

Chapter 2. Manipulation of thermodynamic quantities

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2.1. Evaluation of one characteristic function from another

- 1) Test if your system can yield the value of a state variable that in principle could be used as a characteristic state function.
- 2) Test if it can accept values of a set of variables that are the natural set for another characteristic state function.
- 3) Try to use the value of a site fraction as condition.

Hint

An advanced data bank systems may be composed of modules, one of which stores thermodynamic properties of individual phases as fundamental equations representing some characteristic state function, usually the Gibbs energy, G , as function of its natural set of variables, e.g. T , P and N for G of a pure substance. However, since G is an extensive state function it can be expressed with the molar Gibbs energy, $G = N \cdot G_m$, and it is sufficient to store $G_m(T, P)$ for a pure substance. Multiplying with N is a trivial matter. For a phase with more components, G may be stored as a function of T , P , N_1 , N_2 etc. and, in principle, one could then evaluate G for a set of values of these variables, the natural set for G . However, one still prefers to store the information on G as a function of the molar Gibbs energy. For a simple case one would use a function $G_m(T, P, x_1, x_2, \dots)$ and it is a trivial matter to evaluate N and all the x_i from the set of N_i values. For a phase with sublattices one prefers $G_m(T, P, y_1', y_2', \dots, y_1'', y_2'', \dots)$ where y_i are the site fractions, i.e., mole fractions defined for each sublattice. In a simple case one can also evaluate the site fractions from the set of N_i values. In more complicated cases there is one or more degrees of freedom and there is not only one set of y_i values that satisfies the set of N_i values. The equilibrium set of y_i values is then found by minimizing the Gibbs energy. In the same way, when there is more than one phase and each has

no degree of freedom, there is a degree of freedom for the material to be distributed between the phases. The equilibrium composition and amount of each phase are then again found by minimizing the Gibbs energy.

To the customer all this is like a black box and s/he simply trusts that it contains information stored as a fundamental equation based on the Gibbs energy. S/he will thus give the values of T, P, N_1 , N_2 , etc. when setting the conditions or s/he will use T, P, N and x_1 , x_2 etc. Your data bank system will probably accept the mass, B_i , instead of N_i and the mass fraction, w_i , instead of x_i .

The above conditions are all based on the natural set of variables for G and it is an interesting question whether your data bank system can also accept other sets of variables as conditions. Could it even behave as if it were based on another characteristic state function?

Start with a unary system of your choice and set conditions for the state to be studied. Evaluate S after computing equilibrium. Then, enter the S value as a condition and remove one of the initial conditions. First, remove the initial T value, which makes a conjugate pair with S. Compute equilibrium and evaluate T. Then, enter the T value and, instead, remove the initial P value, which is part of another conjugate pair. Compute equilibrium and evaluate P. Again you should obtain its initial value if the equilibrium module can accept a set of conditions that does not contain one variable from each pair of conjugate variables.

Instructions for using T-C

Choose carbon from the DFECRC database and reject all phases but graphite. Later, go back to the database module, add Fe and reject all phases but bcc and fcc.

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 C
C DEFINED
TDB_DFECRC: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
LIQUID:L :C:
> This is metallic liquid solution phase, with C species
GRAPHITE :C:
TDB_DFECRC: rej p liq
LIQUID:L REJECTED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 11
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'

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 conditions for the natural set of variables for G.

POLY_3: **s-c P=101325 T=1100 N=1**

POLY_3: **sh S**

S=0

POLY_3:

*) You can get no reliable information without first computing equilibrium.

POLY_3: **c-e**

Using global minimization procedure

Calculated 1 grid points in 0 s

POLY_3: **sh S**

S=26.528829

POLY_3:

*) For H the natural set of variables is S, P, N. Use this set by entering the S value.

POLY_3: **s-c S**

Value /26.5288292/:

POLY_3: **c-e**

*** ERROR 2003 IN QMJBSV

*** Degrees of freedom not zero

POLY_3:

*) You must delete an old condition when you have introduced a new one. Inspect the
conditions and decide which one to delete.

POLY_3: **l-c**

P=1.01325E5, T=1100, N=1, S=26.5288

DEGREES OF FREEDOM -1

POLY_3: **s-c T=none**

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 1 grid points in 0 s

6 ITS, CPU TIME USED 0 SECONDS

POLY_3: **sh T**

T=1100.

POLY_3:

*) Fine! It is thus possible to use S, P and N as conditions. It is as if POLY were using a
fundamental equation based on H as the characteristic state function. Now try to delete P
instead.

POLY_3: **s-c P=none T=**

Value /1100/:

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: **sh P**

P=101347.89

POLY_3:

*) This is not quite exact but good enough considering numerical difficulties. This time the variables were T, S and N. It is thus demonstrated that POLY does not even require conditions for one variable from each pair of conjugate variables.

Now you should turn to the bcc and fcc phases in the Fe-C system in order to test if one could exchange w(C) for one of the site fractions.

```
POLY_3: b
TDB_DFECRC: def-el Fe
FE DEFINED
TDB_DFECRC: rej p *
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: **b**

```
POLY version 3.32, Aug 2001
POLY_3: s-c T=1100 P=101325 N=1 w(C)=.002
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/:
```

*) This time you may like to inspect the constitution of the phases, not just their compositions.

