

Chapter 7. Applications of molar Gibbs energy diagrams

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7.2. Instability of binary solutions

Calculate and plot a molar Gibbs energy diagram for the bcc phase in the Fe-Cr system at 500°C under 1 atm.

Hint

- 1) Since pure Fe and Cr are both bcc, there will be only one phase to be fetched from the database. From your first run you may get a Gm curve with two minima. The bcc phase should thus have a miscibility gap at this low temperature and your equilibration module may have a procedure for identify two bcc phases, an Fe rich phase, bcc#1, and a Cr rich phase, bcc#2. Try to accomplish this if it does not happen automatically.
- 2) Use the pure elements at the actual temperature as references.

Instructions for using T-C

When searching for the state of equilibrium by minimizing the Gibbs energy, it is possible to find a local minimum and stop there. In POLY this can be prevented by applying a global minimization procedure, which searches for an even lower Gibbs energy by scanning over a wide range of compositions or constitutions. That procedure can be turned off or activated by the command set-min followed by options. When there is a miscibility gap in a phase, this procedure will find the other side of the miscibility gap and then consider two phase, #1 and #2. By turning this procedure off and on you can thus obtain different results. As default, this procedure is normally turned on and a miscibility gap will be found automatically.

It may be instructive to see the two minima. If you don't get them on your first run, try to inactivate the automatic procedure.

Prompts, commands and responses

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

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

```
VA DEFINED
TDB_DFECRC: def-el Fe Cr
FE CR DEFINED
TDB_DFECRC: rej p *
LIQUID:L FCC_A1 BCC_A2
HCP_A3 SIGMA REJECTED
TDB_DFECRC: rest p bcc
BCC_A2 RESTORED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 34
FUNCTIONS ....
```

List of references for assessed data

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

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

-OK-

```
TDB_DFECRC: go pol
```

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

*) Compute an equilibrium using as one condition a value of the variable you like to vary, e.g. $x(\text{Cr})$.

```
POLY_3: s-c P=101325 T=673 N=1 x(Cr)=.1
POLY_3: c-e
Using global minimization procedure
Calculated 137 grid points in 0 s
Found the set of lowest grid points in 0 s
Creating a new composition set BCC_A2#2
Calculated POLY solution 0 s, total time 0 s
```

POLY_3:
*) Observe the note: "Creating a new composition set BCC_A2#2". POLY has thus detected the miscibility gap. Now you can start stepping and preferably across the whole system.

```
POLY_3: s-a-v
Axis number: /1/:
Condition /NONE/: x(Cr)
Min value /0/:
Max value /1/:
Increment /.025/:
```

POLY_3: **step**
 Option? /NORMAL/:

Phase Region from 0.100000 for:
 BCC_A2#1
 BCC_A2#2
 Calculated 36 equilibria

Phase Region from 0.939244 for:
 BCC_A2#2
 Calculated 6 equilibria

Phase Region from 0.100000 for:
 BCC_A2#1
 BCC_A2#2
 Calculated 3 equilibria

Phase Region from 0.934860E-01 for:
 BCC_A2#1
 Calculated 7 equilibria

*** Buffer saved on file: USERPROFILE\RESULT.POLY3

POLY_3:

*) Time to go to the postprocessor for plotting a diagram.

POLY_3: **post**

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

POST: **s-d-a x m-f Cr**

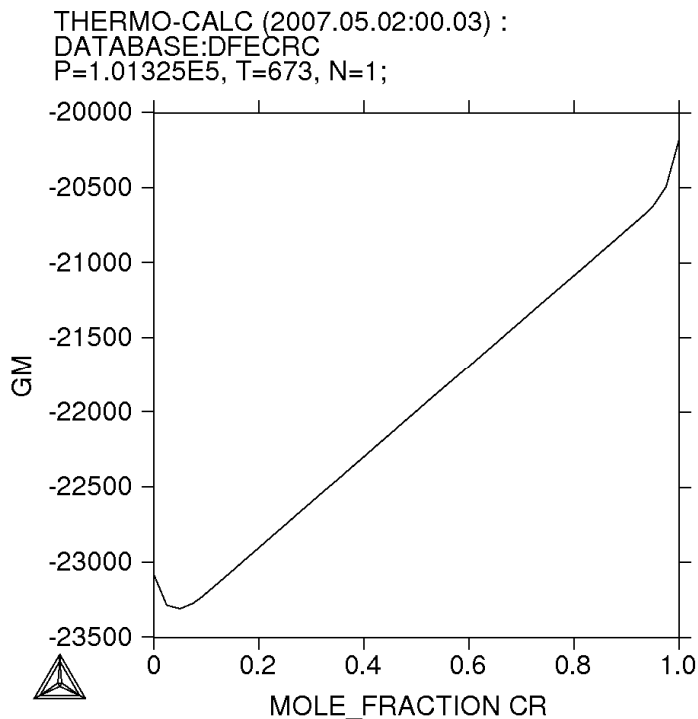
POST:

*) The symbol m-f Cr stands for "mass fraction of Cr", which is usually denoted by $x(\text{Cr})$.
 Sometimes one likes to specify the values for individual phases and uses $x(\text{bcc}, \text{Cr})$ or more
 generally $x(*, \text{Cr})$. M-f Cr is identical to the latter symbol.

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

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:



POST:

*) The two-phase states in the central part of the diagram are represented by a straight line, the common tangent. If you also like to see the metastable and unstable parts of the Gibbs energy of the homogeneous phase, you have to step through the computations again with an option "separate".

POST: **b**

POLY_3: **step**

Option? /NORMAL/: **sep**

Convergence problems, increasing smallest sitefraction from 1.00E-30 to hardware precision 2.00E-12. You can restore using SET-NUMERICAL-LIMITS

Phase Region from 0.497537 for:
BCC_A2#1
BCC_A2#2

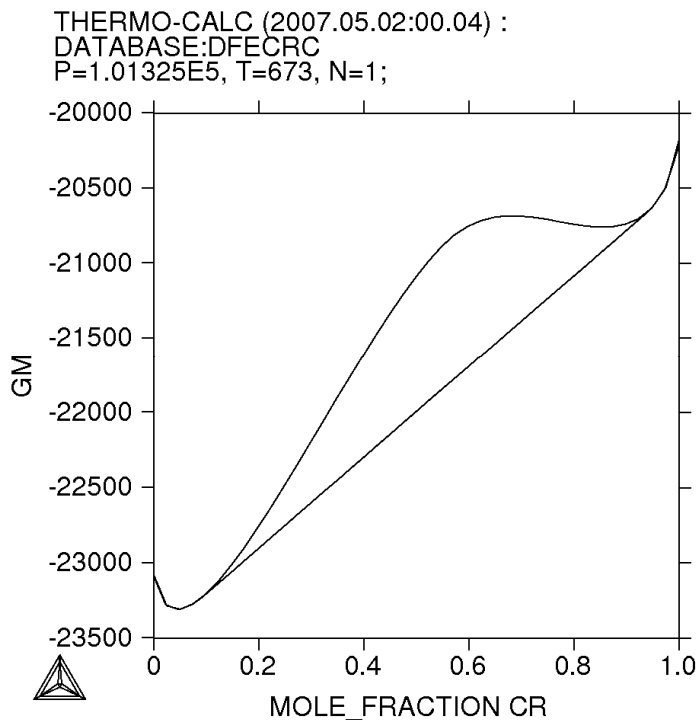
Phase Region from 0.497537 for:
BCC_A2#1
BCC_A2#2

*** Buffer saved on file *** USERPROFILE\RESULT.POLY3

POLY_3: **post**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:



POST:

*) G_m is here given relative to the SER references. You may prefer to use the pure elements at the current temperature. You can then introduce them by going back to POLY. If you then like to use them in POST, you call for Gmr instead of Gm.

