

Chapter 6. Stability

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6.5A. Limit of stability

Compare numerically the values of $(\partial T / \partial S)_{V,N}$ and $(\partial T / \partial S)_{P,N}$ 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_PGEO:
```

*) Notice that this database is mainly for oxides and O is thus defined automatically.

However, you don't want to include O.

```
TDB_PGEO: rej-el O
O REJECTED
```

```

TDB_PGEO: def-el C
  C DEFINED
TDB_PGEO: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
  DIAMOND      :C1:
  GRAPHITE     :C1:
TDB_PGEO: rej p gra
  GRAPHITE REJECTED
TDB_PGEO: get
  REINITIATING GES5 .....
  ELEMENTS .....
  SPECIES .....
  PHASES .....
  PARAMETERS ...
  Rewind to read functions          1
  FUNCTIONS ....
  -OK-
TDB_PGEO: 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;

```

*) You change to a new set of independent variables by introducing V instead of P.

```

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:

```

*) Finally, you should again introduce S as an independent variable.

```

POLY_3: s-c T=none S=
Value /19.84063161/:
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 $\text{der}V$ and $\text{der}P$ 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 $\text{der}P$ being smaller than $\text{der}V$.
- 3) It is interesting to see that $(\partial Y / \partial X) = 1 / (\partial X / \partial Y)$ 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 $B = 2(\partial \mu_c / \partial N_c)_{T,P,\mu_2,\dots,\mu_{c-1},N_1}$. 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_1 . 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_DFECRC: **def-el Fe C**

FE C

DEFINED

TDB_DFECRC: **rej p ***

LIQUID:L FCC_A1 BCC_A2

HCP_A3 CEMENTITE

GRAPHITE REJECTED

TDB_DFECRC: **rest p fcc**

FCC_A1 RESTORED

TDB_DFECRC: **get**

REINITIATING GES5

ELEMENTS

SPECIES

PHASES

PARAMETERS ...

Rewind to read functions 29

FUNCTIONS

List of references for assessed data

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

'Byeong-Joo Lee, unpublished revision (1991); C-Cr-Fe-Ni'

'P. Gustafson, Scan. J. Metall. vol 14, (1985) p 259-267 TRITA 0237 (1984);
 C-Fe'

'J-O Andersson, B. Sundman, CALPHAD Vol 11, (1987), p 83-92 TRITA 0270
 (1986); CR-Fe'

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

-OK-

TDB_DFECRC: **go pol**

POLY version 3.32, Aug 2001

POLY_3:

*) Remember not to give the composition of the system with x_C and N . You need N_C and N_{Fe}
 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 $\partial\mu_{Cr} / \partial N_{Cr}$ 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

```

'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:
```

*) 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/:
```

```
Control minimization step size /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 $N(\text{Fe})$ and $x(\text{Fe})$ are both equal to 0.94. However, when $N(\text{Cr})$ is increased during a derivation, $N(\text{Fe})$ must also increase if $x(\text{Fe})$ should stay constant. The effect on $\mu(\text{Cr})$ will thus be less.

```
POLY_3: s-c x(Fe)=none mu(Fe)=
Value /-24676.72301/:
POLY_3: c-e
  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/:
POLY_3: c-e
  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 $\mu(\text{Cr})$ cannot vary when all the other potentials are constant.

```
POLY_3: s-c mu(C)=none x(C)=
Value /.00999999969/:
POLY_3: c-e
  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 $N(\text{Cr})$ is here the only quantity defining the size. It does not affect the composition and $\mu(\text{Cr})$ cannot vary with $N(\text{Cr})$.

```
POLY_3: s-c mu(Fe)=none x(Fe)=
Value /.9400000018/:
POLY_3: c-e
  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 $N(\text{Cr})$ since $x(\text{C})$ and $x(\text{Fe})$ are already given and, consequently, $x(\text{C})$ cannot vary, nor $\mu(\text{Cr})$.