```
Options /VWCS/: N
Output from POLY-3, equilibrium =          1, label A0 , database: DFECRC
```

```
Conditions:
T=1100, P=1.01325E5, N=1, W(C)=2E-3
DEGREES OF FREEDOM 0
```

```
Temperature 1100.00 K ( 826.85 C), Pressure 1.013250E+05
Number of moles of components 1.00000E+00, Mass 5.54423E+01
Total Gibbs energy -4.90638E+04, Enthalpy 3.17008E+04, Volume 7.24065E-06
```

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	9.2319E-03	2.0000E-03	3.5177E-02	-3.0615E+04	SER
FE	9.9077E-01	9.9800E-01	4.5925E-03	-4.9236E+04	SER

```

BCC_A2                               Status ENTERED           Driving force  0.0000E+00
Number of moles 1.4953E-01, Mass 8.3481E+00           Mass fractions:
FE 9.99907E-01  C  9.33735E-05
Constitution:
Sublattice 1, Number of sites  1.0000E+00
FE 1.00000E+00
Sublattice 2, Number of sites  3.0000E+00
VA 9.99855E-01  C  1.44732E-04

```

```

FCC_A1                               Status ENTERED           Driving force  0.0000E+00
Number of moles 8.5047E-01, Mass 4.7094E+01           Mass fractions:
FE 9.97662E-01  C  2.33798E-03
Constitution:
Sublattice 1, Number of sites  1.0000E+00
FE 1.00000E+00
Sublattice 2, Number of sites  1.0000E+00
VA 9.89104E-01  C  1.08963E-02

```

POLY_3:

*) Using the N option, the whole constitution is now presented, i.e., the fractions of the phases and the site fractions on their sublattices. Much more information is available but you have to ask for it by the command **show**. Try some.

POLY_3: **sh s Sm(bcc) Sm(fcc)**

S=73.422333

SM(BCC_A2)=71.973154

SM(FCC_A1)=73.677135

POLY_3:

*) Try to use the site fraction of C in fcc as a condition and delete another, related condition.

POLY_3: **s-c w(C)=none y(fcc,C#2)=**

Value /.01089625966/:

POLY_3: **c-e**

Normal POLY minimization, not global

Convergence problems, increasing smallest sitefraction from 1.00E-30

to hardware precision 2.00E-12. You can restore using SET-NUMERICAL-LIMITS

*** ERROR 1611 IN QEQUIL

*** TOO MANY ITERATIONS

Give the command INFO TROUBLE for help

POLY_3:

*) Maybe your set of conditions was not logical although you tried to replace a condition with a related one. Inspect the set.

POLY_3: **l-c**

T=1100, P=1.01325E5, N=1, Y(FCC_A1,C#2)=1.08963E-2

DEGREES OF FREEDOM 0

POLY_3:

*) Now you may realize that the equilibrium constitution of fcc is directly related to the temperature of the equilibrium. You could not prescribe values of both at the same time.

Delete the T condition and instead take back the alloy composition.

POLY_3: **s-c w(C)=.002 T=none**

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=1980.7016

POLY_3:

*) This is an unexpected result. You should inspect this equilibrium in detail.

POLY_3: **1-e**

OUTPUT TO SCREEN OR FILE /SCREEN/:

Options /VWNS/:

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

Conditions:

P=1.01325E5, N=1, W(C)=2E-3, Y(FCC_A1,C#2)=1.08963E-2

DEGREES OF FREEDOM 0

Temperature 1980.70 K (1707.55 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 5.54423E+01

Total Gibbs energy -1.24190E+05, Enthalpy 6.66737E+04, Volume 7.74613E-06

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	9.2319E-03	2.0000E-03	1.4534E-03	-1.0760E+05	SER
FE	9.9077E-01	9.9800E-01	5.2589E-04	-1.2434E+05	SER

BCC_A2 Status ENTERED Driving force 0.0000E+00

Number of moles 1.0000E+00, Mass 5.5442E+01

Mass fractions:

FE 9.98000E-01 C 2.00000E-03

Constitution:

Sublattice 1, Number of sites 1.0000E+00

FE 1.00000E+00

Sublattice 2, Number of sites 3.0000E+00

VA 9.96894E-01 C 3.10598E-03

*) This equilibrium does not seem to concern the bcc/fcc equilibrium you were interested in.

It is a one-phase state of bcc. It is evident that the condition on w(C) at the same time as

y(fcc,C#2) does not really add anything. If you are really interested in knowing the

temperature where y(fcc,C#2) has a certain value when bcc is in equilibrium with fcc, then

you should fix the two phases and remove the condition on w(C) and another one, which

should be N=1 unless you like to let P differ from 1 atm.

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

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

POLY_3: **1-c**

P=1.01325E5, Y(FCC_A1,C#2)=1.08963E-2

FIXED PHASES

BCC_A2=1 FCC_A1=1

DEGREES OF FREEDOM 0

POLY_3: **c-e**

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

Calculated 274 grid points in 0 s

9 ITS, CPU TIME USED 0 SECONDS

POLY_3: **sh T**

T=1793.0299

POLY_3:

*) This is a correct value, which could be confirmed by listing the equilibrium, but it may be

unexpected. Actually, the bcc/fcc equilibrium at low temperatures disappears above 1184 K

but it returns at much higher temperatures. In order to find the point you are interested in, you

could set a lower temperature as a start value. Instead of the value T=1980.7 K, which was

automatically taken as a start value from the current state of equilibrium.

POLY_3: **s-s-v T**

Value: /1793.029875/: 1000

POLY_3: **c-e**

Normal POLY minimization, not global

