

## Chapter 4. Practical handling of multicomponent systems

[Problem 4.1. Partial quantities](#)

[Problem 4.2. Relations for partial quantities](#)

[Problem 4.3. Alternative variables for composition](#)

[Problem 4.5. The tie-line rule](#)

[Problem 4.6. Different sets of components](#)

[Problem 4.7. Constitution and constituents](#)

[Problem 4.8. Chemical potentials in a phase with sublattices](#)

### 4.1. Partial quantities

Evaluate the diffusion potential in CuZn with 50 mass% Zn at 700°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  $N_{\text{Zn}}$  and removing the same amount of Cu,  $dN_{\text{Cu}} = -dN_{\text{Zn}}$ . The total number of moles,  $N$  is thus constant and the diffusion potential is obtained directly as  $(\partial G / \partial N_{\text{Zn}})_N$ . One could also use Eq. 6.43 in the textbook, giving the diffusion potential in our binary as  $dG_m/dx_{\text{Zn}}$  which is identical to  $(\partial G / \partial x_{\text{Zn}})_{N=1}$ .

#### 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  $x_{\text{Zn}}$  and use it as a condition instead of  $w_{\text{Zn}}$  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  $(\partial G / \partial x_{\text{Zn}})_{N=1}$ . Then you can evaluate the value of  $N_{\text{Zn}}$ , 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  $N_{\text{Cu}}$  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°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**

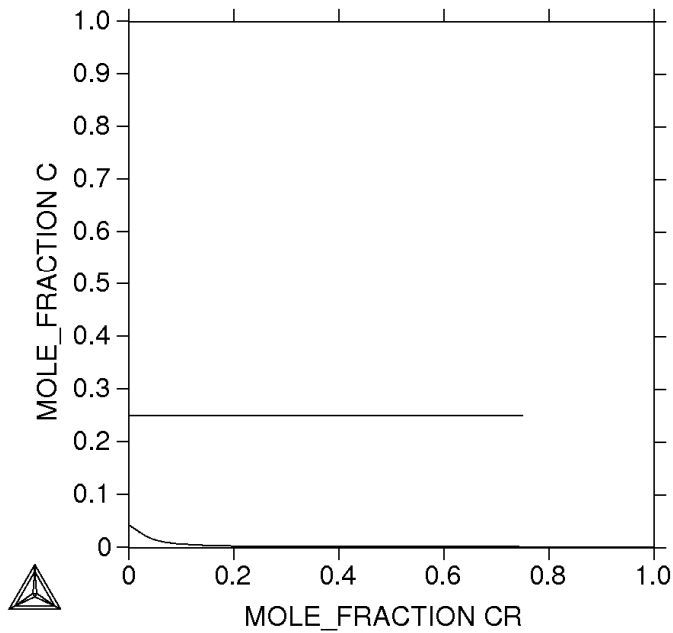
POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

Setting automatic diagram axis

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.05:20.00) :  
 DATABASE:DFECRC  
 P=1E5, T=1073, N=1;



POST:

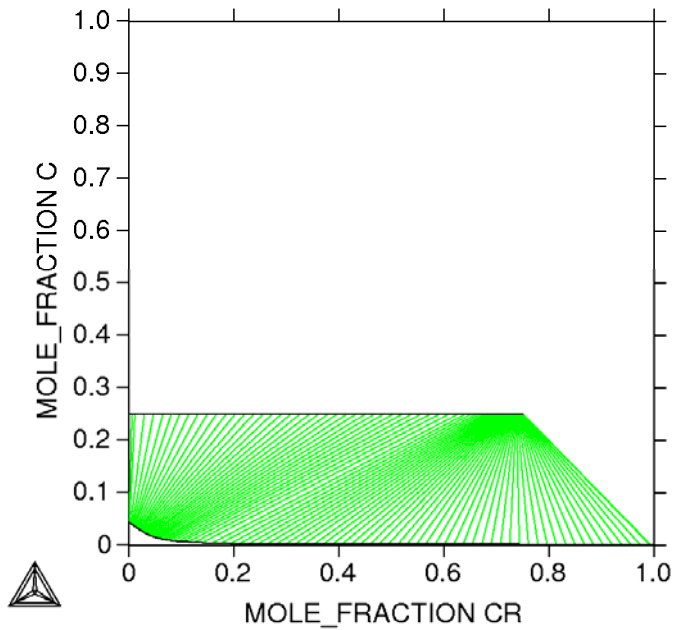
\*) You must order the tie-lines to be shown if you like them to be. You can decide what fraction of the computed ones you like to see plotted. Now choose all of them (fraction=1).

