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

Chapter 6. Stability

Problem 6.5A. Limit of stability
Problem 6.5B. Limit of stability
Problem 6.5C. Limit of stability
Problem 6.5D. Limit of stability
Problem 6.6. Limit of stability of alloys
Problem 6.9. Le Chatelier's principle

6.5A. Limit of stability

Compare numerically the values of \( \left( \frac{\partial T}{\partial S} \right)_{N} \) and \( \left( \frac{\partial T}{\partial S} \right)_{P} \) for pure diamond at 1000 K and 1 atm. Both expressions are used for defining stability.

**Hint**

The only difference between the two partial derivatives is that different quantities are kept constant. They are thus based on different sets of independent state variables.

**Instructions for using T-C**

T-C has a special operator for the evaluation of partial derivatives with respect to a state variable that could be either a potential or an extensive variable. Sometimes it works best with the potential in the denominator. Try both ways in the present cases.

**Prompts, commands and responses**

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

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

O VA DEFINED
STEAM OXYGEN HYDROGEN
REJECTED
CARBON_MONOXIDE CARBON_DIOXIDE METHANE
REJECTED
TDB_PGE0:

*) Notice that this database is mainly for oxides and O is thus defined automatically.
However, you don't want to include O.
TDB_PGE0: `rej-el O`
O REJECTED
TDB_PGE0: def-el C
C DEFINED
TDB_PGE0: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
DIAMOND :C1:
GRAPHITE :C1:
TDB_PGE0: rej p gra
GRAPHITE REJECTED
TDB_PGE0: get
REINITIATING GES5  ...... 
ELEMENTS  ...... 
SPECIES  ...... 
PHASES  .......
PARAMETERS ...
Rewind to read functions  1 
FUNCTIONS ....
-OK-
TDB_PGE0: go pol

POLY version 3.32, Aug 2001

POLY_3:
  *) You must define the system as given. That will directly give the correct set of independent
variables for one of the derivatives.
POLY_3: s-c P=101325 T=1000 N=1
POLY_3: c-e
Using global minimization procedure
Calculated 1 grid points in 0 s
POLY_3: ent-sym var derP1=1/S.T;
  *) In order to take the derivative with respect to S, that variable must be included in the set of
independent variables, i.e., it must have been used as a condition for the state of equilibrium.
POLY_3: s-c T=none S=
Value /19.84063161/:
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated 1 grid points in 0 s
  6 ITS, CPU TIME USED 0 SECONDS
POLY_3: ent-sym var derP2=T.S;

POLY_3: s-c P=none S=none T=1000 V=
Value /3.436459517E-06/:
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated 1 grid points in 0 s
  7 ITS, CPU TIME USED 0 SECONDS
POLY_3: ent-sym var derV1=1/S.T;

POLY_3: s-c T=none S=
Value /19.84063161/:
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated 1 grid points in 0 s
  6 ITS, CPU TIME USED 0 SECONDS
POLY_3: ent-sym var derV2=T.S;

*) Finally, you should again introduce S as an independent variable.
POLY_3: s-c T=none S=
Value /19.84063161/:
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated 1 grid points in 0 s
  6 ITS, CPU TIME USED 0 SECONDS
POLY_3: ent-sym var derV2=T.S;
POLY_3: eval
Name(s):
DERP1=46.544542
DERP2=46.544542
DERV1=47.169399
DERV2=47.169399
POLY_3: exit
CPU time  0 seconds
Comments

1) The two derivatives \( \text{derV} \) and \( \text{derP} \) have different values simply because there is a difference in what variables are kept constant.

2) They are both used for defining stability but it is known that the one using a potential as constant, instead of the conjugate extensive variable, should be smaller according to Eq. 6.30. That is indeed demonstrated by \( \text{derP} \) being smaller than \( \text{derV} \).

3) It is interesting to see that \( \frac{\partial Y}{\partial X} = \frac{1}{\partial X / \partial Y} \) but in order to get this satisfactory result you must use different sets of independent variables by including \( X \) in the first case and \( Y \) in the second.

6.5B. Limit of stability

Evaluate the stability of a supersaturated fcc alloy of Fe with 20 mol% C at 1200 and 1000 K and 1 atm.

**Hint**

A system is least stable against fluctuations of one extensive state variable while all but one of the other conjugate pairs are represented by the potential. The exception is one that has been chosen to define the size of the system, e.g. \( N_i \) where \( i \) is the main component. The preferable expression for the stability of the system would thus be \( B = 2(\partial \mu / \partial N_i)_{T,P,\mu_2,\cdots,\mu_n} \). However, it should be remembered that inside an unstable region this quantity may again turn positive while other expressions of stability have turned negative. It should thus be used only inside a stable region and when approaching an unstable region.