```
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 $\partial\mu_{Cr}/\partial N_{Cr}$ with μ_C and N_{Fe} and $\partial\mu_C/\partial N_C$ with μ_{Cr} 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

```

'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:

*) 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**

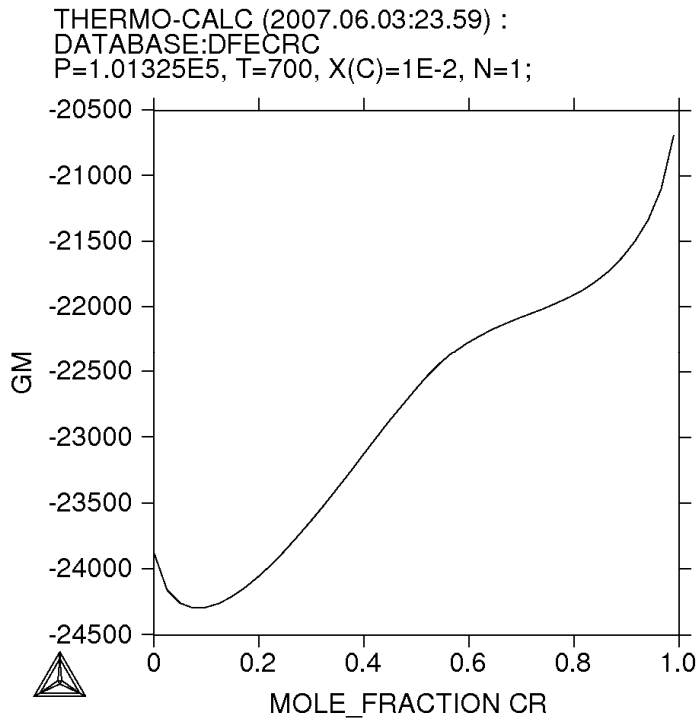
POLY-3 POSTPROCESSOR VERSION 3.2 , last update 2002-12-01

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

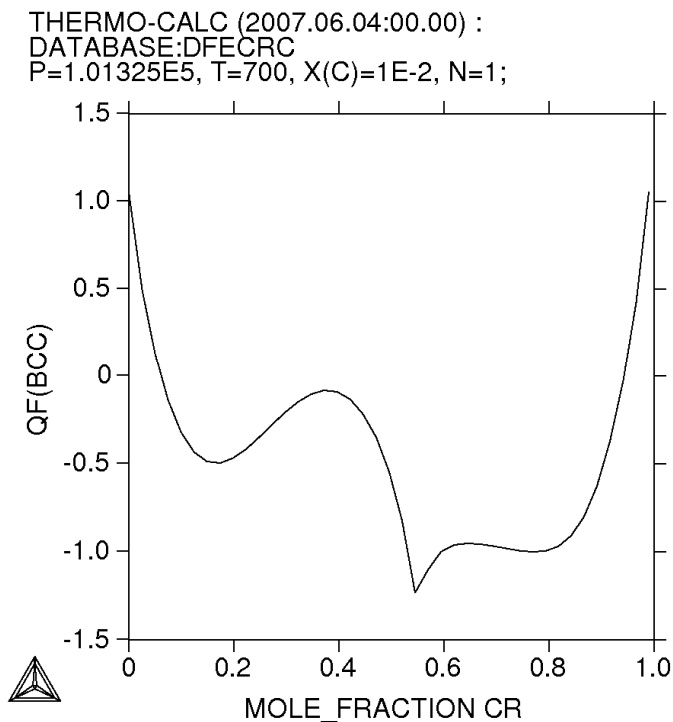
POST: **s-d-a y Gm**

POST: **plot**

OUTPUT TO SCREEN OR FILE /SCREEN/:



POST: **s-d-a y QF(bcc)**
 POST: **plot**
 OUTPUT TO SCREEN OR FILE /SCREEN/:



POST: **b**
 POLY_3:
 *) 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

POLY_3:

*) Now you should introduce the set of independent variables for the first partial derivative.

POLY_3: **s-c x(Cr)=none N(Cr)=.05 N=none N(Fe)=.94**

POLY_3: **s-c x(C)=none mu(C)=**

Value /29447.02446/:

POLY_3: **c-e**

6 ITS, CPU TIME USED 0 SECONDS

POLY_3:

*) 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.

POLY_3: **ent-sym fun stabCr=mu(Cr).N(Cr);**

POLY_3: **ent-sym var stCr05=stabCr;**

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

Value /-27169.30695/:

POLY_3: **c-e**

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: **ent-sym fun stabC=mu(C).N(C);**

POLY_3: **ent-sym var stC05=stabC;**

POLY_3: **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

STCR05=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

STC05=92759.74

QF(BCC_A2)=0.12733409

POLY_3:

*) 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.

POLY_3: **s-c N(C)=none x(C)=.01 mu(Cr)=none x(Cr)=.06 N(Fe)=.93**

POLY_3: **c-e**

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: **s-c x(Cr)=none N(Cr)=.06 x(C)=none mu(C)=**

Value /27201.66822/:

POLY_3: **c-e**

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: **ent-sym var stCr06=stabCr;**

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

Value /-26297.18603/:

POLY_3: **c-e**

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: **ent-sym var stC06=stabC;**

POLY_3: **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

STCR06=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
POLY_3: c-e
```

```
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 G_m 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 $(\partial\mu_2/\partial N_2)_{T,P,\mu_3,N_1}$ and $(\partial\mu_3/\partial N_3)_{T,P,\mu_2,N_1}$ 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 $\mu_2 = (\partial G/\partial N_2)_{T,P,N_3,N_1}$ 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, $G_{ij} = (\partial\mu_i/\partial N_j)_{T,P,N_i,N_k}$, 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 CR C
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
```