POST: **b**

POLY_3: **set-ref Fe bcc**

Temperature /*/:

Pressure /1E5/:

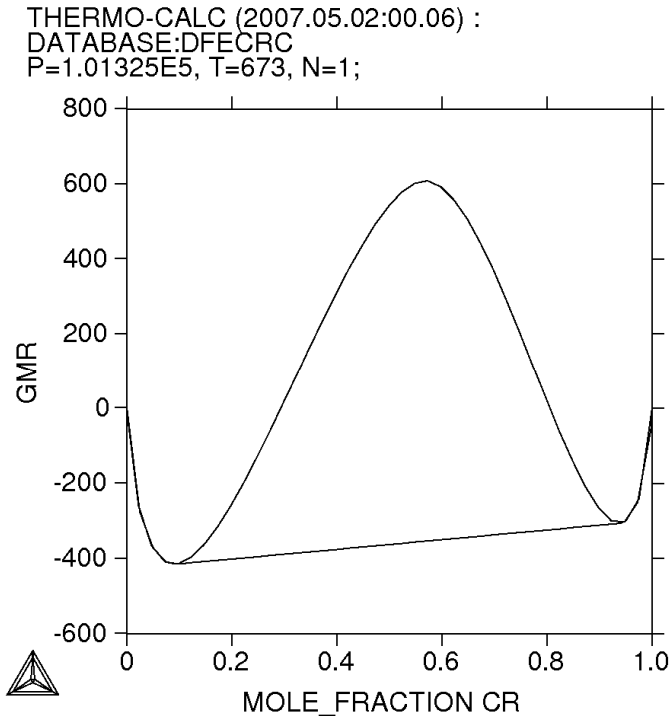
POLY_3: **set-ref Cr bcc**

Temperature /*/:

```

Pressure /1E5/:
POLY_3: post
POST: s-d-a y Gmr
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:

```



```

POST: exit
CPU time          0 seconds

```

Comments

POLY can automatically find the other side of a miscibility gap.

7.3. Illustration of the Gibbs-Duhem relation.

Define a system at 1000 K and 1 atm, with the elements Fe, Cr and C and with the phases bcc, graphite and cementite, $(\text{Fe,Cr})_3\text{C}$. Then, define Fe_3C_1 and Cr_3C_1 as new components instead of Fe and Cr. Make bcc and graphite dormant and compute the equilibrium between cementite, with equal amounts of Fe and Cr, and graphite. Evaluate the potential of a hypothetical component Fe_1Cr_1 . Finally, evaluate the same potential if the C activity is just half as high as for graphite. Evaluate the difference in Fe_1Cr_1 potential with what one should expect. Fig. 7.6 can be used as an illustration.

Hint

- 1) Equilibrium with graphite simply means that the C activity is 1, if graphite is used as reference. The second case can then be treated in exactly the same way but with a C activity of 0.5.

- 2) The potential of Fe for an equilibrium is equal to the potential of Fe_3C_1 minus the potential of C and divided by 3. Similarly for Cr and the potential for Fe_1Cr_1 is the sum of the two.

Instructions for using T-C

- 1) The new components must be introduced as the first action in POLY.
- 2) One should get the correct value for Fe_1Cr_1 in SER if SER is used for cementite and graphite. However, the choice of reference has no effect on the difference in a potential.

Prompts, commands and responses

```

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

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

VA DEFINED
TDB_DFECRC: def-el Fe Cr C
FE CR C
DEFINED
TDB_DFECRC: rej p *
LIQUID:L FCC_A1 BCC_A2
HCP_A3 SIGMA CEMENTITE
M3C2 M7C3 M23C6
GRAPHITE REJECTED
TDB_DFECRC: rest p bcc gra cem
BCC_A2 GRAPHITE CEMENTITE
RESTORED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 37
FUNCTIONS ....

```

List of references for assessed data

```

'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
-425, also in NPL Report DMA(A)195 Rev. August 1990'
'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
C-FE'
'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
(1986); CR-FE'
'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
C-CR-FE'

```

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

-OK-

TDB_DFECRC: go pol

POLY version 3.32, Aug 2001

POLY_3:

*) Now at the beginning of the session on POLY, you should define the whole new set of components.

POLY_3: **def-comp Fe3C1 Cr3C1 C**

POLY_3: **set-ref C gra**

Temperature /*/:

Pressure /1E5/:

POLY_3: **ch-st p gra=dor**

POLY_3: **ch-st p bcc=dor**

POLY_3: **s-c P=1E5 T=1000 N(Fe3C1)=1 N(Cr3C1)=1 acr(C)=1**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 137 grid points in 0 s

15 ITS, CPU TIME USED 0 SECONDS

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VWCS/:

Output from POLY-3, equilibrium = 1, label A0, database: DFECRC

Conditions:

P=1E5, T=1000, N(Fe3C1)=1, N(Cr3C1)=1, ACR(C)=1

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.000000E+05

Number of moles of components 2.00000E+00, Mass 3.47551E+02

Total Gibbs energy -3.48499E+05, Enthalpy 1.44449E+05, Volume 2.40157E-05

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
FE3C1	1.0000E+00	5.1662E-01	1.0043E-08	-1.5312E+05	SER
CR3C1	1.0000E+00	4.8338E-01	6.2354E-11	-1.9538E+05	SER
C	0.0000E+00	-1.0222E-17	1.0000E+00	0.0000E+00	GRAPHITE

CEMENTITE Status ENTERED Driving force 0.0000E+00

Number of moles 2.0000E+00, Mass 3.4755E+02 Mass fractions:

FE3C1 5.16621E-01 CR3C1 4.83379E-01 C 0.00000E+00

GRAPHITE Status DORMANT Driving force 0.0000E+00

Number of moles 0.0000E+00, Mass 0.0000E+00 Mass fractions:

C 1.00000E+00 FE3C1 0.00000E+00 CR3C1 0.00000E+00

*) According to the Hint, the potential of Fe_1Cr_1 is given as follows. Observe that $\mu(\text{C})$ is the symbol when SER is used. A few lines earlier when ACR(C) was used, the letter R indicates that the special reference was used.

POLY_3: **ent-sym fun muFeCr=(mu(Fe3C1)+mu(Cr3C1)-2*mu(C))/3;**

POLY_3:

*) When you are going to use an expression for a symbol several times, then you should define it as a function. If you then like to store the current value you should define that as a variable.

POLY_3: **ent-sym var mu1=muFeCr;**

POLY_3:

*) Next, use a different value of $\text{acr}(\text{C})$ as a condition.

POLY_3: **s-c acr(C)=.5**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

```
Using already calculated grid
 10 ITS, CPU TIME USED  0 SECONDS
POLY_3:
```

*) Everytime you call for the function muFeCr, it will be evaluated from the current conditions. mu2 on the next line will thus get a different value than the earlier mu1.

```
POLY_3: ent-sym var mu2=muFeCr;
POLY_3: ent-sym var diff=mu2-mu1;
POLY_3: sh diff
      DIFF=3842.1194
POLY_3: exit
CPU time          0 seconds
```

Comments

The value 3842.1194 is the difference in chemical potential of Fe_1Cr_1 in the Fe-Cr cementite due to the two C activities. The change in activity gives a change in potential of $RT\ln(1/0.5)$. Comparison with Fig. 7.9 shows that one should divide by 3 because of the composition of cementite, M_3C but one should also multiply by 2 because the hypothetical component Fe_1Cr_1 was here defined for two atoms. $(3/2)RT\ln(1/0.5) = 3842.1194$.

7.4. Two-phase equilibria in binary systems

The database lists four carbides in the Cr-C system, Cr_{23}C_6 , Cr_3C , Cr_7C_3 and Cr_3C_2 , and together with the end-members, bcc-Cr and graphite, it makes six phases. Examine the phase equilibria by computing the equilibrium for alloy compositions in all the regions between phases.

Hint

For all the alloy compositions, let all the phases be present and note the degree of instability, i.e. the negative value of the driving force for formation, of all the phases not taking part in the equilibrium.