**Instructions for using T-C**

T-C offers the possibility of evaluating the partial derivative of a state variable under constant values of a set of independent state variables. The first state variable may then be regarded as a state function, function of that set of variables. You can make that evaluation by using those constant values as conditions for the equilibrium.

When the partial derivative represents a stability condition, then the denominator is an extensive variable and in order to define the size of the system one of the variables to be kept constant must also be extensive and one may choose the amount of the main component, \( N_i \). For a binary case one may choose \( T \) and \( P \) as the remaining independent variables. Usually, one may thus have a proper set of independent variables from the beginning and for a binary system one may thus evaluate the stability without changing the set of variables.

For a binary A-B system you can directly use the given \( T \), \( P \), \( N_A \) and \( N_B \) as conditions and that would be a complete set of independent variables.

**Prompts, commands and responses**

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

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

VA DEFINED
TDB_DFECCR: def el Fe C
FE C
DEFINED
TDB_DFECCR: rej p *
LIQUID: FCC_A1 BCC_A2
HCP_A3 CEMENTITE
GRAPHITE REJECTED
TDB_DFECCR: rest p fcc
FCC_A1 RESTORED
TDB_DFECCR: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 29
FUNCTIONS ....

List of references for assessed data

-425, also in NPL Report DMA(A)195 Rev. August 1990'
'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
C-Fe'
(1986); CR-Fe'

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

-O.K-
TDB_DFECCR: go pol

POLY version 3.32, Aug 2001
POLY_3:
*) Remember not to give the composition of the system with xC and N. You need NC and NFe
when later evaluating the partial derivative.
POLY_3: s-c P=101325 T=1200 N(C)=.2 N(Fe)=.8
POLY_3: c-e
Using global minimization procedure
Calculated 19648 grid points in 0 s
Found the set of lowest grid points in 0 s
Calculated POLY solution 0 s, total time 0 s
POLY_3:
*) Introduce a function for the stability because you will use it several times.
POLY_3: ent-sym fun stab=mu(C).N(C);
POLY_3: sh stab

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

STAB=153193.58

POLY_3: s-c T=1000

POLY_3: c-e

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: sh stab

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

STAB=142107.57

POLY_3: s-c T=800

POLY_3: c-e

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: sh stab

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

STAB=131021.55

POLY_3:

*) You have thus found that the stability decreases at lower temperatures. Can that be taken as an indication that you are approaching a miscibility gap that exists at higher C contents that widens towards lower temperatures? Examine the stability for higher C contents at 800 K.

POLY_3: s-c N(C)=.3 N(Fe)=.7

POLY_3: c-e

POLY_3: sh stab

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

STAB=137861.05

POLY_3: s-c N(C)=.4 N(Fe)=.6

POLY_3: c-e

POLY_3: sh stab

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

STAB=165457.06

POLY_3: exit

CPU time 4 seconds

Comments
1) The stability for this C content decreases at lower temperatures but that is not a sign of a miscibility gap at higher C contents and lower temperatures.

2) It is not possible to step in N(C) in order to get a curve for the stability as function of the C content. The reason is that one would also have to adjust the value of N(Fe), which is not possible in POLY's stepping procedure. To set the condition for Fe as N=1 does not help because the stability can be evaluated only if N(Fe) is used as a condition, i.e. as an independent variable.

6.5C. Limit of stability

The stability can be defined in many ways. Each method expresses the stability in its own way and the resulting values for the same case may differ appreciably. However, there are two general principles. 1) A method using a set of independent variables containing a potential gives a lower value than a method using the conjugate extensive variable. 2) At the limit of stability all methods using potentials except for two extensive variables give the value zero. Test if your data bank system can confirm the first principle. The second one will be tested in Problem 6.5D.

**Hint**

You may consider the bcc phase in the Fe-Cr-C system at 1 atm and 700 K and for 1 mol\% C and 5 mol\% Cr.

**Instructions for using T-C**

1) Always start by first computing the equilibrium for the given composition and then changing the condition for one of the contents to a condition for another variable. Then you should compute the same equilibrium with this new definition and finally evaluate the stability using the "." operator.