```

Testing POLY result by global minimization procedure
Calculated          274  grid points in          0  s
 18 ITS, CPU TIME USED  0 SECONDS
POLY_3: sh T
T=1100.
POLY_3: exit
CPU time          0  seconds

```

Comments

- 1) From the stored fundamental equation one can compute an equilibrium after defining the conditions using its natural set of variables. All characteristic state functions can then be evaluated from the state of equilibrium but also many other properties.
- 2) It is also possible to define the conditions using the natural set of variables for another characteristic state function. In fact, the conditions can be defined in various ways with a considerable flexibility. It is not even necessary to use one state variable from each pair of conjugate variables when defining the conditions but any set of conditions may not be appropriate.
- 3) The requirement that a phase must take part in the equilibrium plays the role of a condition.
- 4) It should be mentioned that there is actually a second solution to the final set of conditions for the Fe-C system. By setting the start value $T=1900$ you should get the value $T=1793.0299$. That is another correct solution. The bcc/fcc equilibrium disappears over 911°C but it returns at very much higher temperatures.
- 5) By properly adjusting a start value you can help POLY to find the equilibrium you are interested in.

2.2. Internal variables at equilibrium

At equilibrium $D=0$ and the driving force, D , can be evaluated in different ways that all should give the same result. For instance, $D = -(\partial G / \partial \xi)_{T,p} = -(\partial F / \partial \xi)_{T,v}$ where ξ is an internal variable.

Demonstrate this by a numerical calculation on an Fe-C alloy with 1 mol% C at 1 bar and 1050 K.

Hint

- 1) First you must choose a system with an internal variable. For systems with more than one phase, the fraction of a phase is such a variable. For one-phase systems with a variable degree of order, one can choose some site fraction as the internal variable. For a gas, there may be a variable constitution due to reactions between molecules. For the present demonstration it may be convenient to choose a binary system with two phases, which can both dissolve the two components.
- 2) With a binary bcc+fcc alloy you may establish two slightly different constitutions by computing equilibrium at two temperatures, 1 K apart. Define this difference as $\Delta \xi = N_{fcc2} - N_{fcc1}$ where N_{fcc} is the amount of the fcc phase. Examine their properties at a quite different temperature where they are far from equilibrium. In order not to change their constitutions at that

temperature you must evaluate the bcc and fcc phases separately and for extensive properties you can then add the contributions from the phases.

- 3) For the first constitution you evaluate V_1 , G_1 and F_1 . For the second one you evaluate G_2 and approximate the driving force according to G as $DFG = -(G_2 - G_1) / (N_{fcc2} - N_{fcc1})$ for the values of T and P used as conditions. To get the corresponding quantity for the Helmholtz energy, F , you must compare two states of the same T and V , not P . When you first evaluate V_2 for the second constitution you find that it differs from V_1 because of the difference in constitution, mainly in the amounts of the phases. You must find a new pressure that makes the volume of the second constitution equal to V_1 . Just try a different P and evaluate its effect on V_2 . Then you may find the proper P by extrapolation.

Instructions for using T-C

Remember that the Helmholtz energy has the symbol A instead of F in T-C. Choose an Fe-C alloy with 1 mol% C at 1 atm. Establish the equilibrium constitution at 999 and 1000 K and study the properties at 1050 K.

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:
  *) For case 1, equilibrate the alloy at 1000 K.
POLY_3: s-c P=1E5 T=1000 N=1 x(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:
  *) Store information on the constitution.
POLY_3: ent-sym var Nbcc1=NP(bcc);
POLY_3: ent-sym var Nfcc1=NP(fcc);
POLY_3: ent-sym var xCbcc1=x(bcc,C);
POLY_3: ent-sym var xCfcc1=x(fcc,C);
POLY_3:
  *) Increase T to 1050 K and consider each phase as its own system. Start with the fcc
  constituent by excluding bcc.
POLY_3: ch-st p bcc=dor
POLY_3: s-c T=1050 x(C)=xCfcc1 N=Nfcc1
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:
  *) It is now possible to evaluate various properties of the fcc phase with the composition from
  1000 K. Remember that T-C uses A as the symbol for Helmholtz energy, which we denote
  by F.
POLY_3: ent-sym var Vfcc1=V;
POLY_3: ent-sym var Gfcc1=G;
POLY_3: ent-sym var Ffcc1=A;
POLY_3:
  *) Next, study a system composed of the bcc constituent.
POLY_3: ch-st p fcc=dor
POLY_3: ch-st p bcc=ent 1
POLY_3: s-c x(C)=xCbcc1 N=Nbcc1
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:
  *) When you now evaluate the properties of bcc you can also evaluate the values for the
  whole alloy in case 1.
POLY_3: ent-sym var Vbcc1=V;
POLY_3: ent-sym var V1=Vfcc1+Vbcc1;
POLY_3: ent-sym var G1=Gfcc1+G;
POLY_3: ent-sym var F1=Ffcc1+A;
POLY_3:
  *) This will be the initial state and you should evaluate the changes of G and F when the
  constitution is changed to the one characteristic of 999 K, i.e. case 2. Compute that state by
  entering fcc. Bcc is already entered.
POLY_3: ch-st p fcc=ent 1