Instructions for using T-C

If you get problems when computing equilibrium, try set-all-start values and respond F for Forced instead of N, which stands for No.

Prompts, commands and responses

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

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

VA DEFINED
TDB_DFECRC: def-el Cr C
CR C DEFINED
TDB_DFECRC: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
LIQUID:L :C CR:
> This is metallic liquid solution phase, with C species
FCC_A1 :CR:C VA:
```

```

BCC_A2      :CR:C VA:
HCP_A3      :CR:VA C:
CEMENTITE   :CR:C:
M3C2        :CR:C:
M7C3        :CR:C:
M23C6       :CR:CR:C:
GRAPHITE    :C:
TDB_DFECRC: rej p fcc hcp
  FCC_A1                    HCP_A3  REJECTED
TDB_DFECRC: get
  REINITIATING GES5 .....
  ELEMENTS .....
  SPECIES .....
  PHASES .....
  PARAMETERS ...
  Rewind to read functions          45
  FUNCTIONS ....

```

List of references for assessed data

```

'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
  -425, also in NPL Report DMA(A)195 Rev. August 1990'
'J-O Andersson, Calphad Vol 11 (1987) p 271-276, TRITA 0314; C-CR'
'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
  Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'
'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
'J-O Andersson, Met. Trans A, Vol 19A, (1988) p 627-636 TRITA 0207 (1986);
  C-CR-FE'

```

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

-OK-

```
TDB_DFECRC: go pol
```

```

POLY version 3.32, Aug 2001
POLY_3: set-ref C gra
Temperature /*/:
Pressure /1E5/:
POLY_3: s-c T=1000 P=101325 N=1 x(C)=.2
POLY_3: c-e
  Using global minimization procedure
  Calculated      279  grid points in          0  s
  Found the set of lowest grid points in      0  s
  Calculated POLY solution      0 s, total time  0  s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/: XP
  Output from POLY-3, equilibrium =      1, label A0 , database: DFECRC

Conditions:
T=1000, P=1.01325E5, N=1, X(C)=0.2
DEGREES OF FREEDOM 0

Temperature 1000.00 K ( 726.85 C), Pressure 1.013250E+05
Number of moles of components 1.00000E+00, Mass 4.39990E+01
Total Gibbs energy -4.50781E+04, Enthalpy 8.16011E+03, Volume 2.45960E-07

Component      Moles      M-Fraction Activity Potential Ref.stat
C                2.0000E-01 2.0000E-01 3.5879E-04 -6.5957E+04 GRAPHITE
CR               8.0000E-01 8.0000E-01 1.2116E-02 -3.6694E+04 SER

```

LIQUID Status ENTERED Driving force -1.5219E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 9.66620E-01 C 3.33803E-02

BCC_A2 Status ENTERED Driving force 0.0000E+00
 Number of moles 3.3333E-02, Mass 1.7332E+00 Mole fractions:
 CR 1.00000E+00 C 1.25040E-07

CEMENTITE Status ENTERED Driving force -2.6056E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.50000E-01 C 2.50000E-01

GRAPHITE Status ENTERED Driving force -7.9328E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 C 1.00000E+00 CR 0.00000E+00

M23C6 Status ENTERED Driving force 0.0000E+00
 Number of moles 9.6667E-01, Mass 4.2266E+01 Mole fractions:
 CR 7.93103E-01 C 2.06897E-01

M3C2 Status ENTERED Driving force -1.1456E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 6.00000E-01 C 4.00000E-01

M7C3 Status ENTERED Driving force -2.7210E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.00000E-01 C 3.00000E-01

POLY_3:

*) Bcc and M23C6 are stable. Cr3C(cementite) falls between them and cannot form as a stable phase. Show the C activity relative to graphite.

POLY_3: **sh acr(C)**

ACR(C)=3.5878726E-4

POLY_3:

*) Insert a slightly higher C content.

POLY_3: **s-c x(C)=.23**

POLY_3: **c-e**

Using global minimization procedure

Using already calculated grid

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VXCP/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

T=1000, P=1.01325E5, N=1, X(C)=0.23

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 4.27995E+01

Total Gibbs energy -4.57743E+04, Enthalpy 6.99316E+03, Volume 0.00000E+00

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
C	2.3000E-01	2.3000E-01	3.6431E-03	-4.6685E+04	GRAPHITE
CR	7.7000E-01	7.7000E-01	6.6186E-03	-4.1721E+04	SER

LIQUID Status ENTERED Driving force -1.8784E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:

CR 8.68080E-01 C 1.31920E-01

BCC_A2 Status ENTERED Driving force -6.0466E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 1.00000E+00 C 2.49139E-09

CEMENTITE Status ENTERED Driving force -1.3459E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.50000E-01 C 2.50000E-01

GRAPHITE Status ENTERED Driving force -5.6149E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 C 1.00000E+00 CR 0.00000E+00

M23C6 Status ENTERED Driving force 0.0000E+00
 Number of moles 7.5185E-01, Mass 3.2873E+01 Mole fractions:
 CR 7.93103E-01 C 2.06897E-01

M3C2 Status ENTERED Driving force -5.8124E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 6.00000E-01 C 4.00000E-01

M7C3 Status ENTERED Driving force 0.0000E+00
 Number of moles 2.4815E-01, Mass 9.9261E+00 Mole fractions:
 CR 7.00000E-01 C 3.00000E-01

POLY_3:

*) M23C6 and M7C3 are stable. Cr3C does not form in spite of the fact that the alloy composition was here chosen close to the composition of Cr3C.

POLY_3: **sh acr(C)**

ACR(C)=3.6431395E-3

POLY_3: **s-c x(C)=.35**

POLY_3: **c-e**

Using global minimization procedure

Using already calculated grid

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VXCP/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

T=1000, P=1.01325E5, N=1, X(C)=0.35

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 3.80012E+01

Total Gibbs energy -4.54726E+04, Enthalpy 4.21182E+03, Volume 0.00000E+00

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
C	3.5000E-01	3.5000E-01	2.1305E-01	-1.2856E+04	GRAPHITE
CR	6.5000E-01	6.5000E-01	1.1574E-03	-5.6219E+04	SER

LIQUID Status ENTERED Driving force -2.4604E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.40466E-01 C 2.59534E-01

BCC_A2 Status ENTERED Driving force -2.3481E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 9.99926E-01 C 7.40201E-05

```

CEMENTITE                               Status ENTERED           Driving force -4.2521E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.50000E-01 C 2.50000E-01

GRAPHITE                                 Status ENTERED           Driving force -1.5462E+00
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
C 1.00000E+00 CR 0.00000E+00

M23C6                                    Status ENTERED           Driving force -5.4116E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.93103E-01 C 2.06897E-01

M3C2                                     Status ENTERED           Driving force 0.0000E+00
Number of moles 5.0000E-01, Mass 1.8001E+01      Mole fractions:
CR 6.00000E-01 C 4.00000E-01

M7C3                                     Status ENTERED           Driving force 0.0000E+00
Number of moles 5.0000E-01, Mass 2.0000E+01      Mole fractions:
CR 7.00000E-01 C 3.00000E-01
POLY_3:
  *) M7C3 and M3C2 are stable.
POLY_3: sh acr(C)
  ACR(C)=0.21305078
POLY_3: s-c x(C)=.45
POLY_3: c-e
  Using global minimization procedure
  Using already calculated grid
  Found the set of lowest grid points in          0 s
  Calculated POLY solution          0 s, total time 0 s
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
  Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:
T=1000, P=1.01325E5, N=1, X(C)=0.45
DEGREES OF FREEDOM 0

Temperature 1000.00 K ( 726.85 C), Pressure 1.013250E+05
Number of moles of components 1.00000E+00, Mass 3.40028E+01
Total Gibbs energy -4.13308E+04, Enthalpy 4.45886E+03, Volume 4.49815E-07

