

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

---

## Chapter 3. Systems with variable composition

[Problem 3.1. Chemical potential](#)

[Problem 3.2. Molar and integral quantities](#)

[Problem 3.3. Characteristic state functions](#)

[Problem 3.4. Additivity of extensive quantities. Free energy and exergy.](#)

[Problem 3.6A. Calculation of equilibrium](#)

[Problem 3.6B. Calculation of equilibrium](#)

[Problem 3.7. Evaluation of the driving force](#)

[Problem 3.8. Driving force for molecular reactions](#)

### 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,  $\text{Fe}_3\text{C}$ , 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,  $x_{\text{C}}=0.25$ . 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  $\mu_c$  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 listing the system.

```
TDB_DFECRC: 1-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 **change** the **status** of these **phases** 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 **fixed**, 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 set the other conditions 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 list the equilibrium 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
```



\*) The last line says that now there is only 6% C in the interstitial sublattice 2. You may continue by **showing** 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 **changing** the **status** of the **phase cementite** to either dormant or **suspended**. Then try to **compute equilibrium**.

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

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

\*) You should **list** the **conditions** 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 **suspend** the **phase 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  $\sum \mu_i N_i$  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  $\sum \mu_i N_i$  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  $\sum \mu_i N_i$ .

```
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  $\Omega = U - TS - \sum \mu_i N_i = -PV$  and its natural state variables are  $T$ ,  $V$  and  $\mu_i$  because  $d\Omega = d(-PV) = -SdT - PdV - \sum N_i d\mu_i$  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,  $G = \sum \mu_i N_i$ , 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  $\mu_i$ , 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  $\mu_i$  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  $\mu_i$  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  $\mu_i$  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<sup>3</sup> of pure H<sub>2</sub> at 600°C and 1 atm being burned to H<sub>2</sub>O with air containing 20 mol% O<sub>2</sub> and 1.5 mol% H<sub>2</sub>O of 18°C and the resulting gas being cooled to 18°C. Evaluate the free energy that could theoretically be extracted from that system if the air can be regarded as an infinite reservoir of O<sub>2</sub> and recipient of H<sub>2</sub>O, i.e., the exergy. Assume that one can neglect the minute amount of H<sub>2</sub> 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<sub>2</sub> gas. Initially, there are thus two subsystems, the H<sub>2</sub> 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<sub>2</sub> gas must be evaluated from  $U(873\text{ K}, 101325\text{ Pa}) - 291 \cdot S(873\text{ K}, 101325\text{ Pa}) + 101325 \cdot V(873\text{ K}, 101325\text{ Pa})$ . The value of the oxygen is obtained directly from  $\mu_{\text{O}_2}$  of the atmosphere. The Gibbs energy of the final state is obtained from the H<sub>2</sub>O gas at  $\mu_{\text{H}_2\text{O}}$  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<sub>2</sub> and the receipt of H<sub>2</sub>O. The most critical information would be the local H<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub> and assume that the H<sub>2</sub>O 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.,  $P_i = P \cdot y(\text{gas}, i)$ . 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 H<sub>2</sub>O at the temperature and partial pressure of the surroundings with its 1.5% H<sub>2</sub>O.