```

POLY_3: **s-c T=999 x(C)=.01 N=1**

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:

*) Store the new constitution and evaluate the difference in amount of fcc.

POLY_3: **ent-sym var Nbcc2=NP(bcc);**

POLY_3: **ent-sym var Nfcc2=NP(fcc);**

POLY_3: **ent-sym var deltaN=Nfcc2-Nfcc1;**

POLY_3: **ent-sym var xCbcc2=x(bcc,C);**

POLY_3: **ent-sym var xCfcc2=x(fcc,C);**

POLY_3:

*) Take each one of the phases to 1050 K. Start with the fcc constituent by making bcc dormant.

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

POLY_3: **s-c T=1050 x(C)=xCfcc2 N=Nfcc2**

POLY_3: **c-e**

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **ent-sym var Vfcc2=V;**

POLY_3: **ent-sym var Gfcc2=G;**

*) And now the bcc constituent.

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

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

POLY_3: **s-c x(C)=xCbcc2 N=Nbcc2**

POLY_3: **c-e**

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

Calculated POLY solution 0 s, total time 0 s

POLY_3: **ent-sym var Vbcc2=V;**

POLY_3: **ent-sym var V2=Vfcc2+Vbcc2;**

POLY_3: **ent-sym var G2=Gfcc2+G;**

POLY_3:

*) You may now evaluate the driving force according to G and compare the volumes.

POLY_3: **ent-sym var DFG=(G1-G2)/deltaN;**

POLY_3: **sh deltaN Vbcc1 Vbcc2 Vfcc1 Vfcc2 V1 V2**

DELTAN=-2.6550306E-3

Vbcc1=5.3286538E-6

Vbcc2=5.3480902E-6

Vfcc1=1.9439908E-6

Vfcc2=1.9248294E-6

V1=7.2726447E-6

V2=7.2729196E-6

POLY_3:

*) The volume has increased from V1 to V2 mainly because the amount of fcc, the denser phase, has decreased by $\Delta N = -0.0026550306$. In order to find the change of the Helmholtz energy you need the pressure that would make the volume for case 2 equal to V1. As a first attempt you may increase the pressure by 50 atm. Start with the bcc constituent that is already entered.

POLY_3: **s-c P=51E5**

POLY_3: **c-e**

Using global minimization procedure

Calculated 137 grid points in 0 s

Found the set of lowest grid points in 0 s

```

Calculated POLY solution          0 s, total time          0 s
POLY_3: ent-sym var Vbcc3=V;
POLY_3:

```

*) Continue with the fcc constituent.

```

POLY_3: ch-st p bcc=dor
POLY_3: ch-st p fcc=ent 1
POLY_3: s-c x(C)=xCfcc2 N=Nfcc2
POLY_3: c-e
Using global minimization procedure
Calculated          137 grid points in          0 s
Found the set of lowest grid points in          0 s
Calculated POLY solution          0 s, total time          0 s
POLY_3: ent-sym var Vfcc3=V;
POLY_3: ent-sym var V3=Vbcc3+Vfcc3;
POLY_3: sh V1 V3
V1=7.2726447E-6
V3=7.2726966E-6
POLY_3:

```

*) You were quite fortunate. Most of the difference has disappeared. However, you should still make an adjustment by extrapolation.

```

POLY_3: ent-sym var P4=1E5+50E5*(V2-V1)/(V2-V3);
POLY_3: sh P4
P4=6264323.6
POLY_3:

```

*) Try to use this P value. Since you hope that P4 will be good enough, you might evaluate F at the same time that you examine if the volume is kept constant at P4. Remember that fcc is already the entered constituent.

```

POLY_3: s-c P=P4
POLY_3: c-e
Using global minimization procedure
Calculated          137 grid points in          0 s
Found the set of lowest grid points in          0 s
Calculated POLY solution          0 s, total time          0 s
POLY_3: ent-sym var Ffcc4=A;
POLY_3: ent-sym var Vfcc4=V;
POLY_3:

```

*) Continue with the bcc constituent.

```

POLY_3: ch-st p fcc=dor
POLY_3: ch-st p bcc=ent 1
POLY_3: s-c x(C)=xCbcc2 N=Nbcc2
POLY_3: c-e
Using global minimization procedure
Calculated          137 grid points in          0 s
Found the set of lowest grid points in          0 s
Calculated POLY solution          0 s, total time          0 s
POLY_3: ent-sym var Vbcc4=V;
POLY_3: ent-sym var V4=Vfcc4+Vbcc4;
POLY_3: sh V1 V4
V1=7.2726447E-6
V4=7.2726447E-6
POLY_3:

```

*) V has thus been kept constant and the value of P4 can be accepted. Complete the evaluation of the Helmholtz energy.

```

POLY_3: ent-sym var F4=Ffcc4+A;
POLY_3: ent-sym var DFF=(F1-F4)/deltaN;
POLY_3: sh DFG DFF
DFG=151.90466
DFF=152.22376
POLY_3:

```

*) The two methods of evaluating the driving force have not given the same result. The theoretical relation has not been confirmed. The explanation is that Helmholtz energy is suited only for homogeneous systems. If the new pressure is adjusted to keep the volume of the whole system constant, it does not mean that the volume of each phase is kept constant. Inspect the changes of their individual volumes.

```
POLY_3: sh Vbcc1 Vbcc4 Vfcc1 Vfcc4
```

```
Vbcc1=5.3286538E-6
```

```
Vbcc4=5.3478908E-6
```

```
Vfcc1=1.9439909E-6
```

```
Vfcc4=1.9247539E-6
```

```
POLY_3:
```

*) It is evident that the volumes of the phases have not been kept constant and it was not justified to try to evaluate the change in the Helmholtz energy by comparing the states. That would require that one applies different pressures to the two phases, which is not physically possible in reality. In fact, the fcc phase has decreased its amount by $dN=-2.6550306E-6$ and thus its volume. Of course, there is no physical justification to try to compensate for that effect by decreasing the pressure. It would even have to be strongly negative in order to expand the fcc phase back to V_{fcc1} . Helmholtz energy can thus be used for homogeneous systems only.

```
POLY_3: exit
```

```
CPU time          0 seconds
```

Comments

- 1) The positive value of DFG means that there is a driving force for the growth of the fcc phase at 1050 K if the system has first been equilibrated at 1000 K.
- 2) Of course, T-C was not constructed to produce this kind of test of a theoretical relation. It is encouraging that it is nevertheless possible to make this kind of test, although a little awkward.
- 3) This exercise has demonstrated that the Helmholtz energy is not suited for systems with more than one phase.

2.4A. Experimental conditions

Evaluate C_V and C_P for pure Cr at 500°C and 1 atm.

Hint

The heat capacities can be obtained from the second derivatives of F and G with respect to T but can also be obtained from first derivatives, e.g. $C_P = -TG_{TT} = (\partial H / \partial T)_P = T(\partial S / \partial T)_P$ and $C_V = (\partial U / \partial T)_V = T(\partial S / \partial T)_V$.

Instructions for using T-C

- 1) POLY can give first-order partial derivatives of state functions directly by using the period sign "." as an operator but one must be careful and consider what variable is kept constant.
- 2) This kind of operation works only if the set of independent variables is composed of the variable in the denominator and those in the subscript. You should thus use them when defining

the conditions for the state of equilibrium. That is how a state variable becomes independent in POLY.

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
Use one of these databases

DALMGSI = TCS Demo Al-Mg-Si Alloys TDB v1
DFECRC  = TCS Demo Fe-Cr-C Alloys TDB v1
PURE4   = SGTE Unary (Pure Elements) TDB v4
PSUB    = TCS Public Pure Substances TDB v1
PBIN    = TCS Public Binary Alloys TDB v1
PKP     = Kaufman Binary Alloys TDB v1
PCHAT   = Chatenay-Malabry Binary Alloys TDB v1
PTERN   = TCS Public Ternary Alloys TDB v1
PG35    = G35 Binary Semi-Conductors TDB v1
PION    = TCS Public Ionic Solutions TDB v2
PAQ2    = TCS Public Aqueous Solution TDB v2
PGEO    = Saxena Pure Minerals Database v1
PFRIB   = Fridberg Dilute Fe-Alloys MDB v1
USER    = User defined Database

DATABASE NAME /DALMGSI/: PTERN
Current database: TCS Public Ternary Alloys TDB v1

VA DEFINED
TDB_PTERN: def-el Cr
CR DEFINED
TDB_PTERN: l-sys
ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:
LIQUID:L      :CR:
  > This is metallic liquid solution phase, with C species
BCC_A2        :CR:VA:
FCC_A1         :CR:VA:
TDB_PTERN: rej p *
LIQUID:L      BCC_A2          FCC_A1
REJECTED

TDB_PTERN: rest p bcc
BCC_A2 RESTORED
TDB_PTERN: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions          11
FUNCTIONS ....

```

List of references for assessed data

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