Component           Moles      M-Fraction Activity Potential Ref.stat
C                   4.5000E-01 4.5000E-01 1.0000E+00 0.0000E+00 GRAPHITE
CR                  5.5000E-01 5.5000E-01 4.1286E-04 -6.4790E+04 SER

LIQUID              Status ENTERED           Driving force -2.7618E+00
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 6.93947E-01 C 3.06053E-01

BCC_A2              Status ENTERED           Driving force -3.3777E+00
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 9.99652E-01 C 3.47717E-04

CEMENTITE           Status ENTERED           Driving force -8.1176E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.50000E-01 C 2.50000E-01

GRAPHITE            Status ENTERED           Driving force 0.0000E+00
Number of moles 8.3333E-02, Mass 1.0009E+00      Mole fractions:
C 1.00000E+00 CR 0.00000E+00

```

```

M23C6                      Status ENTERED          Driving force -1.0388E+00
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.93103E-01 C 2.06897E-01

M3C2                      Status ENTERED          Driving force 0.0000E+00
Number of moles 9.1667E-01, Mass 3.3002E+01      Mole fractions:
CR 6.00000E-01 C 4.00000E-01

M7C3                      Status ENTERED          Driving force -2.5770E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.00000E-01 C 3.00000E-01
POLY_3:
  *) M3C2 and graphite are stable.
POLY_3: sh acr(C)
  ACR(C)=1
POLY_3:
  *) Cr3C(cementite) is never stable in this system. Force it to be in equilibrium with bcc.
POLY_3: ch-st p *=dor
POLY_3: ch-st p bcc cem=fix 1
POLY_3: s-c N=none x(C)=none
POLY_3: c-e
  Normal POLY minimization, not global
  Testing POLY result by global minimization procedure
  Calculated 138 grid points in 0 s
  17 ITS, CPU TIME USED 0 SECONDS
POLY_3: sh acr(C)
  ACR(C)=1.0173557E-3
POLY_3:
  *) Force Cr3C to be in equilibrium with M23C6.
POLY_3: ch-st p bcc=dor
POLY_3: ch-st p m23=fix 1
POLY_3: c-e
  Normal POLY minimization, not global
  Testing POLY result by global minimization procedure
  Calculated 2 grid points in 0 s
  10 ITS, CPU TIME USED 0 SECONDS
POLY_3: l-e
OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VXCP/:
  Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:
T=1000, P=1.01325E5
FIXED PHASES
CEMENTITE=1 M23C6=1
DEGREES OF FREEDOM 0

Temperature 1000.00 K ( 726.85 C), Pressure 1.013250E+05
Number of moles of components 3.30000E+01, Mass 1.43597E+03
Total Gibbs energy -1.49568E+06, Enthalpy 2.47366E+05, Volume 0.00000E+00

Component      Moles      M-Fraction Activity Potential Ref.stat
C              7.0000E+00 2.1212E-01 4.3347E-02 -2.6095E+04 GRAPHITE
CR            2.6000E+01 7.8788E-01 3.4690E-03 -4.7092E+04 SER

LIQUID                      Status DORMANT          Driving force -1.9908E+00
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.93565E-01 C 2.06435E-01

```


CEMENTITE Status FIXED Driving force 0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02 Mole fractions:
 CR 7.50000E-01 C 2.50000E-01

GRAPHITE Status DORMANT Driving force -7.4991E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 C 1.00000E+00 CR 0.00000E+00

M23C6 Status DORMANT Driving force 2.5061E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.93103E-01 C 2.06897E-01

M3C2 Status DORMANT Driving force -8.5041E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 6.00000E-01 C 4.00000E-01

M7C3 Status FIXED Driving force 0.0000E+00
 Number of moles 1.0000E+01, Mass 4.0001E+02 Mole fractions:
 CR 7.00000E-01 C 3.00000E-01

POLY_3: **sh acr(C)**
 ACR(C)=5.5356977E-4
 POLY_3:

*) The list shows that bcc and M23C6 have positive driving forces for this equilibrium.

POLY_3: **ch-st p m7=dor**

POLY_3: **ch-st p m3=fix 1**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 2 grid points in 0 s

10 ITS, CPU TIME USED 0 SECONDS

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VXCP/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

T=1000, P=1.01325E5

FIXED PHASES

CEMENTITE=1 M3C2=1

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 9.00000E+00, Mass 3.48009E+02

Total Gibbs energy -3.99718E+05, Enthalpy 4.09174E+04, Volume 0.00000E+00

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
C	3.0000E+00	3.3333E-01	3.8889E-02	-2.6998E+04	GRAPHITE
CR	6.0000E+00	6.6667E-01	3.5968E-03	-4.6792E+04	SER

LIQUID Status DORMANT Driving force -1.9843E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.96628E-01 C 2.03372E-01

BCC_A2 Status DORMANT Driving force -1.2145E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 9.99986E-01 C 1.35518E-05

CEMENTITE Status FIXED Driving force 0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02 Mole fractions:
 CR 7.50000E-01 C 2.50000E-01

GRAPHITE Status DORMANT Driving force -3.2471E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 C 1.00000E+00 CR 0.00000E+00

M23C6 Status DORMANT Driving force 6.2378E-03
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.93103E-01 C 2.06897E-01

M3C2 Status FIXED Driving force 0.0000E+00
 Number of moles 5.0000E+00, Mass 1.8001E+02 Mole fractions:
 CR 6.00000E-01 C 4.00000E-01

M7C3 Status DORMANT Driving force 2.8347E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.00000E-01 C 3.00000E-01
 POLY_3: **sh acr(C)**
 ACR(C)=3.8888654E-2
 POLY_3:

*) The list shows that M23C6 and M7C3 have now positive driving forces. Finally, study the equilibrium between graphite and Cr3C.

POLY_3: **ch-st p m3=dor**
 POLY_3: **ch-st p gra=fix 1**
 POLY_3: **c-e**

Normal POLY minimization, not global
 Testing POLY result by global minimization procedure
 Calculated 2 grid points in 0 s
 10 ITS, CPU TIME USED 0 SECONDS

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VXCP/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

T=1000, P=1.01325E5

FIXED PHASES

CEMENTITE=1 GRAPHITE=1

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 5.00000E+00, Mass 1.80010E+02

Total Gibbs energy -1.92689E+05, Enthalpy 3.37377E+04, Volume 5.39778E-06

Component	Moles	M-Fraction	Activity	Potential	Ref.stat
C	2.0000E+00	4.0000E-01	1.0000E+00	0.0000E+00	GRAPHITE
CR	3.0000E+00	6.0000E-01	1.2186E-03	-5.5791E+04	SER

LIQUID Status DORMANT Driving force -2.0004E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 7.13137E-01 C 2.86863E-01

BCC_A2 Status DORMANT Driving force -2.2957E+00
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mole fractions:
 CR 9.99652E-01 C 3.47730E-04

CEMENTITE Status FIXED Driving force 0.0000E+00
 Number of moles 4.0000E+00, Mass 1.6800E+02 Mole fractions:
 CR 7.50000E-01 C 2.50000E-01

GRAPHITE Status FIXED Driving force 0.0000E+00
 Number of moles 1.0000E+00, Mass 1.2011E+01 Mole fractions:

```

C 1.00000E+00 CR 0.00000E+00

M23C6                      Status DORMANT      Driving force -1.8037E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.93103E-01 C 2.06897E-01

M3C2                      Status DORMANT      Driving force 6.4941E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 6.00000E-01 C 4.00000E-01

M7C3                      Status DORMANT      Driving force 4.9994E-01
Number of moles 0.0000E+00, Mass 0.0000E+00      Mole fractions:
CR 7.00000E-01 C 3.00000E-01
POLY_3: sh acr(C)
ACR(C)=1
POLY_3:
      *) Cr3C2 and M7C3 have now positive driving forces.
POLY_3: exit
CPU time          0 seconds

```

Comments

It may seem strange that bcc got a positive driving force for the equilibrium Cr₃C(cementite)+M₇C₃ although it is never stable in this system. It is related to the very low C activity for that equilibrium, which is connected to a higher Cr activity, according to the Gibbs-Duhem relation.

7.5. Allotropic phase boundaries

Fcc and bcc Fe have the same Gibbs energy at 1 atm and 911°C. That phase equilibrium represents an end-point of a T₀ line that extends into all binary Fe-X phase diagram. Compute and plot that line for the Fe-C system up to 1 mass% C.

Hint

The T₀ line is sometimes regarded as an allotropic phase boundary. In principle, it is evaluated from the condition G_m(fcc) = G_m(bcc) but different data bank systems may have different methods of computing that kind of equilibrium.

Instructions for using T-C

T-C has a special procedure for the computation of T₀ lines.

Prompts, commands and responses

```

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

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

VA DEFINED

```

```

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

```

List of references for assessed data

```

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

```

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

-OK-

```
TDB_DFECRC: go pol
```

```

POLY version 3.32, Aug 2001
POLY_3:

```

*) Start with an initial equilibrium and map the phase diagram.