2) Start by examining methods based on \( \partial \mu_C / \partial N_C \) where T, P and two quantities related to Fe and C are kept constant. Try the combinations \((N_C;N_Fe), (N_C;x_Fe), (N_C;\mu_Fe), (\mu_C;\mu_Fe), (x_C;\mu_Fe)\) and \((x_C;x_Fe)\).

**Prompts, commands and responses**

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

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

VA DEFINED
TDB_DFECRC: def-el Fe Cr C
FE                      CR                      C
DEFINED
TDB_DFECRC: rej p *
LIQUID:L                FCC_A1                  BCC_A2
HCP_A3                  SIGMA                   CEMENTITE
M3C2   M7C3   M23C6

GRAPHITE REJECTED

TDB DFECRC: rest p bcc
BCC A2 RESTORED

TDB DFECRC: get
REINITIATING GES5 ..... ELEMENTS ..... SPECIES ..... PHASES ..... PARAMETERS ...
Rewind to read functions 33 FUNCTIONS ....

List of references for assessed data

'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'

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

-OK-

TDB DFECRC: go pol

POLY version 3.32, Aug 2001

POLY_3:

*) You like to know the stability at a given composition. You are not interested in looking for a composition with a lower Gibbs energy. You could thus inactivate the global minimization procedure.

POLY_3: set-min
Settings for global minimization:
Use global minimization /Y/: N
Settings for general calculations:
Force positive definite Phase Hessian /N/: N
Control minimization step size /N/: N
POLY_3: s-c P=101325 T=700 N(Cr)=.05 N(C)=.01 N(Fe)=.94
POLY_3: c-e
Global equilibrium calculation turned off, you can turn it on with
SET_MINIMIZATION_OPTIONS Y,,,;
8 ITS, CPU TIME USED 0 SECONDS

POLY_3: ent-sym fun stabCr=mu(Cr).N(Cr);
POLY_3: sh stabCr
STABCR=94553.346

POLY_3: s-c N(Fe)=none x(Fe)=
Value /.94/:

POLY_3: c-e
6 ITS, CPU TIME USED 0 SECONDS

POLY_3: sh stabCr
STABCR=52753.451

POLY_3:
*) One could possibly expect to get the same result here since \(N(Fe)\) and \(x(Fe)\) are both equal to 0.94. However, when \(N(Cr)\) is increased during a derivation, \(N(Fe)\) must also increase if \(x(Fe)\) should stay constant. The effect on \(\mu(Cr)\) will thus be less.

POLY_3: \(s-c \ x(Fe)=none \ \mu(Fe)=\)
Value /-24676.72301/:  
6 ITS, CPU TIME USED 0 SECONDS
POLY_3: \(sh \ stabCr\)
STABCR=11570.964

POLY_3:
*) This is a lowest stability value in agreement with Eq. 6.30.

POLY_3: \(s-c \ N(C)=none \ \mu(C)=\)
Value /29447.02461/:  
6 ITS, CPU TIME USED 0 SECONDS
POLY_3: \(sh \ stabCr\)
STABCR=0

POLY_3:
*) This result is expected from the Gibbs-Duhem relation because \(\mu(Cr)\) cannot vary when all the other potentials are constant.

POLY_3: \(s-c \ \mu(C)=none \ x(C)=\)
Value /.00999999969/:  
6 ITS, CPU TIME USED 0 SECONDS
POLY_3: \(sh \ stabCr\)
STABCR=-2.3453967E-12

POLY_3:
*) This is practically zero considering the limited accuracy of the numerical calculations. The explanation is that \(N(Cr)\) is here the only quantity defining the size. It does not affect the composition and \(\mu(Cr)\) cannot vary with \(N(Cr)\).

POLY_3: \(s-c \ \mu(Fe)=none \ x(Fe)=\)
Value / .9400000018/:  
6 ITS, CPU TIME USED 0 SECONDS
POLY_3: \(sh \ stabCr\)
STABCR=2.2458789E-10

POLY_3:
*) This is also practically zero and here it is more immediately evident that the composition cannot vary with \(N(Cr)\) since \(x(C)\) and \(x(Fe)\) are already given and, consequently, \(x(C)\) cannot vary, nor \(\mu(Cr)\).

POLY_3: \(exit\)
CPU time 0 seconds

Comment

1) A stability expression based on two extensive variables kept constant will get more severe, i.e., get a lower numerical value, if one of those variables is replaced by its conjugate intensive variable.

2) In all partial derivatives, expressing stability, there must be at least one extensive variable in addition to the one used in the derivative.

6.5D. Limit of stability
Test the second principle defined in Problem 6.5C.

