

Chapter 11. Directions of phase boundaries

[Problem 11.5. Congruent melting points](#)

[Problem 11.6. Vertical phase boundaries](#)

11.5. Congruent melting points

Determine the curvatures of the two phase boundaries at the congruent transformation point for bcc/sigma in the Fe-Cr system.

Hint

You may evaluate the curvature of a curve from three points. The transformation point is one and you may compute one point on each side by requiring that T should be 0.1 K lower, for instance.

Instructions for using T-C

With POLY you can evaluate the slope at any point of a phase boundary directly. You don't need to use the equation derived in Section 11.4. It would thus be possible to evaluate the curvature from the slopes in two points. On the other hand, it often happens that a phase changes its properties rather suddenly at a composition close to the transformation point. It may thus be interesting to study the slopes in the two points mentioned in the Hint and check if it would be necessary to make two evaluations of the curvature by using two points on each side of the congruent point.

Prompts, commands and responses

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

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

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

```
PARAMETERS ...
Rewind to read functions          25
FUNCTIONS ....
```

List of references for assessed data

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

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

-OK-

TDB_DFECRC: **go pol**

POLY version 3.32, Aug 2001

POLY_3:

*) The two phases must have the same composition when they are in equilibrium at the transformation point.

POLY_3: **s-c P=101325 w(bcc,Cr)-w(sigma,Cr)=0**

POLY_3: **ch-st p sigma bcc=fix 1**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 274 grid points in 0 s

8 ITS, CPU TIME USED 0 SECONDS

POLY_3: **sh T**

T=1105.2128

POLY_3:

*) You have found the transformation temperature and may call it the congruent temperature.

POLY_3: **ent-sym var Tcon=T;**

POLY_3:

*) You have already shown the congruent temperature and could easily enter a slightly lower temperature as a condition for the two new points. In order to avoid the risk of making a typing error you could instead enter a symbol for it.

POLY_3: **ent-sym var Tnew=Tcon-0.1;**

POLY_3: **s-c T=Tnew**

POLY_3:

*) You must remove another condition and that should be the one that is no longer valid.

POLY_3: **s-c w(bcc,Cr)-w(sigma,Cr)=none**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 274 grid points in 0 s

26 ITS, CPU TIME USED 0 SECONDS

POLY_3:

*) Store and show the compositions and slopes of the phases at this temperature.

POLY_3: **ent-sym var xb1=x(bcc,Cr);**

POLY_3: **ent-sym var xs1=x(sigma,Cr);**

POLY_3: **ent-sym var slob1=x(bcc,Cr).T;**

POLY_3: **ent-sym var slos1=x(sigma,Cr).T;**

POLY_3: **eval**

POLY_3:

XB1=0.44974952

XS1=0.45332381

SLOB1=2.3473964E-2

SLOS1=5.6520113E-3

POLY_3:

*) The slopes are positive and this equilibrium is thus situated to the left of the congruent point. The other point for each curve is situated to the right and can be found by giving a start value on that side.

POLY_3: **s-s-v y(bcc,Cr)=.6**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Using already calculated grid

10 ITS, CPU TIME USED 0 SECONDS

POLY_3: **ent-sym var xb2=x(bcc,Cr);**

POLY_3: **ent-sym var xs2=x(sigm,Cr);**

POLY_3: **ent-sym var slob2=x(bcc,Cr).T;**

POLY_3: **ent-sym var slos2=x(sigm,Cr).T;**

POLY_3:

*) You can now evaluate the curvatures defined as $d^2T/dx^2 = d(dT/dx)/dx$

POLY_3: **ent-sym var curvb=(1/slob2-1/slob1)/(xb2-xb1);**

POLY_3: **ent-sym var curvs=(1/slos2-1/slos1)/(xs2-xs1);**

POLY_3: **eval**

Name(s):

TCON=1105.2128

TNEW=1105.1128

XB1=0.44974952

XS1=0.45332381

SLOB1=2.3473964E-2

SLOS1=5.6520113E-3

XB2=0.45922615

XS2=0.45562949

SLOB2=-2.3917906E-2

SLOS2=-5.8721891E-3

CURVB=-8907.1779

CURVS=-150594.82

POLY_3: **exit**

CPU time 0 seconds

Comments

Slob1 and slob2 have almost the same magnitude and so have slos1 and slos2. The two-phase field is thus fairly symmetric around the congruent point and there is no sign of a drastic change of properties at the congruent composition. It was not necessary to evaluate different values for the curvatures on the two sides of the congruent point.