POST: **s-t-st 1**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.05:20.02) :  
 DATABASE:DFECRC  
 P=1E5, T=1073, N=1;



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**

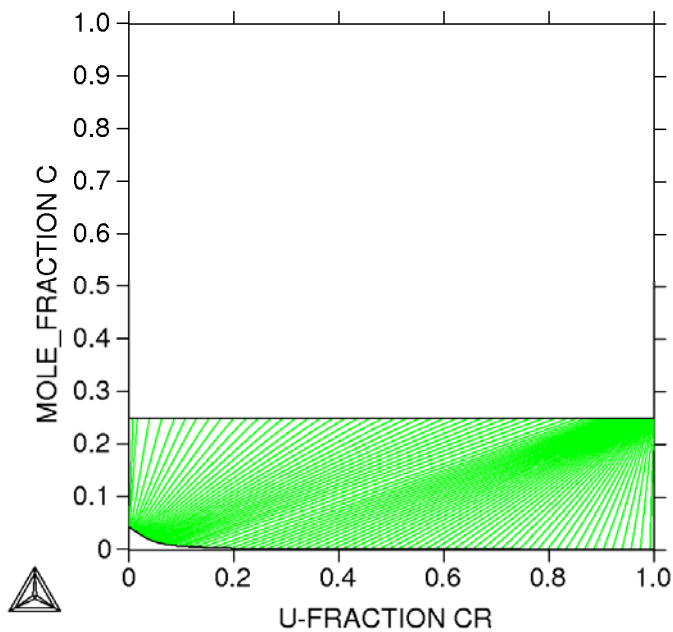
FOR COMPONENT : **Cr**

COMPONENTS IN DENOMINATOR : /C CR FE/: **Cr Fe**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

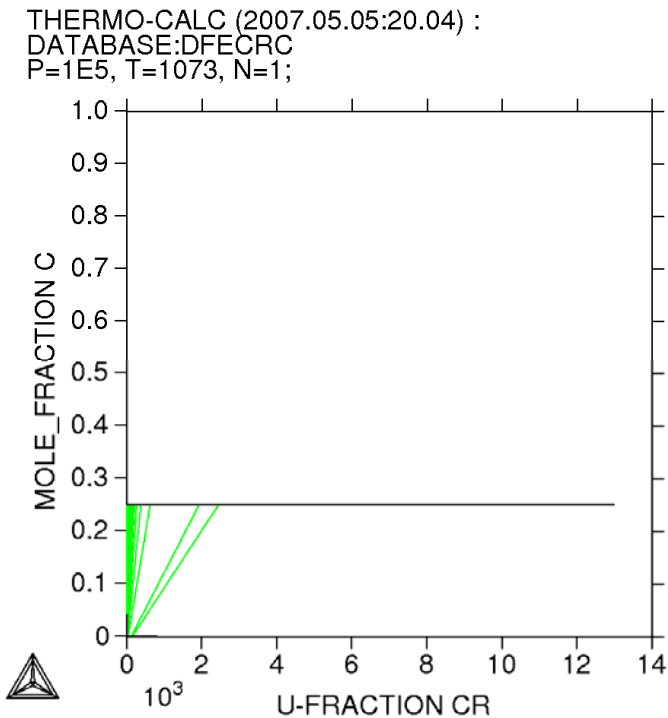
THERMO-CALC (2007.05.05:20.02) :  
 DATABASE:DFECRC  
 P=1E5, T=1073, N=1;



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 `set-scaling-status` 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

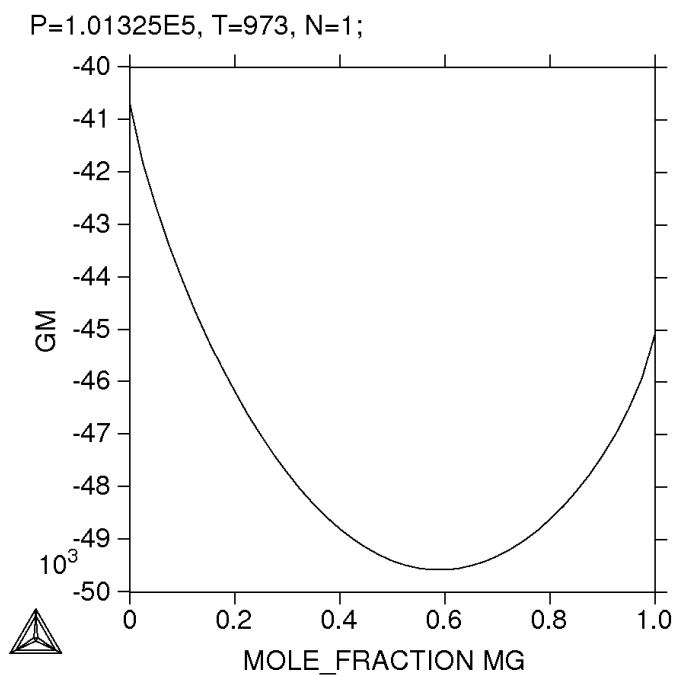
  Phase Region from 0.300000 for:
    LIQUID
  Calculated 31 equilibria

  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 references. 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:

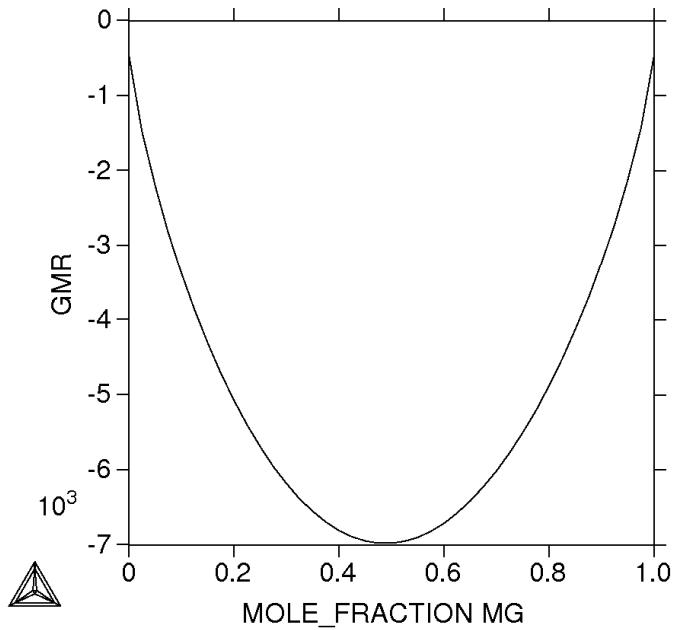
\*) The new references will be applied if you add the letter **r** to the symbol. You only need to redefine the axis you like to change.

POST: **s-d-a y Gmr**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.01:21.07) :  
 DATABASE:DALMGSI  
 P=1.01325E5, T=973, N=1;



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**

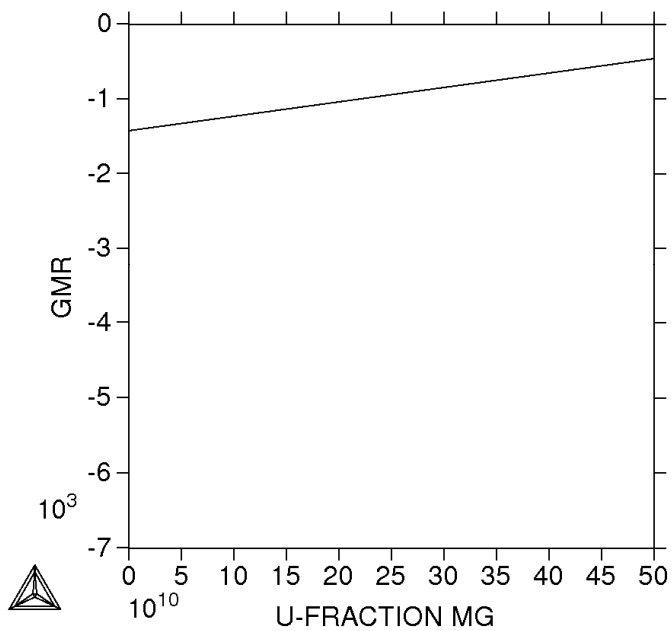
FOR COMPONENT : **Mg**

COMPONENTS IN DENOMINATOR : /AL MG/: **Al**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.01:21.09) :  
 DATABASE:DALMGSI  
 P=1.01325E5, T=973, N=1;



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 set the scaling status 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/:

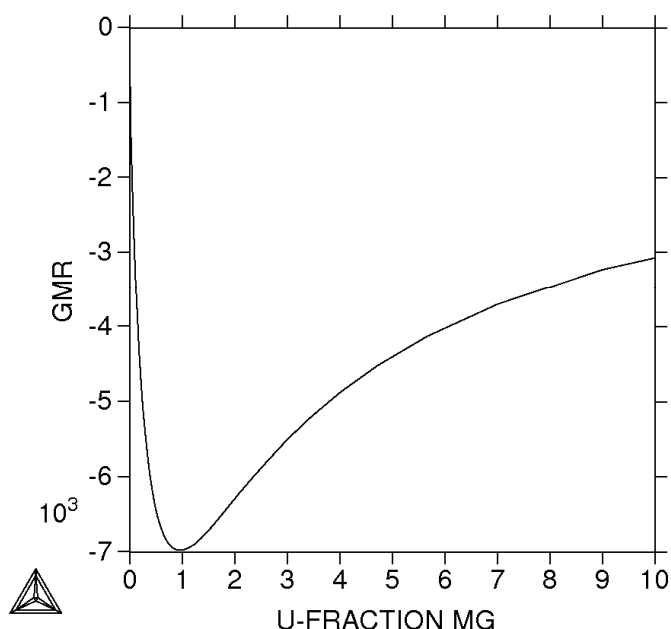
MIN VALUE : 0

MAX VALUE : 10

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.01:21.10) :  
 DATABASE:DALMGS1  
 P=1.01325E5, T=973, N=1;



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<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O 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 6.0000E-01 H 4.0000E-01

Constitution:

H2O1 7.5000E-01 H2 2.5000E-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:
```

\*)  $y(\text{gas}, \text{O}_2)$  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  $RT\ln(\text{fraction})$  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  $y(\text{fcc},\text{C}\#2)=0.0645$ . 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: 1-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°C and 1 atm. Then, apply this distribution to 500°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

```



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 sublattices. 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.