```

-OK-
TDB_PTERN: go pol

POLY version 3.32, Aug 2001
POLY_3:
  *) For Cp the set of independent variables is T, P and N although N is usually omitted when
  writing the partial derivative of a pure element.
POLY_3: s-c P=101325 T=773 N=1
POLY_3: c-e
  Using global minimization procedure
  Calculated 1 grid points in 0 s
POLY_3: ent-sym var CP=H.T;
POLY_3:
  *) For Cv the set of independent variables is T, V and N.
POLY_3: s-c P=none V=
Value /7.323224298E-06/:
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 CV=U.T;
POLY_3: eval
Name(s):
  CP=28.810421
  CV=27.74913
POLY_3: exit
  CPU time 0 seconds

```

Comments

A partial derivative of a state function with respect to one variable while one or several other variables are kept constant can be evaluated only if all those variables make a set of independent variables. In POLY it is necessary to use that set when defining the conditions for the state of equilibrium and that is when the constant values are fixed.

2.4B. Experimental conditions

One mole of N₂ gas at 400°C and 1 atm is compressed adiabatically and reversibly to 100 kbar. Evaluate the new temperature.

Hint

$\Delta S = Q/T + \Delta_{ip}S = 0 + 0 = 0$. The final state should thus have the same entropy as the initial state. You should evaluate S for the initial state and then find the temperature where S has the same value at the higher P .

Instructions for using T-C

In order to evaluate S of the initial state from POLY, you must first compute its equilibrium. Then you should remove the condition on T and instead introduce the S value.

Prompts and commands

SYS: **go da**

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

VA DEFINED

TDB_DALMGSI: **sw psub**

Current database: TCS Public Pure Substances TDB v1

VA DEFINED

TDB_PSUB: **def-el N**

N DEFINED

TDB_PSUB: **l-sys**

ELEMENTS, SPECIES, PHASES OR CONSTITUENTS: /CONSTITUENT/:

GAS:G :N N2 N3:

> Gaseous Mixture, using the ideal gas model

TDB_PSUB:

*) For pure N this database only had the gas phase. However, there are several species and for a realistic calculation one should include them. For the present exercise you may reject them.

TDB_PSUB: **rej sp ***

VA N N2

N3 REJECTED

TDB_PSUB: **rest sp N2**

N2 RESTORED

TDB_PSUB: **get**

REINITIATING GES5

ELEMENTS

SPECIES

PHASES

PARAMETERS ...

FUNCTIONS

List of references for assessed data

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

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

-OK-

TDB_PSUB: **go pol**

POLY version 3.32, Aug 2001

POLY_3:

*) Set the initial conditions. Remember that the size of the system must be defined in some way. N=1 is the simplest.

POLY_3: **s-c P=101325 T=673 N=1**

POLY_3: **c-e**

Using global minimization procedure

Calculated 1 grid points in 0 s

POLY_3:

*) Set S as a condition instead of T. The value of S should be the same as for the equilibrium you have just computed. You should also set a new P value as condition. For a pure element a new value may be processed immediately and change the state. In the present case it may thus change the current value of S and in order to use the old S value as condition it must be fetched before the new P value is introduced.

POLY_3: **s-c T=None S=**


```

REJECTED
CARBON_MONOXIDE          CARBON_DIOXIDE          METHANE
REJECTED
TDB_PGEO:

```

*) Since O is automatically defined as an element in this database, you should reject it for the present application.

```

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: s-c T=673 P=101325 N=1
POLY_3: c-e
Using global minimization procedure
Calculated          1 grid points in          0 s
POLY_3:

```

*) To keep track of what happens later, it may be wise to show some properties of this equilibrium.

```

POLY_3: sh S U
S=12.08605011
U=6670.2495
POLY_3: ent-sym var U0=U;
POLY_3: s-c T=none S=
Value /12.08605011/:
POLY_3:

```

*) Now you can change P.

```

POLY_3: s-c P=1E10
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated          1 grid points in          0 s
6 ITS, CPU TIME USED 0 SECONDS
POLY_3: sh T U
T=686.92129
U=7029.4067
POLY_3: ent-sym var W1=U-U0;
POLY_3: sh W1
W1=359.15716
POLY_3: exit
CPU time          0 seconds

```

Comments

- 1) The work of compression will be 360 J/mol, which is not very much, the reason being that diamond has a very low compressibility.
- 2) For a unary system the state will be changed in POLY as soon as a new P value is introduced as a condition.

2.6A. Use of various derivatives

Evaluate α and κ_T for an Fe alloy with 0.5 mass% C at 850 and 750°C under 1 atm.

Hint

- 1) Expressed with first-order derivatives we find $\alpha = (\partial V / \partial T)_P / V$ and $\kappa_T = -(\partial V / \partial P)_T / V$.
- 2) At 850°C the alloy is inside the fcc one-phase field. At 750°C it is inside the bcc+fcc two-phase field. There you may evaluate the properties for the whole as well as for each phase.

Instructions for using T-C

- 1) You can make the evaluation for the whole system at T=1023 without considering that it is a two-phase state of equilibrium.
- 2) These cases have the same independent variables, P and T, in addition to the usual N.

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: **s-c P=101325 T=1123 N=1 w(C)=.005**

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:

*) Now, use the operator "." for evaluating partial derivatives.

POLY_3: **ent-sym var alphal=V.T/V;**

POLY_3: **ent-sym var kappal=-V.P/V;**

POLY_3:

*) All the symbols will be evaluated at the end. The discussion is postponed until then. Now,
go to the lower temperature.

POLY_3: **s-c T=1023**

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:

*) For a reason soon to become evident, it will be interesting to inspect the constitution of this
state of equilibrium.

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=1023, N=1, W(C)=5E-3

DEGREES OF FREEDOM 0

Temperature 1023.00 K (749.85 C), Pressure 1.013250E+05

Number of moles of components 1.00000E+00, Mass 5.48462E+01

Total Gibbs energy -4.31762E+04, Enthalpy 2.92590E+04, Volume 7.17030E-06

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
C	2.2832E-02	5.0000E-03	1.7010E-01	-1.5067E+04	SER
FE	9.7717E-01	9.9500E-01	5.7801E-03	-4.3833E+04	SER

BCC_A2 Status ENTERED Driving force 0.0000E+00

Number of moles 1.7391E-01, Mass 9.7063E+00 Mass fractions:

FE 9.99833E-01 C 1.67230E-04