```
POLY_3: s-c P=101325 T=1000 N=1 w(C)=.003
```

```
POLY_3: c-e
```

Using global minimization procedure

```
Calculated          274 grid points in          0 s
```

```
Found the set of lowest grid points in          0 s
```

```
Calculated POLY solution          0 s, total time 0 s
```

```
POLY_3: s-a-v 1 w(C) 0 .05
```

```
Increment /.00125/:
```

```
POLY_3: s-a-v 2 T 500 1200
```

```
Increment /17.5/:
```

```
POLY_3: map
```

Automatic saving workspaces on

```
USERPROFILE\RESULT.POLY3
```

Organizing start points

No initial equilibrium added, trying to fix one

Automatic saving workspaces on

```
USERPROFILE\RESULT.POLY3
```

Using ADDED start equilibria

```
Global search for miscibility gaps 1 2 3 4 5 6 7 8 9 10 11 12
```

```
Found          2 zero phase fraction lines to start mapping
```

```
Phase region boundary 1 at: 1.902E-04 1.000E+03
```

```
BCC_A2
```

```

** FCC_A1
Calculated 100 equilibria, continuing
Calculated 200 equilibria, continuing
Mapping terminated 1
Calculated 226 equilibria

```

```

Phase region boundary 2 at: 1.902E-04 1.000E+03
BCC_A2

```

```

** FCC_A1
Mapping terminated 1
*** Last buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3: post

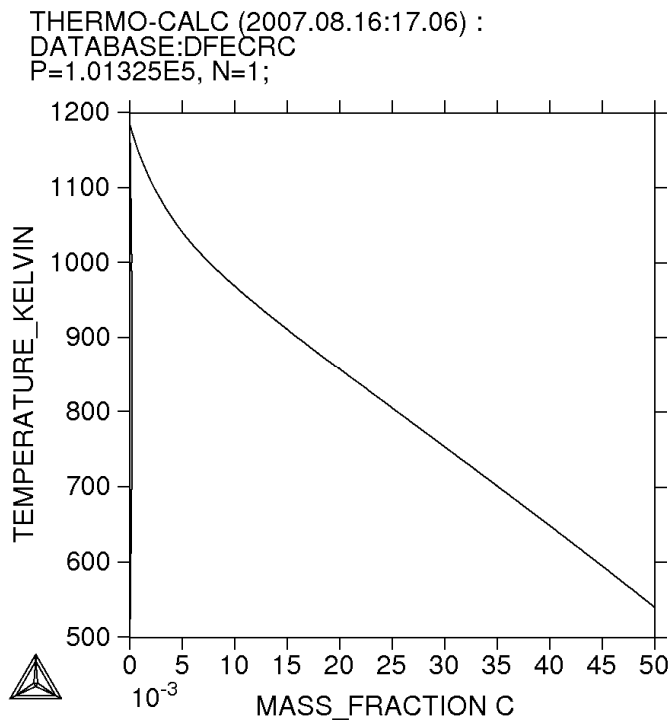
```

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

Setting automatic diagram axis

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:



POST: **b**

POLY_3:

*) POLY has a special stepping option for T_0 lines. You start by setting the x axis variable as for normal stepping. Here you must also give the second axis variable as none since it was entered in the previous plot.

POLY_3: **s-a-v 1 w(c) 0 .02**

Increment /5E-04/:

POLY_3: **s-a-v 2 none**

POLY_3: **step**

Option? /NORMAL/:

*) Inspect the options.

Option? /NORMAL/: ?

The following options are available:

NORMAL	Stepping with given conditions
INITIAL_EQUILIBRIA	An initial equilibrium stored at every step
EVALUATE	Specified variables evaluated after each step

SEPARATE_PHASES Each phase calculated separately
 T-ZERO T0 line calculation
 PARAEQUILIBRIUM Paraequilibrium diagram
 MIXED_SCHEIL Scheil with fast diffusing elements
 Option? /NORMAL/: **T-zero**
 Name of first phase: **bcc**
 Name of second phase: **fcc**

Phase Region from 0.300000E-02 for:

BCC_A2
 FCC_A1
 3.000000E-03 962.48
 2.500000E-03 984.59
 2.000000E-03 1009.05
 1.500000E-03 1037.79
 1.000000E-03 1074.51
 5.000000E-04 1121.53
 5.000000E-10 1184.79

Phase Region from 0.227025E-03 for:

BCC_A2
 FCC_A1
 2.270245E-04 1153.42
 7.270245E-04 1098.63
 1.227025E-03 1056.76
 1.727025E-03 1023.98
 2.227025E-03 997.57
 2.727025E-03 974.33
 3.227025E-03 952.97
 3.727025E-03 932.87
 4.227025E-03 913.68
 4.727025E-03 895.17
 5.227025E-03 877.17
 5.727025E-03 859.58
 6.227025E-03 842.31
 6.727025E-03 825.30
 7.227025E-03 808.47
 7.727025E-03 791.81
 8.227025E-03 775.26
 8.727025E-03 758.80
 9.227025E-03 742.40
 9.727025E-03 726.03
 1.022702E-02 709.68
 1.072702E-02 693.32
 1.122702E-02 676.92
 1.172702E-02 660.49
 1.222702E-02 644.00
 1.272702E-02 627.42
 1.322702E-02 610.76
 1.372702E-02 593.99
 1.422702E-02 577.09
 1.472702E-02 560.05
 1.522702E-02 542.85
 1.572702E-02 525.48
 1.622702E-02 507.93
 1.672702E-02 490.16
 1.722702E-02 472.17
 1.772702E-02 453.92
 1.822702E-02 435.41
 1.872702E-02 416.60
 1.922702E-02 397.47