**Hint**

As for Problem 6.5C you may again consider the bcc phase in the Fe-Cr-C system at 1 atm and 700 K and for 1 mol% C. There is a bcc miscibility gap and the stability limit, i.e., the spinodal, falls close to 6 mol% Cr. You may thus examine the stability for 5, 6 and 7 mol% Cr.

**Instructions for using T-C**

1) For each alloy you should first compute the equilibrium for the given composition and then change one of the contents to the chemical potential of the same compound. Then you should compute the same equilibrium with this new definition and can finally evaluate a stability using the "." operator.

2) For all three alloys use $\frac{\partial \mu_C}{\partial N_C}$ with $\mu_C$ and $N_{Fe}$ and $\frac{\partial \mu_C}{\partial N_C}$ with $\mu_C$ and $N_{Fe}$ as independent variables but also the quantity QF that POLY can evaluate directly for any state of equilibrium.

**Prompts, commands and responses**

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

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

VA DEFINED
TDB_DFECRC: def-el Fe Cr C
FE                      CR                      C
DEFINED
TDB_DFECRC: rej p *
LIQUID:L                FCC_A1                  BCC_A2
HCP_A3                  SIGMA                  CEMENTITE
M3C2                    M7C3                  M23C6
GRAPHITE REJECTED
TDB_DFECRC: rest p bcc
BCC_A2 RESTORED
TDB_DFECRC: get
REINITIATING GES5 ..... 
ELEMENTS ...... 
SPECIES ...... 
PHASES ...... 
PARAMETERS .... 
Rewind to read functions 33 
FUNCTIONS ....

List of references for assessed data

'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.'
   (1986); CR-Fe'
'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'
   C-CR-Fe'

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

-OK-
TDB_DFECRC: go pol

POLY version 3.32, Aug 2001

POLY_3:
   *) You should prevent POLY from reacting to the miscibility gap and split alloys into two
   phases. You should thus omit the global minimization procedure.

POLY_3: set-min N
   Settings for global minimization:
   Settings for general calculations:
   Force positive definite Phase Hessian /N/:  
   Control minimization step size /N/: 
   POLY_3: s-c P=101325 T=700 x(Cr)=.05 x(C)=.01 N=1
   POLY_3: c-e
   Global equilibrium calculation turned off, you can turn it on with
   SET_MINIMIZATION_OPTIONS Y,,,;
   8 ITS, CPU TIME USED 0 SECONDS

POLY_3:
   *) You like to step across the system and then plot Gm and QF as functions of the Cr content.

POLY_3: s-a-v 1 x(Cr) 0 .99
   Increment /.02475/: 

POLY_3: step
   Option? /NORMAL/:
   No initial equilibrium, trying to add one 0

   Phase Region from 0.500000E-01 for:
      BCC_A2
   Calculated 41 equilibria

   Phase Region from 0.500000E-01 for:
      BCC_A2
   Calculated 6 equilibria
   *** Buffer saved on file: USERPROFILE\RESULT.POLY3

POLY_3: post

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

POST: s-d-a x m-f Cr
POST: s-d-a y Gm
POST: plot
OUTPUT TO SCREEN OR FILE /SCREEN/:
*) Start again from the initial alloy. The Cr content has been varied during the stepping procedure and should be restored.

POLY_3: s-c x(Cr) = .05
POLY_3: c-e

6 ITS, CPU TIME USED 0 SECONDS
Now you should introduce the set of independent variables for the first partial derivative.

\[
\text{POLY}_3: \quad s-c \ x(Cr)=\text{none} \ N(Cr)=.05 \ N=\text{none} \ N(Fe)=.94
\]

Value /29447.02446/:

\[
\text{POLY}_3: \quad c-e
\]

6 ITS, CPU TIME USED 0 SECONDS

\[
\text{POLY}_3: \quad *) \text{ You will evaluate partial derivatives several times and should thus defined functions for them. In order to save the value from an evaluation, you should further save it as a variable.}
\]

\[
\text{POLY}_3: \quad \text{ent-sym fun stabCr}=\mu(Cr).N(Cr);
\]

\[
\text{POLY}_3: \quad \text{ent-sym var stCr05}=\text{stabCr};
\]

Value /-27169.30695/:

\[
\text{POLY}_3: \quad c-e
\]