```

FCC_A1                Status ENTERED        Driving force  0.0000E+00
Number of moles 8.2609E-01, Mass 4.5140E+01        Mass fractions:
FE 9.93961E-01  C    6.03918E-03
POLY_3:

```

*) This is a two-phase state, which is important for the interpretation of the result.

```
POLY_3: ent-sym var alpha2=V.T/V;
```

```
POLY_3:
```

*) You will soon see that this quantity is negative, which is unusual for the thermal expansivity. You should thus examine the values for the individual phases.

```
POLY_3: ent-sym var alp2fcc=Vm(fcc).T/Vm(fcc);
```

```
POLY_3: ent-sym var alp2bcc=Vm(bcc).T/Vm(bcc);
```

```
POLY_3: ent-sym var kappa2=-V.P/V;
```

```
POLY_3: ent-sym var kap2fcc=-Vm(fcc).P/Vm(fcc);
```

```
POLY_3: ent-sym var kap2bcc=-Vm(bcc).P/Vm(bcc);
```

```
POLY_3: eval
```

```
Name(s):
```

```
ALPHA1=7.5819633E-5
```

```
KAPPA1=6.3682434E-12
```

```
ALPHA2=-5.828903E-5
```

```
ALP2FCC=1.7330685E-4
```

```
ALP2BCC=5.1466861E-5
```

```
KAPPA2=1.0846535E-11
```

```
KAP2FCC=2.9966318E-12
```

```
KAP2BCC=5.936857E-12
```

```
POLY_3: exit
```

```
CPU time          0 seconds
```

Comments

The numbers show that both bcc and fcc have positive alpha values but the two-phase mixture has a negative value (ALPHA2). The explanation is that the amount of bcc decreases at higher temperatures and bcc has the largest molar volume. At 850°C the alloy fell inside the fcc one-phase field.

2.6B. Various derivatives

Test numerically the relation $(\partial U / \partial V)_T = T(\partial P / \partial T)_V - P$ on two Cr alloys with 5 or 10 mass% Fe, both kept at 800° C and 1 atm.

Hint

Both partial derivatives are based on the same two independent variables, T and V, but the experimental conditions are given through T and P. You should thus compute equilibrium and then introduce the computed V value as a condition for a new computation of equilibrium. Both partial derivatives can then be evaluated from the new description of the equilibrium based on the correct set of independent variables.

Instructions for using T-C

Use the special operator "." for the evaluation of partial derivatives.

Prompts, commands and responses

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

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

```
VA DEFINED
TDB_DFECRC: def-el Cr Fe
CR FE DEFINED
TDB_DFECRC: rej p *
LIQUID:L FCC_A1 BCC_A2
HCP_A3 SIGMA REJECTED
TDB_DFECRC: rest p bcc
BCC_A2 RESTORED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 22
FUNCTIONS ....
```

List of references for assessed data

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

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

-OK-

```
TDB_DFECRC: go pol
```

```
POLY version 3.32, Aug 2001
POLY_3: s-c P=101325 T=1073 w(Fe)=.05 N=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:
```

*) Change to the wanted set of independent variables.

```
POLY_3: s-c P=none V=
Value /7.395233554E-06/:
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated 137 grid points in 0 s
6 ITS, CPU TIME USED 0 SECONDS
POLY_3:
```

*) Now you could define the wanted quantities. If you do it as functions you could repeat the evaluation for the next alloy much quicker.

```
POLY_3: ent-sym fun LHS=U.V;
```

```
POLY_3: ent-sym fun RHS=T*P.T-P;
POLY_3: eval
Name(s):
```

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

```
LHS=7.6662711E9
```

```
RHS=7.6662711E9
```

```
POLY_3:
```

*) The two value are equal and the relation was confirmed. Set conditions for the other alloy and repeat the evaluation. Remember to restore the pressure for the first computation of equilibrium.

```
POLY_3: s-c w(Fe)=.1
```

```
POLY_3: s-c V=none P=101325
```

```
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:
```

*) Change to the wanted set of independent variables.

```
POLY_3: s-c P=none V=
```

```
Value /7.3921799E-06/:
```

```
POLY_3: c-e
```

Normal POLY minimization, not global

Testing POLY result by global minimization procedure

```
Calculated          137  grid points in          0  s
```

```
6 ITS, CPU TIME USED  0 SECONDS
```

```
POLY_3:
```

*) Since you used functions you can evaluate the wanted quantities directly.