11.6. Vertical phase boundaries

The phase boundary bcc/fcc in the Fe-C system is retrograde, i.e., the solubility of C in bcc which starts from zero at the transition point of 911°C reaches a maximum value at some lower temperature and then decreases and approaches zero at low temperatures. Evaluate the temperature of maximum solubility with high accuracy.

Hint

Rather than just comparing the solubility at various temperatures it may be more accurate to evaluate the slope of the phase boundary and evaluate where it goes through zero.

Instructions for using T-C

In T-C you can evaluate the slope directly using the “.” operator. You don’t need to use the equation in Section 11.4.

Prompts, commands and responses

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

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

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

List of references for assessed data

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

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

-OK-

```
TDB_DFECRC: go pol
```

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

```
POLY_3:
```

*) You must start with an initial equilibrium. Bcc transforms to fcc at 911°C and you should thus choose a somewhat lower temperature. Even though you know what phases you like to take part in the equilibrium, it is often convenient to start prescribing the composition of the system.

```
POLY_3: s-c P=101325 T=850 N=1 w(C)=.01
```

```
POLY_3: c-e
```

```
Using global minimization procedure
Calculated 274 grid points in 0 s
Found the set of lowest grid points in 0 s
```

Calculated POLY solution 0 s, total time 0 s
 POLY_3:

*) Since you like to step along the bcc boundary when in equilibrium with fcc, it is convenient to use **fix 1** for bcc and **fix 0** for fcc as conditions for the single equilibrium introducing the stepping procedure. Instead you should remove the conditions for N and w(C).

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

POLY_3: **ch-st p fcc=fix 0**

POLY_3: **s-c N=none w(C)=none**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 274 grid points in 0 s

6 ITS, CPU TIME USED 0 SECONDS

POLY_3:

*) Before starting to step, you could just as well enter a symbol for the slope, which you will need later on.

POLY_3: **ent-sym fun slope=x(bcc,C).T;**

POLY_3: **s-a-v 1**

Condition /NONE/: **T**

Min value /0/: **800**

Max value /1/: **900**

Increment /2.5/:

POLY_3: **step**

Option? /NORMAL/:

No initial equilibrium, trying to add one 0

Phase Region from 850.000 for:

BCC_A2

FCC_A1

Calculated 23 equilibria

Phase Region from 850.000 for:

BCC_A2

FCC_A1

Calculated 23 equilibria

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

POLY_3: **post**

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

Setting automatic diagram axis

POST:

*) In practice, it is quite common to use mass% rather than mole fraction. Use that quantity for the x axis and the slope for the y axis.

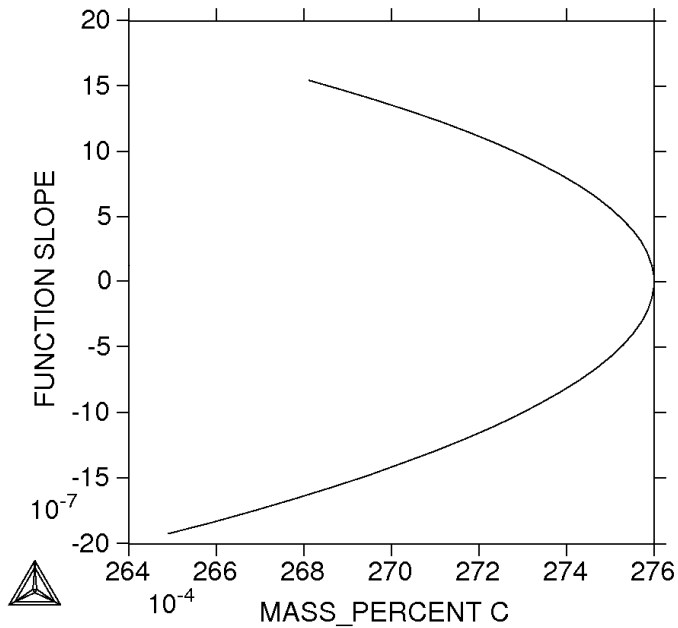
POST: **s-d-a x w-p C**

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

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

THERMO-CALC (2007.05.19:08.52) :
 DATABASE:DFECRC
 P=1.01325E5, FIXED PHASES: BCC_A2=1FCC_A1=0;