6 ITS, CPU TIME USED 0 SECONDS

\[
\text{POLY}_3: \quad \text{ent-sym fun stabC}=\mu(C).N(C);
\]

\[
\text{POLY}_3: \quad \text{ent-sym var stC05}=\text{stabC};
\]

\[
\text{POLY}_3: \quad \text{sh stCr05 stC05 QF(bcc)}
\]

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

\[
\text{STC05}=14288.414
\]

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

\[
\text{STC05}=92759.74
\]

QF(BCC_A2)=0.12733409

\[
\text{POLY}_3: \quad *) \text{ All these quantities are positive and agree that this alloy is not in a region of instability. Now, do the same for the next alloy. Start with its composition.}
\]

\[
\text{POLY}_3: \quad s-c \ N(C)=\text{none} \ x(C)=.01 \ \mu(Cr)=\text{none} \ x(Cr)=.06 \ N(Fe)=.93
\]

\[
\text{POLY}_3: \quad c-e
\]

6 ITS, CPU TIME USED 0 SECONDS

\[
\text{POLY}_3: \quad s-c \ x(Cr)=\text{none} \ N(Cr)=.06 \ x(C)=\text{none} \ \mu(C)=
\]

Value /27201.66822/:

\[
\text{POLY}_3: \quad c-e
\]

6 ITS, CPU TIME USED 0 SECONDS

\[
\text{POLY}_3: \quad \text{ent-sym var stCr06}=\text{stabCr};
\]

Value /-26297.18603/:

\[
\text{POLY}_3: \quad c-e
\]

6 ITS, CPU TIME USED 0 SECONDS

\[
\text{POLY}_3: \quad \text{ent-sym var stCr06}=\text{stabC};
\]

\[
\text{POLY}_3: \quad \text{sh stCr06 stC06 QF(bcc)}
\]

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

\[
\text{STC06}=779.57015
\]

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

STC06=6313.5985
QF(BCC_A2)=8.4326953E-3

POLY_3:

*) The values of all these quantities have decreased considerably. You are approaching the limit of stability. Continue to the third alloy.

POLY_3: s-c N(C)=none x(C)=.01 mu(Cr)=none x(Cr)=.07 N(Fe)=.92

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: s-c x(Cr)=none N(Cr)=.07 x(C)=none mu(C)=

Value /25010.47882/:

POLY_3: c-e

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: ent-sym var stCr07=stabCr;

POLY_3: s-c mu(C)=none N(C)=.01 N(Cr)=none mu(Cr)=

Value /-25583.61545/:

POLY_3: c-e

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: ent-sym var stC07=stabC;

POLY_3: sh stCr07 stC07 QF(bcc)

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

STCR07=-7473.93

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

STC07=-73357.28
QF(BCC_A2)=-9.5413995E-2

POLY_3:

*) This time all the values are negative and this alloy is thus inside the region of instability.

POLY_3: exit
CPU time 0 seconds

Comments

1) You have confirmed that the three methods of expressing the stability give very different values but they agree on the limit of stability.

2) The QF symbol represents a further method of expressing the stability that has been normalized in order to give comparable values under different conditions. The sharp break in the middle of the diagram indicates that there was a change of method. It will be further discussed in Problem 6.6.

3) If you draw a double tangent to the Gm curve you may find that the miscibility gap starts above about 20 mol% Cr. And the curve indicates that the inflection point falls at about 40 mol% Cr. However, then you found that the limit of stability falls at about 7 mol% Cr. The explanation is
that the system is really three-dimensional and the double tangent in your section at a constant value of 1 mol% C cannot be used.

6.6. Limit of stability of alloys

Compare the value of \[
\begin{vmatrix}
G_{22} & G_{23} \\
G_{32} & G_{33}
\end{vmatrix}
\] with \((\partial \mu_2 / \partial N_2)_{T,P,N_1,N_i}\) and \((\partial \mu_3 / \partial N_3)_{T,P,N_2,N_i}\) for the fcc phase in an Fe alloy with 1 mol% C and 5 mol% Cr at 1200 K and 1 atm.

**Hint**

The determinant is equal to \(G_{22}G_{33} - G_{23}G_{32}\) where \(G_2\) is identical to \((\partial G / \partial N_2)_{T,P,N_1,N_i}\) in a ternary system. The set of independent variables are thus \(T, P, N_1, N_2\) and \(N_3\) for all the quantities in the determinant. Each partial derivative involves a chemical potential.