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

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

-OK-

TDB_DFECRC: **go pol**

POLY version 3.32, Aug 2001

POLY_3: **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 $(\partial\mu_2/\partial N_2)_{T,P,\mu_3,N_1}$, where 1 stands for Fe, 2 stands

for C and 3 for Cr. You should thus use μ_{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 BFeFeC=mu(Fe).N(Fe);**

POLY_3: **s-c mu(Cr)=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: **ent-sym var BFeFeCr=mu(Fe).N(Fe);**

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

Value /-24676.72301/:

POLY_3: **c-e**

```

6 ITS, CPU TIME USED 0 SECONDS
POLY_3: ent-sym var BCrCrC=mu(Cr).N(Cr);
POLY_3: ent-sym var BCCCr=mu(C).N(C);
POLY_3:

```

*) As explained in the comments, you are also asked to evaluate the following products.

```

POLY_3: ent-sym var pCrCrFe=BCrCrFe*GCC;
POLY_3: ent-sym var pCCFe=BCCFe*GCrCr;
POLY_3: ent-sym var pFeFeCr=BFeFeCr*GCC;
POLY_3: ent-sym var pCCCr=BCCCr*GFeFe;
POLY_3: ent-sym var pFeFeC=BFeFeC*GCrCr;
POLY_3: ent-sym var pCrCrC=BCrCrC*GFeFe;
POLY_3: eval

```

Name(s):

```

GFEFE=85.78498
GCC=613836.07
GCRCR=94553.346
GFEC=5276.6037
GFECR=-2668.0784
GCCR=-221967.36
DETFEC=2.4815368E7
DETFECR=992614.73
DETCCR=8.7707438E9
STAB=0.12733409
BCCFE=92759.74
BFEFEC=10.497933
BCRCRFE=14288.414
BFEFECR=40.426703
BCRCRC=11570.964
BCCCR=289274.1
PCRCRFE=8.7707438E9
PCCFE=8.7707438E9
PFEFECR=2.4815368E7
PCCCR=2.4815373E7
PFEFEC=992614.73
PCRCRC=992614.93
POLY_3: exit
CPU time          0 seconds

```

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 $QF(\text{phase})$ that POLY can give directly has been normalized in a very approximate way, comparable to multiplying by x_1x_2/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**

Name(s):
 T1=1800
 VM1=4.9278451E-2
 HM1=-59481.526
 SM1=86.601345
 SF1=259.57338
 POLY_3: **go tab**
 TAB:

*) In addition to the usual properties given in the table, you like to add the volume.