POST:

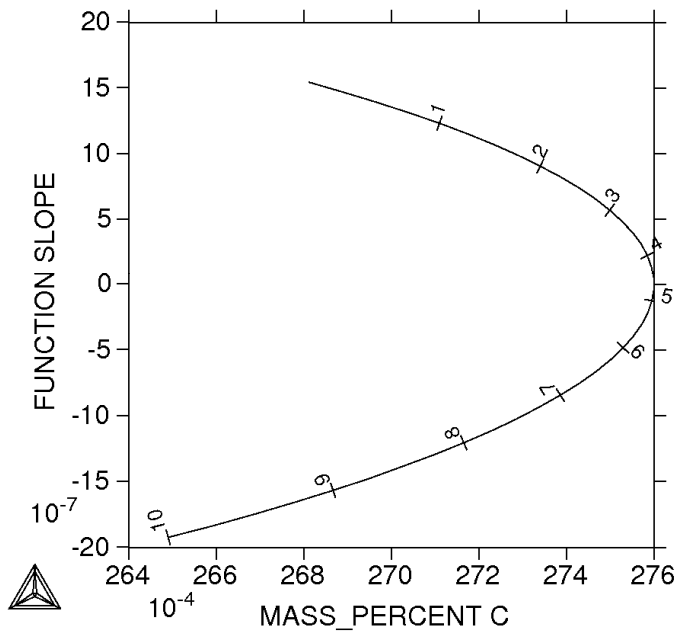
*) The maximum solubility is clearly shown. In order to get a rough idea of the temperature, you can introduce T as a third z axis and show its values as tic marks.

POST: **s-d-a z T**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:

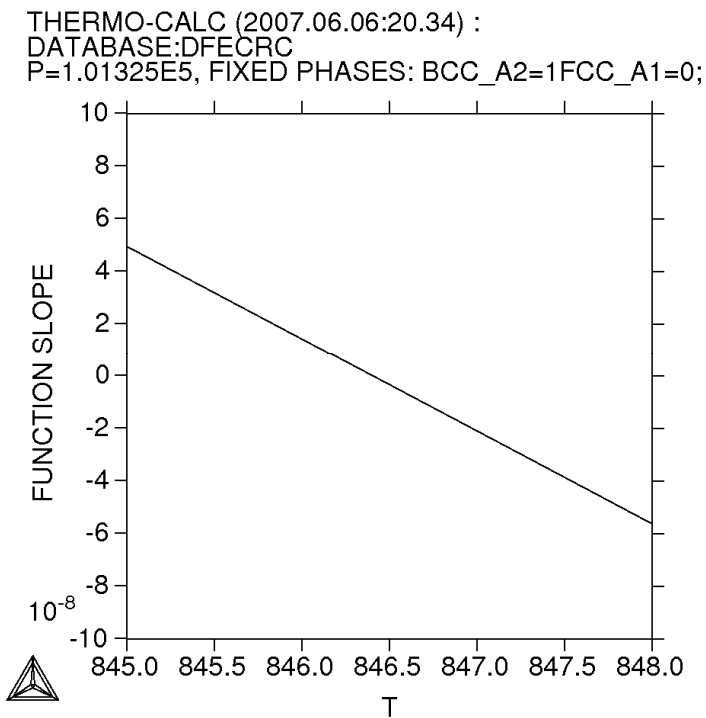
THERMO-CALC (2007.05.19:08.53) :
 DATABASE:DFECRC
 Z-AXIS = 800.0 + 10.00 * Z



POST:

*) From the tic marks you can see very well that the wanted temperature is between 845 and 848 K. In order to evaluate it with higher accuracy you could magnify the slope between these temperatures.

```
POST: s-d-a z none
POST: s-d-a x T
POST: s-s-s x 845 848
POST: s-s-s y n -1E-7 1E-7
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
```



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

Comments

It is easy to read the wanted temperature with good accuracy from the plot of the slope, $T = 846.4$ K.