**Instructions for using T-C**

Of course, the \(G_{ij}\) quantities can also be expressed as partial derivatives, \(G_{ij} = (\partial \mu_i / \partial N_j)_{T,P,N_1,N_i}\), where the subscript \(k\) represents all the other components. Notice that \(G_{ij} = G_{ji}\). All the quantities required for solving this problem are thus available with the operator "," but you must be careful with the choices of conditions, which will define the set of independent variables.

POLY can directly give information on the stability through a quantity available under the symbol QF(phase).

**Prompts, commands and responses**

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

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

VA DEFINED
TDB_DFECRC: def-el Fe Cr C
FE C
CR

DEFINED
TDB_DFECRC: rej p *
TDB_DFECRC: rest p bcc
TDB_DFECRC: get
REINITIATING GES5 ..... ELEMENTS ..... SPECIES ..... PHASES ..... PARAMETERS ..... Rewind to read functions 100 FUNCTIONS ..... 

List of references for assessed data


'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.'


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

-OK-

TDB_DFECRC: go pol

POLY version 3.32, Aug 2001

POLY_3: set-min N

Settings for global minimization:
Settings for general calculations:
Force positive definite Phase Hessian /N/:
Control minimization step size /N/:

POLY_3: s-c P=101325 T=700 N(Fe)=.94 N(C)=.01 N(Cr)=.05

POLY_3: c-e

Global equilibrium calculation turned off, you can turn it on with
SET_MINIMIZATION_OPTIONS Y,,,,
7 ITS, CPU TIME USED 0 SECONDS

POLY_3:

*) Start by evaluating and saving all the G_{ij} etc. but omitting all with i<j due to symmetry.

POLY_3: ent-sym var GFeFe=mu(Fe).N(Fe);
POLY_3: ent-sym var GCC=mu(C).N(C);
POLY_3: ent-sym var GCrCr=mu(Cr).N(Cr);
POLY_3: ent-sym var GFeC=mu(Fe).N(C);
POLY_3: ent-sym var GFeCr=mu(Fe).N(Cr);
POLY_3: ent-sym var GCCr=mu(C).N(Cr);

POLY_3: ent-sym var detFeC=GFeFe*GCC-GFeC**2;
POLY_3: ent-sym var detFeCr=GFeFe*GCrCr-GFeCr**2;
POLY_3: ent-sym var detCCr=GCC*GCrCr-GCCr**2;

POLY_3: ent-sym var stab=QF(bcc);

POLY_3:

*) Change a condition in order to evaluate \( \frac{\partial \mu_2}{\partial N_2} \), where 1 stands for Fe, 2 stands for C and 3 for Cr. You should thus use \( \mu_{Cr} \) as a condition.

POLY_3: s-c N(Cr)=none mu(Cr)=
Value /-27169.30695/;

POLY_3: c-e

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: ent-sym var BCCFe=mu(C).N(C);
POLY_3: ent-sym var BFeFe=mu(Fe).N(Fe);

POLY_3: s-c mu(Fe)=none N(Cr)=.05 N(C)=none mu(C)=
Value /29447.02446/;

POLY_3: c-e

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: ent-sym var BCrCrFe=mu(Cr).N(Cr);

POLY_3: s-c mu(Cr)=none N(Cr)=.01 N(Fe)=none mu(Fe)=
Value /-24676.72301/;

POLY_3: c-e
As explained in the comments, you are also asked to evaluate the following products.

\[
\begin{align*}
\text{POLY}_3: & \quad \text{ent-sym var } p\text{CrCrFe}=\text{BCrCrFe}\star\text{GCC}; \\
\text{POLY}_3: & \quad \text{ent-sym var } p\text{CCFe}=\text{BCCFe}\star\text{GCrCr}; \\
\text{POLY}_3: & \quad \text{ent-sym var } p\text{FeFeCr}=\text{BFeFeCr}\star\text{GCC}; \\
\text{POLY}_3: & \quad \text{ent-sym var } p\text{CCCr}=\text{BCCCr}\star\text{GFeFe}; \\
\text{POLY}_3: & \quad \text{ent-sym var } p\text{FeFeC}=\text{BFeFeC}\star\text{GCrCr}; \\
\text{POLY}_3: & \quad \text{ent-sym var } p\text{CrCrC}=\text{BCrCrC}\star\text{GFeFe}; \\
\end{align*}
\]

Name(s):