```

1.972702E-02      377.99
2.000000E-02      367.19
*** Buffer saved on file USERPROFILE\RESULT.POLY3
POLY_3: post

```

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

Setting automatic diagram axis

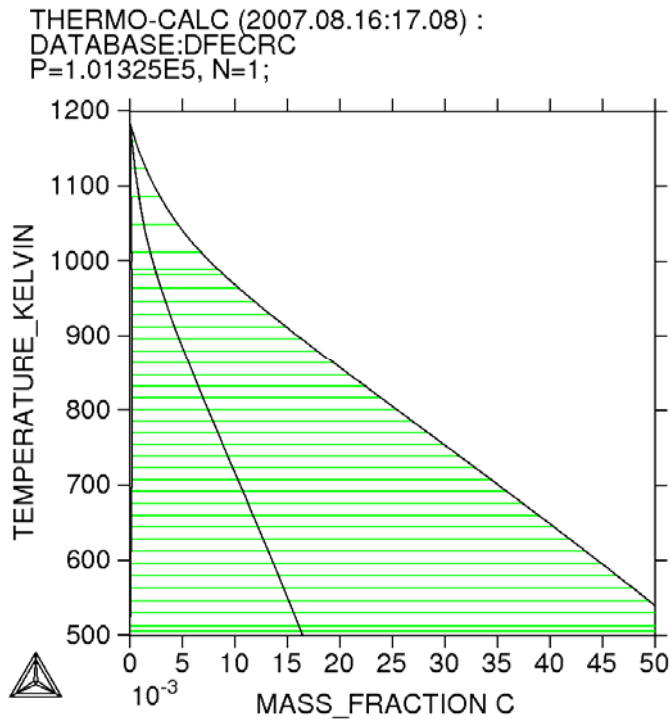
POST:

*) In order to indicate that the three lines in the diagram are not just any lines, it may be helpful to identify the phase boundaries by setting the tie-line status and accepting every third one, for instance.

POST: **s-t-st 3**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:



POST: **exit**

CPU time 1 seconds

Comments

It is worth noting that the T_0 line does not necessarily fall close to the middle of the two phase boundaries.

7.6. Effect of a pressure difference on a two-phase equilibrium

Compute the effect of a pressure increase to 100 atm on the bcc phase when in equilibrium with fcc of 1 atm in the Fe-C system at 1000°C.

Hint

One way to compute the equilibrium between two phases, when only one of them is under an increased pressure, would be to go to the module where the properties are stored and change the molar volume of the other phase to zero. With T-C you have another possibility.

Instructions for using T-C

In POLY there is a special option "set-phase-addition" that allows you to make an addition to the Gibbs energy of an individual phase, α . One could thus account for the effect of an increased pressure on that phase, e.g. caused by the surface energy of a curved interface to another phase, by adding the term $V^\alpha \cdot \Delta P$ to the expression for G^α stored in the database. Of course, the volume must be expressed for the same amount of phase as the Gibbs energy in the database, i.e., for one formula unit. That would correctly give the effect if the α phase is incompressible, which is a reasonable approximation for condensed phases. For a gas phase in a bubble inside a condensed α phase one would have to evaluate the change of constitution caused by the increased pressure. That would also have an effect on the Gibbs energy.

Prompts, commands and responses

```

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

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

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

```

List of references for assessed data

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

'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
C-Fe'
'Pingfang Shi (2006), TCS PTERN Public Ternary Alloys Database, v1.2;
Modified L0(BCC,Fe,C) and L0(BCC,Cr,C) parameters at high temperatures.'

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

-OK-

TDB_DFECRC: **go pol**

POLY version 3.32, Aug 2001

POLY_3:

*) Start with an ordinary equilibrium between the two phases.

POLY_3: **s-c P=101325 T=1000 N=1 w(C)=.003**

POLY_3: **c-e**

Using global minimization procedure

Calculated 274 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VWCS/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

P=1.01325E5, T=1000, N=1, W(C)=3E-3

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 5.52422E+01

Total Gibbs energy -4.18471E+04, Enthalpy 2.65541E+04, Volume 7.22976E-06

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	1.3798E-02	3.0000E-03	2.6736E-01	-1.0968E+04	SER
FE	9.8620E-01	9.9700E-01	6.1890E-03	-4.2279E+04	SER

BCC_A2	Status	ENTERED	Driving force	0.0000E+00
Number of moles	6.1420E-01,	Mass	3.4277E+01	Mass fractions:
FE	9.99810E-01	C	1.90214E-04	

FCC_A1	Status	ENTERED	Driving force	0.0000E+00
Number of moles	3.8580E-01,	Mass	2.0965E+01	Mass fractions:
FE	9.92406E-01	C	7.59399E-03	

POLY_3:

*) You would be interested in studying the effect of a pressure increase in the bcc phase on the equilibrium composition of the fcc phase. The term $V^{bcc}(P-P_0)$ should thus be added to the Gibbs energy of bcc from the database. You should realize that G is expressed for one formula unit in the database and V should be evaluated for the same unit. It can be obtained from POLY using the symbol Vf, where f stands for formula unit, followed by the name of the phase.

POLY_3: **ent-sym var wCfcc1=w(fcc,C);**

POLY_3: **ent-sym var VdelP=(100-1)*101325*Vf(bcc);**

POLY_3:

*) With the command **special options** you can choose the **set-phase-addition** command and thus add the value of VdelP to the G function obtained from the database.

POLY_3: **special options**

Which option? /SET_MISCIBILITY_GAP/: ?

No such option, use one of

```

SET_MISCIBILITY_GAP
SET_MAJOR_CONSTITUENTS
MISC_GAP_TEST_INTERVAL
SET_PHASE_ADDITION
LIST_PHASE_ADDITION
SET_BREAK_CONDITION
SET_PRESENT_PHASE
OUTPUT_AT_MAP_AND_STEP
T-ZERO TEMPERATURE
PARAEQUILIBRIUM
STABILITY_CHECK
NEVER_ADJUST_MINIMUM_Y
TOGGLE_ALTERNATE_MODE
SHOW_OUTPUT_FILE

```

Which option? /SET_MISCIBILITY_GAP/: **set-ph-add**

Phase with addition: **bcc**

Addition to G per mol formula unit: **Vdelp**

POLY_3: **c-e**

Using global minimization procedure

Using already calculated grid

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VWCS/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

P=1.01325E5, T=1000, N=1, W(C)=3E-3

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 5.52422E+01

Total Gibbs energy -4.18054E+04, Enthalpy 2.69429E+04, Volume 7.21888E-06

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	1.3798E-02	3.0000E-03	2.0159E-01	-1.3316E+04	SER
FE	9.8620E-01	9.9700E-01	6.2452E-03	-4.2204E+04	SER

BCC_A2 Status ENTERED Driving force 0.0000E+00

Number of moles 5.1669E-01, Mass 2.8840E+01 Mass fractions:

FE 9.99856E-01 C 1.43596E-04

FCC_A1 Status ENTERED Driving force 0.0000E+00

Number of moles 4.8331E-01, Mass 2.6402E+01 Mass fractions:

FE 9.93880E-01 C 6.12020E-03

POLY_3:

*) Save the new composition of the fcc phase.

POLY_3: **ent-sym var wCfcc2=w(fcc,C);**

POLY_3: **eval**

Name(s):

WCFCC1=7.5939899E-3

VDELDP=73.338681

WCFCC2=6.1202042E-3

POLY_3: **exit**

CPU time 0 seconds

Comments

- 1) The mass fraction of C in fcc has thus decreased from $WC_{FCC1}=0.007594$ to $WC_{FCC2}=0.006120$. Those values were given already in the two lists of the states of equilibrium.
- 2) POLY can directly give extensive quantities per formula unit using symbols with an f instead of m, e.g. V_f instead of V_m . However, this works only for a phase. Even if there is only one phase in the system, you should thus write $V_f(\text{phase})$.

7.7. Driving force for the formation of a new phase

An fcc phase of Fe with 1.5 mass% C at 1000°C and 1 atm is supersaturated with respect to graphite and cementite. Compute the driving forces for their nucleation. Plot the driving forces as functions of the C content of fcc up to 2 mass% C.

Hint

You should remember the difference between the driving force for the first stage of formation, the so-called nucleation, and the driving force for the whole reaction until equilibrium has been established, i.e. the integrated driving force. See Section 7.7 in the textbook.

Instructions for using T-C

POLY automatically gives the driving force for each dormant phase but as a dimensionless quantity by dividing with RT .

Prompts, commands and responses