POLY\_3: **ent-sym var** PiH<sub>2</sub>O=0.015\*101325;

POLY\_3: **s-c T=291 P=PiH<sub>2</sub>O 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=PIH<sub>2</sub>O, 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:

H<sub>2</sub>O1 1.00000E+00 H<sub>2</sub> 2.00000E-12 O<sub>2</sub> 2.00000E-12

POLY\_3:

\*) The very low amounts of H<sub>2</sub> and O<sub>2</sub> 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: 1-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 **change the status of all three phases 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 solidification 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°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  1873.000000000000
QSTEPP  773.000000000000
QSTEPP  1323.000000000000
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**

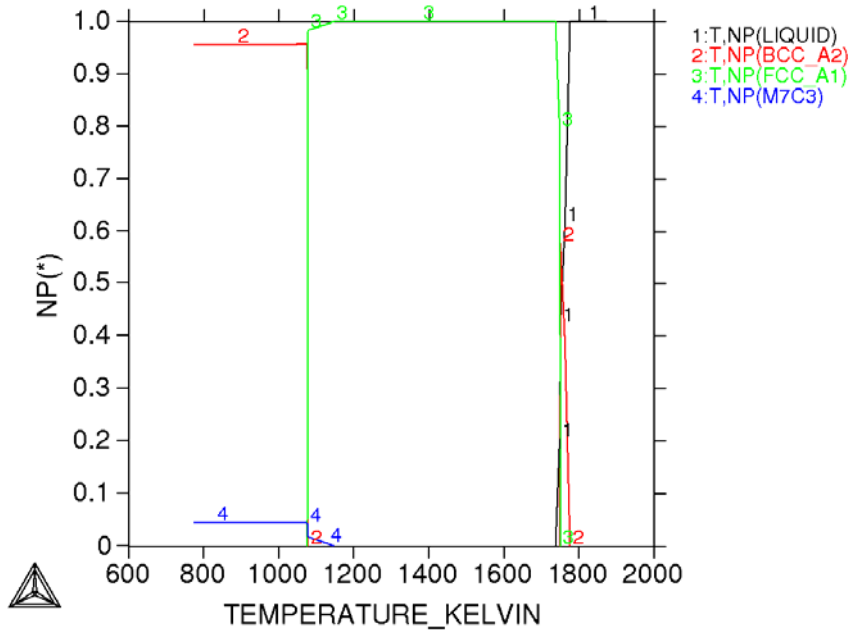
POST:

\*) **F** was the option mentioned in the instructions. That is all needed.

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.05:16.33) :  
 DATABASE:DFECRC  
 P=1.01325E5, N=1, W(CR)=5.31913E-2, W(C)=2.91252E-3;



POST:

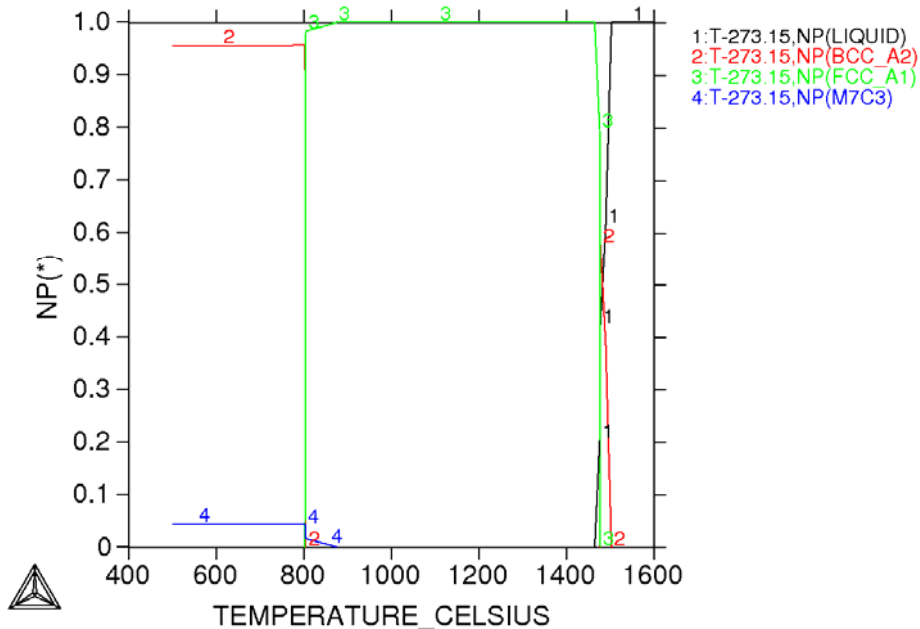
\*) Change the temperature axis to degree Celsius.

POST: **s-d-a x T-C**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.05:16.38) :  
 DATABASE:DFECRC  
 P=1.01325E5, N=1, W(CR)=5.31913E-2, W(C)=2.91252E-3;



POST:

\*) Make the information more visible between 1700 and 1800 K.

POST: **s-s-s x**

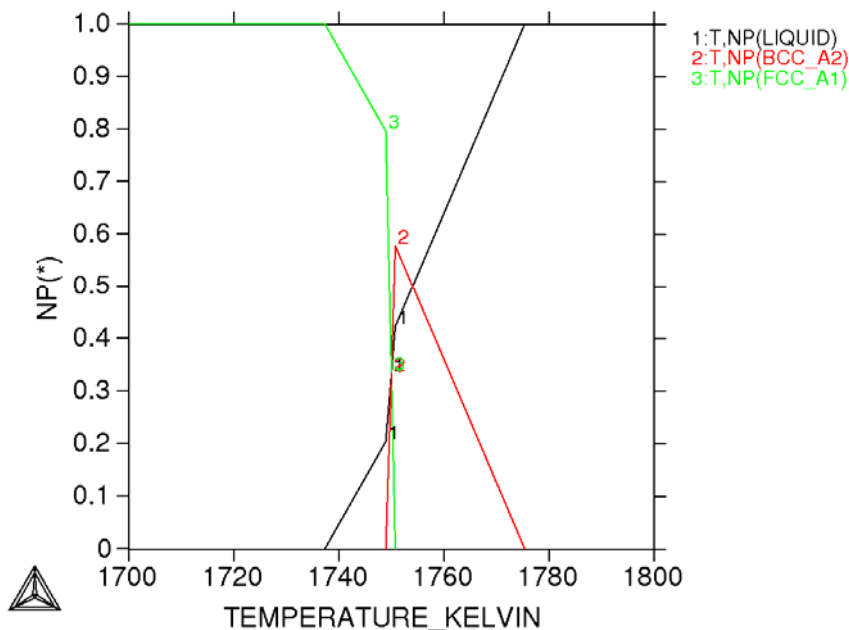
AUTOMATIC SCALING (Y OR N) /N/:

MIN VALUE : 1700 1800

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/ :

THERMO-CALC (2007.05.12:09.27) :  
 DATABASE:DFECRC  
 P=1.01325E5, N=1, W(CR)=5.31913E-2, W(C)=2.91252E-3;



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 **entering the symbol for a variable 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 1.01325E+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<sub>2</sub>, 30% O<sub>2</sub> and 10% H<sub>2</sub>O at 2000 K and 1 bar. (a) What is the driving force for the formation of more H<sub>2</sub>O? (b) What is the average driving force per mole of H<sub>2</sub>O 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,  $G_1$ , 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  $G_{m1} = G_1 / (2 \cdot 0.6 + 2 \cdot 0.3 + 3 \cdot 0.1) = G_1 / 2.1$  and there will be  $N_{m1} = 0.1 / 2.1$  mole of  $H_2O$  molecules. Then, compare with  $G_2$  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  $G_{m2} = G_2 / 2.1015$  and it will have  $N_{m2} = 0.1015$  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 H2O. 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



```
*****
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<sub>2</sub>O 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 set initial amounts of the species. Otherwise, in POLY you must give the composition in terms of elements. If you make a mistake, you can set an initial amount equal to the negative of the incorrect entry. Or you could delete all the entered conditions including the entered amounts with the command set-conditions **\*=none**. Or you could list the conditions and identify what you like to remedy. Finally, you could always **reinitiate** 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<sub>2</sub>O molecules in order to know how many has formed, compared to the initial state. You can get the fraction of H<sub>2</sub>O 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.