GFEFE=85.78498
GCC=613836.07
GCCR=94553.346
GFEC=5276.6037
GECR=-2668.0784
GCCR=-221967.36
DETFEC=2.4815368E7
DETFECR=992614.73
DETFCCR=8.7707438E9
STAB=0.12733409
BCCFE=92759.74
BFEFEC=10.497933
BCRCRFE=14288.414
BFEFECR=40.426703
BCRCRC=11570.964
PCRCRFE=8.7707438E9
PCCFE=8.7707438E9
PFEFECR=2.4815368E7
PCCCR=2.4815373E7
PFEFEC=992614.73
PCRCRC=992614.93

Comments

1) In this exercise you were primarily interested in the three determinants because each one of them treated two components in equivalent ways. Indeed they are all positive in the present case but their values differ much. Next you were interested in the six B-quantities which were supposed to express the stability as based on partial derivatives. All of them are also positive but again they differ much. However, when they were multiplied by the correct second derivative of G, their values were modified to agree in pairs and each pair agrees with one of the determinants. The reason of this agreement is given by Eq. 6.35 where the second factor is identical to a second derivative of G for a ternary system and there are no more factors.

2) One may wonder what method of expressing the stability of an alloy should be preferred. It may seem that the partial derivatives have the most direct thermodynamic basis but unfortunately they give different values. The method based on a determinant may be preferred because it treats both solutes in the same way. However, it does not have the same value if constructed with different pairs of components. It must be accepted that the stability has different values depending on what kind of fluctuation one considers. However, all the alternatives discussed identify the same limit of stability.
3) The particular stability function QF(phase) that POLY can give directly has been normalized in a very approximate way, comparable to multiplying by x1x2/RT for a binary system. It is not comparable to any of the stabilities discussed here but it also predicts the same limit of stability.

6.9. Le Chatelier's principle

Consider the internal process $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ when a gas with 2 mole of H and 1 mole of O from the equilibrium at 1800 K and 1 atm is (a) compressed adiabatically to 10 bar so rapidly that no reaction can occur. Evaluate T and the molar volume, $V_m$. Then, suppose (b) there is time for the process to go to a new equilibrium under 10 bar but still without any exchange of heat. Finally suppose (c) the temperature will eventually return to 1800 K but still under 10 bar. Evaluate the final $V_m$. Compare the resulting T and $V_m$ with initial values and discuss how the results can be used as examples of Le Chatelier’s principle.

**Hint**

(a) For the adiabatic compression, S is not changed because there is no internal reaction. That can be used as a condition for finding the new state after compression. However, it is a frozen-in state and would have to be evaluated from a module that can handle states of non-equilibrium. S will change during (b) due to the internal process but not H because there is no exchange of enthalpy with the surroundings during an isobaric adiabatic change. The final state (c) is easily found as the state of equilibrium at 1800 K.

**Instructions for using T-C**

When using the TAB module in T-C you should remember that it gives properties per mole of formula units, in this case mole of species, not mole of atoms. POLY normally works with mole per atom or component but can deliver extensive quantities per formula unit under symbols with the subscript $f$ instead of $m$.

**Prompts, commands and responses**

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

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

VA  DEFINED
TDB_PSUB: def-sp O2 H2 H2O1
O2                      H2                      H2O1
DEFINED
TDB_PSUB: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/: 
GAS:G        :H2 H2O1 O2:
H2O1_L       :H2O1:
TDB_PSUB: rej p H2O_L
H2O_L REJECTED
TDB_PSUB: get
REINITIATING GES5 ..... 
ELEMENTS .....
SPECIES ......
PHASES ......
PARAMETERS ...
FUNCTIONS ......

List of references for assessed data

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

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

-OK-

TDB_PSUB: go pol

POLY version 3.32, Aug 2001

POLY_3: s-c P=101325 T=1800

POLY_3:
*) The proportions of H and O are such that they correspond exactly to 1 mole of H2O and you could just as well enter that as the initial amount.

POLY_3: s-i-a N(H2O1)=1
POLY_3: c-e
Using global minimization procedure
Calculated 8409 grid points in 0 s
Found the set of lowest grid points in 0 s
Calculated POLY solution 0 s, total time 0 s

POLY_3: l-e

OUTPUT TO SCREEN OR FILE /SCREEN/:
Options /VWCS/:
*) Choose option N in order to see the constitution.
Options /VWCS/: N

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

Conditions:
P=1.01325E5, T=1800, N(H)=2, N(O)=1
DEGREES OF FREEDOM 0

Temperature 1800.00 K (1526.85 C), Pressure 1.013250E+05
Number of moles of components 3.00000E+00, Mass 1.80148E+01
Total Gibbs energy -6.46092E+05, Enthalpy -1.78445E+05, Volume 1.47835E-01