```

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

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

VA DEFINED
TDB_DFECRC: def-el Fe C
FE C DEFINED
TDB_DFECRC: rej p *
LIQUID:L FCC_A1 BCC_A2
HCP_A3 CEMENTITE M7C3
M23C6 GRAPHITE REJECTED
TDB_DFECRC: rest p fcc gra cem
FCC_A1 GRAPHITE CEMENTITE
RESTORED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 31
FUNCTIONS ....

```

List of references for assessed data

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

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

-OK-

TDB_DFECRC: go pol

POLY version 3.32, Aug 2001

POLY_3:

*) Start by computing the equilibrium for the supersaturated fcc alone in order later to be able
to evaluate its driving forces for nucleation. The other phases should thus be dormant.

POLY_3: s-c P=101325 T=1000 N=1 w(C)=.015

POLY_3: ch-st p cem gra=dor

POLY_3: c-e

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: l-e

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VWCS/:

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

P=1.01325E5, T=1000, N=1, W(C)=1.5E-2

DEGREES OF FREEDOM 0

Temperature 1000.00 K (726.85 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 5.29484E+01

Total Gibbs energy -4.00586E+04, Enthalpy 3.03308E+04, Volume 7.03164E-06

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	6.6125E-02	1.5000E-02	7.4084E-01	-2.4941E+03	SER
FE	9.3388E-01	9.8500E-01	5.8705E-03	-4.2718E+04	SER

Phase	Status	Driving force
CEMENTITE	DORMANT	2.1434E-01
Number of moles 0.0000E+00, Mass 0.0000E+00		
Mass fractions:		
FE 9.33106E-01	C 6.68943E-02	

Phase	Status	Driving force
FCC_A1	ENTERED	0.0000E+00
Number of moles 1.0000E+00, Mass 5.2948E+01		
Mass fractions:		
FE 9.85000E-01	C 1.50000E-02	

Phase	Status	Driving force
GRAPHITE	DORMANT	1.2225E+00
Number of moles 0.0000E+00, Mass 0.0000E+00		
Mass fractions:		
C 1.00000E+00	FE 0.00000E+00	

POLY_3:

*) Step in order to obtain the properties of the supersaturated fcc over the range of
composition.

POLY_3: s-a-v

Axis number: /1/:

Condition /NONE/: w(C)

Min value /0/: .005

```

Max value /1/: .025
Increment /5E-04/:
POLY_3: step
Option? /NORMAL/:
  looking for miscibility gaps..at:
  QSTEPP 2.5000000000000000E-002
  QSTEPP 5.0000000000000000E-003
  QSTEPP 1.5000000000000000E-002
  No new miscibility gap found!

Phase Region from 0.250000E-01 for:
  FCC_A1
  Calculated 43 equilibria
  *** Buffer saved on file: USERPROFILE\RESULT.POLY3
POLY_3:

```

*) All the necessary computations have now been done because for any equilibrium that has been computed, POLY can give you the driving force of a dormant phase through the symbol DGM.

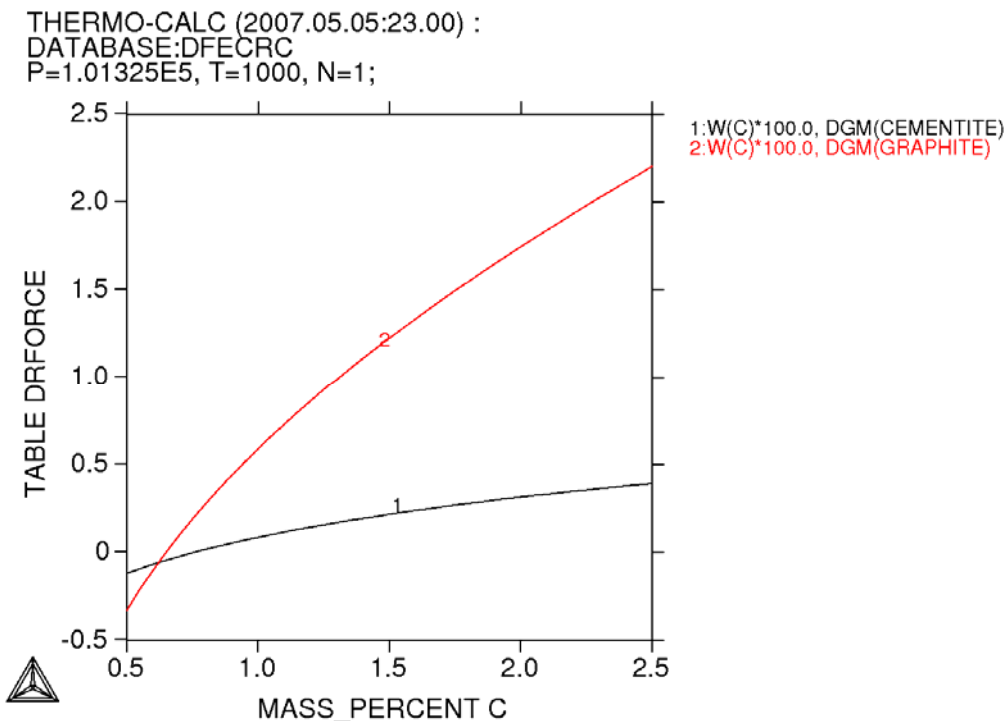
```
POLY_3: post
```

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

```

POST: s-d-a x w-p C
POST: ent-sym tab DrForce=dgm(cem),dgm(gra);
POST: s-d-a y DrForce
COLUMN NUMBER /*/:
POST: set-lab f
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:

```



```

POST: exit
CPU time 0 seconds

```

Comments

The driving force for graphite turns positive above about 0.65 mass% C, for cementite not until about 0.75 mass% C. Cementite is thus a metastable phase. At increasing C contents the driving force for graphite increases much faster than for cementite. The reason is that the mole fraction of C is much higher in graphite. You may illustrate that effect with a molar Gibbs energy diagram. Place the three curves such that the common tangent to cementite and graphite is parallel to the tangent to the fcc curve at a mass percent of about 0.6 where the two curves intersect. Then draw tangents for higher C contents in fcc.

7.8. Partitionless transformation under local equilibrium

Consider the partitionless solidification of an Al-Mg alloy with 2 mass% Mg under 1 atm. Suppose heat conduction is very efficient and the system is thin enough to be kept at a homogeneous temperature, which is decreased until the right temperature for partitionless solidification has been established. Compute the driving force for diffusion in the liquid between the solidification front and the interior of the liquid.

Hint

- 1) You must first find the temperature where the conditions for partitionless solidification are fulfilled. It is required that the new phase should grow with the composition of the bulk of the liquid. You should thus start by computing at what temperature the solid phase with that composition is in equilibrium with liquid. That should also yield the composition of the liquid at the interface. Then it is easy to take the difference in Mg content inside the liquid, i.e., between the interface to solid and the bulk, which has the initial content.
- 2) The potential for interdiffusion in a certain position is the difference between the local values of the chemical potentials. In connection to Eq. 4.8 it was also regarded as the driving force for diffusion which was not correct. The driving force for diffusion is the gradient of the diffusion potential. In the present case you are asked to consider the driving force for diffusion between two localities which might mean the difference in potentials.

Instructions for using T-C

In T-C it is convenient to require that a one-phase system of known composition should be in equilibrium with another phase. Apply the command "ch-st p <name>=fix 0" to the solid phase that has formed with the correct composition for partitionless growth.

Prompts, commands and responses

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

VA DEFINED
TDB_DALMGSI: def-el Al Mg
AL MG DEFINED
TDB_DALMGSI: rej p *
LIQUID:L FCC_A1 HCP_A3
```

```

DIAMOND_A4          ALMG_BETA          ALMG_DZETA
ALMG_UPSILON       AL12MG17  REJECTED
TDB_DALMGSI:

```

*) Al has the fcc structure. You should thus restore fcc together with the liquid phase.

```

TDB_DALMGSI: rest p liq fcc
LIQUID:L          FCC_A1  RESTORED
TDB_DALMGSI: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions          2
FUNCTIONS ....

```

List of references for assessed data

```

'Alan Dinsdale, SGTE Data for Pure Elements, Calphad Vol 15(1991) p 317
-425, also in NPL Report DMA(A)195 Rev. August 1990'
'N Saunders, COST project (1994); MG-SI'

```

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

-OK-

```
TDB_DALMGSI: go pol
```

POLY version 3.32, Aug 2001

```
POLY_3:
```

*) Equilibrium with liquid without any material going into the liquid is defined by **liq=fix 0**.