TAB: **ent-fun**
 Name: **Vfroz**
 Function: **V;**
 TAB: **tab-sub gas**
 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/:

O U T P U T F R O M T H E R M O - C A L C
 2007. 5. 5 21.58.19

Column 6: Vfroz V

Phase : GAS Pressure : 1000000.00
 Specie: *

```
*****
  T      Cp      H      S      G      Vfroz
  (K)    (Joule/K) (Joule) (Joule/K) (Joule)
  *****
1800.00  5.00803E+01 -1.78286E+05  2.40538E+02 -6.11254E+05  1.49661E-02
1900.00  5.08907E+01 -1.73237E+05  2.43268E+02 -6.35446E+05  1.57976E-02
2000.00  5.16530E+01 -1.68110E+05  2.45898E+02 -6.59905E+05  1.66290E-02
2100.00  5.23693E+01 -1.62908E+05  2.48435E+02 -6.84622E+05  1.74605E-02
2200.00  5.30413E+01 -1.57637E+05  2.50887E+02 -7.09589E+05  1.82919E-02
2300.00  5.36703E+01 -1.52301E+05  2.53259E+02 -7.34797E+05  1.91234E-02
2400.00  5.42574E+01 -1.46905E+05  2.55556E+02 -7.60238E+05  1.99548E-02
2500.00  5.48034E+01 -1.41451E+05  2.57782E+02 -7.85906E+05  2.07863E-02
2600.00  5.53089E+01 -1.35945E+05  2.59941E+02 -8.11792E+05  2.16177E-02
2700.00  5.57746E+01 -1.30391E+05  2.62037E+02 -8.37892E+05  2.24492E-02
2800.00  5.62021E+01 -1.24792E+05  2.64074E+02 -8.64198E+05  2.32806E-02
2900.00  5.66195E+01 -1.19150E+05  2.66053E+02 -8.90705E+05  2.41121E-02
3000.00  5.70243E+01 -1.13468E+05  2.67979E+02 -9.17407E+05  2.49435E-02
  *****
```

TAB:

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

TAB: **tab-sub gas**
 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/:

OUTPUT FROM THERMO - CALC
2007. 5. 5 21.58.19

Column 6: Vfroz V

Phase : GAS Pressure : 1000000.00
Specie: *

```
*****
  T      Cp      H      S      G      Vfroz
  (K)    (Joule/K) (Joule) (Joule/K) (Joule)
*****
2550.00  5.50612E+01 -1.38705E+05  2.58870E+02 -7.98822E+05  2.12020E-02
2555.00  5.50864E+01 -1.38429E+05  2.58977E+02 -8.00117E+05  2.12436E-02
2560.00  5.51115E+01 -1.38154E+05  2.59085E+02 -8.01412E+05  2.12851E-02
2565.00  5.51365E+01 -1.37878E+05  2.59193E+02 -8.02707E+05  2.13267E-02
2570.00  5.51615E+01 -1.37602E+05  2.59300E+02 -8.04004E+05  2.13683E-02
2575.00  5.51863E+01 -1.37326E+05  2.59407E+02 -8.05300E+05  2.14099E-02
2580.00  5.52110E+01 -1.37050E+05  2.59514E+02 -8.06598E+05  2.14514E-02
2585.00  5.52356E+01 -1.36774E+05  2.59621E+02 -8.07896E+05  2.14930E-02
2590.00  5.52602E+01 -1.36498E+05  2.59728E+02 -8.09194E+05  2.15346E-02
2595.00  5.52846E+01 -1.36222E+05  2.59835E+02 -8.10493E+05  2.15762E-02
2600.00  5.53089E+01 -1.35945E+05  2.59941E+02 -8.11792E+05  2.16177E-02
*****
```

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: b

```
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;
POLY_3:
```

*) 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
```

TB=2505.3707
VMB=7.0103201E-3
VMC=4.9907737E-3

POLY_3: **exit**
CPU time 0 seconds

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 $dV/d(-P)=(0.00717-0.04928)/(-10-(-1))=0.004679$. It is a positive value as expected for a stable system. The total change after the internal process has reached equilibrium is $dV/d(-P)=(0.00701-0.04928)/(-10-(-1))=0.004697$. 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.