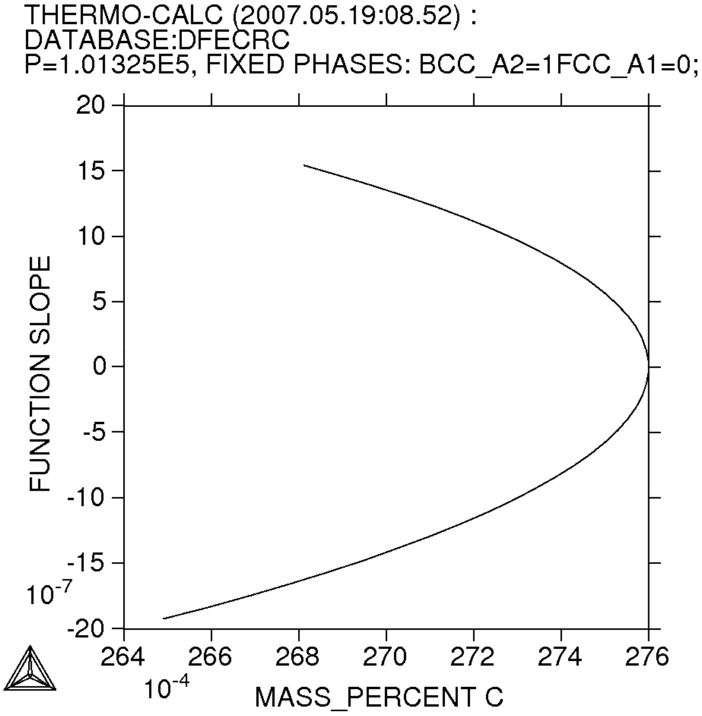
```
POLY_3: ch-st p bcc=fix 1
POLY_3: ch-st p fcc=fix 0
POLY_3: s-c N=none w(C)=none
POLY_3: c-e
 Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated          274  grid points in            0  s
   6 ITS,  CPU TIME USED   0 SECONDS
POLY_3:
```

*) Before starting to step, you could just as well enter a symbol for the slope, which you will need later on.

```
POLY_3: ent-sym fun slope=x(bcc,C).T;
POLY_3: s-a-v 1
Condition /NONE/:  T
Min value /0/:  800
Max value /1/:  900
Increment /2.5/:
POLY_3: step
Option? /NORMAL/:
 No initial equilibrium, trying to add one           0

 Phase Region from    850.000     for:
     BCC_A2
     FCC_A1
 Calculated    23 equilibria

 Phase Region from    850.000     for:
     BCC_A2
     FCC_A1
 Calculated    23 equilibria
 *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

  POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

 Setting automatic diagram axis

POST:
```

*) In practice, it is quite common to use mass% rather than mole fraction. Use that quantity for the x axis and the slope for the y axis.

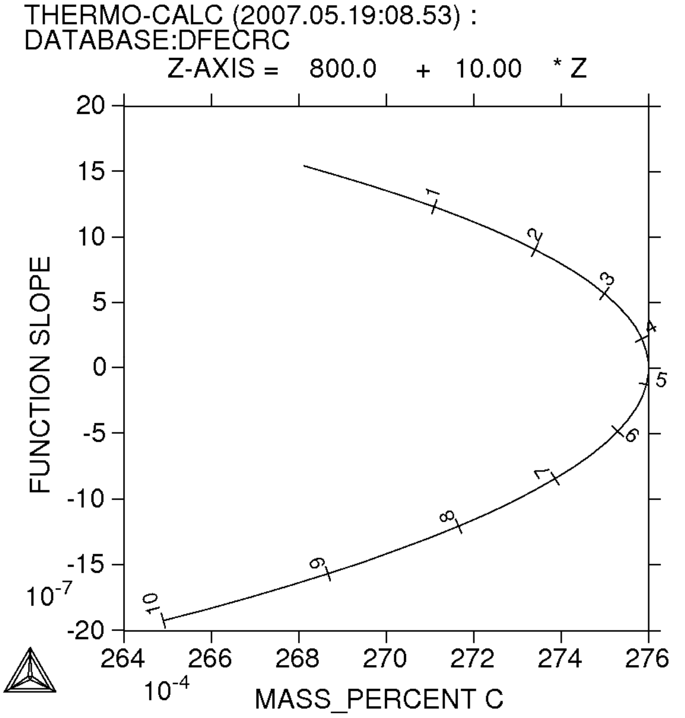
```
POST: s-d-a x w-p C
POST: s-d-a y slope
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) The maximum solubility is clearly shown. In order to get a rough idea of the temperature, you can introduce T as a third z axis and show its values as tic marks.

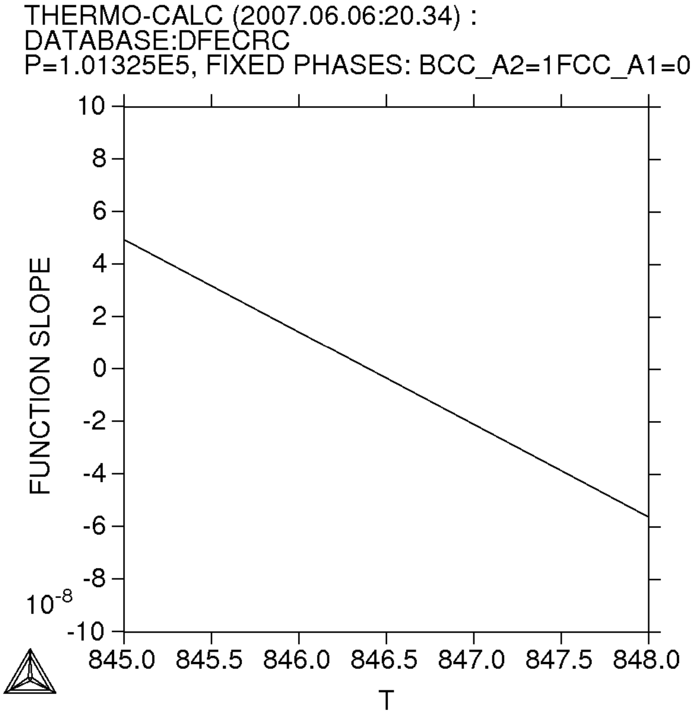
```
POST: s-d-a z T
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST:
```

*) From the tic marks you can see very well that the wanted temperature is between 845 and 848 K. In order to evaluate it with higher accuracy you could magnify the slope between these temperatures.

```
POST: s-d-a z none
POST: s-d-a x T
POST: s-s-s x 845 848
POST: s-s-s y n -1E-7 1E-7
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



```
POST: exit
 CPU time            0  seconds
```

Comments

It is easy to read the wanted temperature with good accuracy from the plot of the slope, T = 846.4 K.