Component  Moles  W-Fraction  Activity  Potential  Ref.stat
H   2.0000E+00 1.1190E-01 2.9517E-06 -1.9057E+05 SER
O   1.0000E+00 8.8810E-01 2.0475E-08 -2.6496E+05 SER

GAS  Status ENTERED  Driving force 0.0000E+00
Number of moles 3.0000E+00, Mass 1.8015E+01
Mass fractions:
O  8.88103E-01  H  1.11897E-01

Constitution:
H2O1 9.97337E-01  H2 1.77564E-03  O2 8.87822E-04

POLY_3:
*) You can see that there is a slight dissociation into H2 and O2. Record the essentials of the state. For the entropy, obtain the value per formula unit to be used in TAB.

POLY_3: ent-sym var T1=T;
POLY_3: ent-sym var Vm1=Vm;
POLY_3: ent-sym var Hm1=Hm;
POLY_3: ent-sym var Sm1=Sm;
POLY_3: ent-sym var Sf1=Sf(gas);
POLY_3: eval
In addition to the usual properties given in the table, you like to add the volume.

**TAB:**  
Name: Vfroz  
Function: V  
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):  
H2 / .001775644781 /  
H2O1 / .9973365328 /  
Pressure / 101325 /: 1E6  
Low temperature limit / 298.15 /: 1800  
High temperature limit / 2000 /: 3000  
Step in temperature / 100 /:  
Output file / SCREEN /:

---

* The wanted value of Sf1 = 259.57338 is found very close to 2600 K. Increase the precision.

**TAB:**  
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):  
H2 / .001775644781 /  
H2O1 / .9973365328 /  
Pressure / 1000000 /:  
Low temperature limit / 1800 /: 2550  
High temperature limit / 3000 /: 2600  
Step in temperature / 100 /: 5  
Output file / SCREEN /:  

---

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<th>T</th>
<th>Cp</th>
<th>H</th>
<th>S</th>
<th>G</th>
<th>Vfroz</th>
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<td>Cp (Joule/K)</td>
<td>H (Joule)</td>
<td>S (Joule/K)</td>
<td>G (Joule)</td>
<td>Vfroz (Joule)</td>
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</tr>
</tbody>
</table>

TAB:

*) You may choose T=2585 and go to POLY in order to use the values of H and Vfroz, both of which are per formula unit.

TAB:

POLY_3: ent-sym var Ta=2585;
POLY_3: ent-sym var Vma=2.14930E-02*Sm1/Sf1;
POLY_3: ent-sym var Hma=-1.36774E+05*Sm1/Sf1;

*) Compute the equilibrium according to (b). You can use the value of Hfa as condition.

POLY_3: s-c P=1E6 T=none Hm=Hma

POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated 8409 grid points in 0 s
10 ITS, CPU TIME USED 0 SECONDS
POLY_3: ent-sym var Tb=T;
POLY_3: ent-sym var Vmb=Vm;

*) Compute the equilibrium according to (c).

POLY_3: s-c Hm=none T=1800

POLY_3: c-e
Using global minimization procedure
Calculated 8409 grid points in 0 s
Found the set of lowest grid points in 0 s
Calculated POLY solution 0 s, total time 0 s

POLY_3: ent-sym var Vmc=Vm;
POLY_3: eval

Name(s):
T1=1800
VM1=4.9278451E-2
HM1=-59481.526
SM1=86.601345
SF1=259.57338
TA=2585
VMA=7.1706996E-3
HMA=-45631.846
Comments

1) This case concerns the effect of an increased P. The conjugate variable to –P is V and for the first change you find \( \frac{dV}{d(-P)} = \frac{0.00717 - 0.04928}{-10 - (-1)} = 0.004679 \). It is a positive value as expected for a stable system. The total change after the internal process has reached equilibrium is \( \frac{dV}{d(-P)} = \frac{0.00701 - 0.04928}{-10 - (-1)} = 0.004697 \). The change has thus increased further by the internal process. This is as expected theoretically because the variable that was primarily changed was a potential and the effect concerned an extensive variable.

2) Usually it is expected that LeChatelier's principle should predict a reversal of the first effect, called LeChatelier's modification. However, that applies when the variable that is primarily changed is an extensive variable and the effect is then studied on a potential.

3) You may think that the temperature obeys LeChatelier's principle because it is first increased from 1800 to 2585 K and then decreased (modified) to 2505 K as an effect of the internal process. However, T is not the conjugate variable to –P and the principle should not be applied to such a combination of variables.