You can thus define a system of fcc with the correct composition for partitionless solidification and compute at what temperature it is in equilibrium with the liquid.

```

POLY_3: s-c P=101325 N=1 w(Mg)=.05
POLY_3: ch-st p liq=fix 0
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated          274 grid points in          0 s
 19 ITS, CPU TIME USED  0 SECONDS
POLY_3: sh T
T=853.05611
POLY_3:

```

*) Store the values of the chemical potentials of this two-phase equilibrium because they apply at the interface.

```

POLY_3: ent-sym var muMgInt=mu(Mg);
POLY_3: ent-sym var muAlInt=mu(Al);
POLY_3:

```

*) Now you should evaluate the chemical potentials in the bulk of the liquid, i.e. with fcc as dormant, assuming that the bulk is at the same temperature as the interface. Its composition is already given as a condition.

```

POLY_3: s-c T=
Value /853.0561072/:
POLY_3: ch-st p fcc=dor
POLY_3: ch-st p liq=ent 1
POLY_3: c-e
Using global minimization procedure
Calculated          137 grid points in          0 s
Found the set of lowest grid points in          0 s
Calculated POLY solution          0 s, total time  0 s

```

POLY_3:

*) The driving force for diffusion is given by the difference in diffusion potential between the two positions in the liquid.

POLY_3: **ent-sym var drf= $\mu(\text{Al}) - \mu(\text{Mg}) - \mu_{\text{AlInt}} + \mu_{\text{MgInt}}$;**

POLY_3: **eval**

Name(s):

MUMGINT=-52533.273

MUALINT=-33518.471

DRF=8843.7844

POLY_3: **exit**

CPU time 0 seconds

Comments

Notice that “partitionless” could be “diffusionless” but not necessarily. In the present case there is local equilibrium and diffusion in the pile-up of Mg in front of the advancing interface.

7.9. Activation energy for a fluctuation

Long ago one had the idea that a small coherent particle could precipitate by a fluctuation in the parent phase first reaching the correct composition and size for a nucleus and then transforming without any diffusion. Consider an fcc Fe alloy with 0.5 mass% C at 1000 K and 1 bar and calculate the activation energy for such a fluctuation being a precursor of a critical nucleus of the new phase.

Hint

You have to know the composition and size of the fcc fluctuation. Suppose they have the same values as the critical nucleus of the new phase according to ordinary nucleation theory. You should then start by evaluating the critical nucleus. 1 J/m^2 may be a reasonable value for the specific surface energy.

Instructions for using T-C

The pressure in the critical nucleus is obtained from its driving force, which POLY calculates for all phases not suspended. If you are not sure what phase would nucleate, you can examine the driving forces for possible phases if you have made them dormant. Remember that POLY gives the dimensionless driving force by dividing its actual value with RT. Thus,

$2\sigma/r = \Delta P = -\Delta G_m / V_m^{new} = (RT / V_m^{new}) \cdot D / RT$. Its content of material would be $4\pi r^3 / 3V_m^{new}$ and the fcc fluctuation should contain the same amount of material. Neglect the possible "surface" energy between the fcc fluctuation and the fcc bulk. Its Gibbs energy would then be $(4\pi r^3 / 3V_m^{new}) \cdot G_m(\text{fcc})$ and this material has been taken from the bulk fcc with its chemical potentials.

Prompts, commands and responses

SYS: **go da**

THERMODYNAMIC DATABASE module running on PC/WINDOWS NT

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

VA DEFINED

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

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

*) If you have no experience with the Fe-C system, it may seem reasonable to keep fcc, bcc, cementite and graphite.

TDB_DFECRC: **rest p fcc bcc cem gra**
 FCC_A1 BCC_A2 CEMENTITE
 GRAPHITE RESTORED
 TDB_DFECRC: **get**
 REINITIATING GES5
 ELEMENTS
 SPECIES
 PHASES
 PARAMETERS ...
 Rewind to read functions 41
 FUNCTIONS

List of references for assessed data

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

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

-OK-

TDB_DFECRC: **go pol**

POLY version 3.32, Aug 2001
 POLY_3:

*) Start with the initial fcc alloy. Compute it as a state of equilibrium in order to get its
 properties. Set all the other phases dormant in order to obtain their driving forces.

POLY_3: **s-c P=101325 T=1050 N=1 w(C)=.004**

POLY_3: **ch-st p bcc cem gra=dor**

POLY_3: **c-e**

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **l-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VWCS/: **P**

Output from POLY-3, equilibrium = 1, label A0 , database: DFECRC

Conditions:

P=1.01325E5, T=1050, N=1, W(C)=4E-3

DEGREES OF FREEDOM 0

Temperature 1050.00 K (776.85 C), Pressure 1.013250E+05
 Number of moles of components 1.00000E+00, Mass 5.50434E+01
 Total Gibbs energy -4.52242E+04, Enthalpy 3.05639E+04, Volume 7.17737E-06

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	1.8331E-02	4.0000E-03	8.6832E-02	-2.1335E+04	SER
FE	9.8167E-01	9.9600E-01	5.3467E-03	-4.5670E+04	SER

BCC_A2 Status DORMANT Driving force 2.7134E-03
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mass fractions:
 FE 9.99877E-01 C 1.22812E-04

CEMENTITE Status DORMANT Driving force -2.3017E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mass fractions:
 FE 9.33106E-01 C 6.68943E-02

FCC_A1 Status ENTERED Driving force 0.0000E+00
 Number of moles 1.0000E+00, Mass 5.5043E+01 Mass fractions:
 FE 9.96000E-01 C 4.00000E-03

GRAPHITE Status DORMANT Driving force -8.5079E-01
 Number of moles 0.0000E+00, Mass 0.0000E+00 Mass fractions:
 C 1.00000E+00 FE 0.00000E+00
 POLY_3:

*) Bcc is the only phase with a tendency to form. You should thus consider a critical nucleus of bcc. Evaluate its radius and size.

POLY_3: **ent-sym var critr=2*1*Vm(bcc)/8.31451/T/DGM(bcc);**

POLY_3: **sh critr**

CRITR=6.183278E-7

POLY_3: **ent-sym var critN=4*3.14*critr**3/3/Vm(bcc);**

POLY_3:

*) Now you find the activation energy for the formation of the critical bcc nucleus.

POLY_3: **ent-sym var Q=DGM(bcc)*8.31451*T*critN;**

POLY_3: **eval**

Name(s):

CRITR=6.183278E-7

CRITN=1.3514482E-13

Q=3.2013704E-12

POLY_3:

*) You cannot yet evaluate the Gibbs energy of the fluctuation but you can evaluate the Gibbs energy of that material before the formation of the fluctuation.

POLY_3: **ent-sym var G0=(x(bcc,C)*mu(C)+x(bcc,Fe)*mu(Fe))*critN;**

POLY_3: **ent-sym var wbccC=w(bcc,C);**

POLY_3:

*) In order to find the Gibbs energy of the fluctuation, you must compute the fcc phase with the correct composition as a state of equilibrium.

POLY_3: **s-c w(C)=wbccC**

POLY_3: **c-e**

Using global minimization procedure

Using already calculated grid

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3:

*) Finally you get the activation energy for the fluctuation before it transforms into the new bcc structure.

POLY_3: **ent-sym var deltaG=critN*Gm-G0;**

POLY_3: **eval**

Name(s):

CRITR=6.183278E-7

```
CRITN=1.3514482E-13
Q=3.2013704E-12
G0=-6.1702231E-9
WBCCC=1.2281177E-4
DELTA G=2.0727424E-11
POLY_3: exit
CPU time          0 seconds
```

Comments

It is interesting to compare the activation energy for the fcc fluctuation, ΔG , with the activation energy for the critical bcc nucleus, Q . ΔG is about 10 times as large. It would thus be cheaper to start the formation of the bcc phase by changing the structure first and then let the minute bcc nucleus grow to and above the critical size.