```
POLY_3: eval
```

```
Name(s):
```

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

```
LHS=7.7502092E9
```

```
RHS=7.7502092E9
```

```
POLY_3:
```

*) Again the relation was confirmed. This time the value was somewhat different because the alloy content was different.

```
POLY_3: exit
```

```
CPU time          0  seconds
```

Comments

When evaluating a partial derivative you must be careful and use the correct set of independent variables, which is done when using them as conditions.

2.7. Comparison between C_V and C_P

Evaluate C_V and C_P for Cr at 500 K and 1 bar.

Hint

C_P is usually measured at 1 atm and can be evaluated from a database as $(\partial H / \partial T)_{P,N}$. For clarity it may be denoted $C_P(T, P_0)$ where P_0 represents 1 atm. For C_V the situation is not quite so clear. Experimentally, one prefers to work under constant pressure and C_V is usually obtained by calculation from other properties, mainly but not only from C_P . C_V may be evaluated from a database as $(\partial U / \partial T)_{V,N}$ and it is evident that one must allow P to change in order to keep V constant when making the small variation of T . However, one could still be interested in the values of C_V when starting from 1 atm at different temperatures. For each temperature one should then first compute the equilibrium at 1 atm as condition. Then one could instead introduce the current volume as condition and compute equilibrium, which should result in the same state of equilibrium. Then one could evaluate $(\partial U / \partial T)_{V,N}$. That quantity could be described as $C_V(T, P_0)$. The alternative would be to keep V constant at its value from room temperature for all temperatures and that would require that P increases with temperature in order to balance the natural thermal expansion. That quantity could be described as $C_V(T, V_0)$. Since all the experimental information usually used when C_V is evaluated from C_P has been obtained from 1 atm, the C_V values usually reported would most probably be $C_V(T, P_0)$.

Instructions for using T-C

$C_P(T, P_0)$ and $C_V(T, P_0)$ can be evaluated by applying the "." operator on the same state of equilibrium at 500°C and 1 atm but the set of independent variables must be different. $C_P(T, P_0)$ is found directly and $C_V(T, P_0)$ after changing the condition on P to the equivalent condition on V . In order to find $C_V(T, V_0)$ you must first find V at room temperature and 1 atm, i.e. V_0 . Then you compute the equilibrium at 500°C and V_0 and directly evaluate $(\partial U / \partial T)_{V,N}$.

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 PTERN
Current database: TCS Public Ternary Alloys TDB v1

VA DEFINED
TDB_PTERN: def-el Cr
CR DEFINED
TDB_PTERN: rej p *
LIQUID:L BCC_A2 FCC_A1
REJECTED
TDB_PTERN: rest p bcc
BCC_A2 RESTORED
TDB_PTERN: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
```

```

PHASES .....
PARAMETERS ...
Rewind to read functions          11
FUNCTIONS ....

```

List of references for assessed data

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

-OK-

TDB_PTERN: **go pol**

```

POLY version 3.32, Aug 2001
POLY_3: s-c T=773 P=101325 N=1
POLY_3: c-e
Using global minimization procedure
Calculated          1 grid points in          0 s
POLY_3: ent-sym var CP=H.T;
POLY_3: s-c P=none V=
Value /7.323224298E-06/:
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 CVP0=U.T;
POLY_3:

```

*) Go back to the equilibrium at 298 K and 1 atm in order to evaluate V_0 and introduce it as condition. Then find the state of equilibrium at 773 K for $V=V_0$.

```

POLY_3: s-c P=101325 V=none T=298
POLY_3: c-e
Using global minimization procedure
Calculated          1 grid points in          0 s
POLY_3: s-c P=none V=
Value /7.230407803E-06/:
POLY_3: s-c T=773
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated          1 grid points in          0 s
21 ITS, CPU TIME USED 0 SECONDS
POLY_3:

```

*) Now you can evaluate $C_V(T, V_0)$.

```

POLY_3: ent-sym var CVV0=U.T;
POLY_3: eval
Name(s):
CP=28.810421
CVP0=27.74913
CVV0=27.41756
POLY_3: exit
CPU time          0 seconds

```

Comments

It is an interesting question how the heat capacities published in tables are defined. Experimentally, it is easiest to measure $C_P(T, P_0)$ and then to derive C_V at each temperature

using Eq. 2.34, which can be written as $C_V = C_P - TV\alpha^2/\kappa_T$. All the quantities C_P , α and κ_T have probably been measured at ordinary pressure. Primarily, one will thus obtain $C_V(T, P_0)$ and publish those values.

2.8. Changing independent variables

Show numerically that $C_V\kappa_T = C_P\kappa_S$ for Cr at 1500 K and 1 atm.

Hint

Remember that $C_V = (\partial U / \partial T)_V$, $C_P = (\partial H / \partial T)_P$, $V\kappa_T = -(\partial V / \partial P)_T$ and $V\kappa_S = -(\partial V / \partial P)_S$.

You have to be careful with the sets of independent variables that are not the same for all the partial derivatives.

Instructions for using T-C

Again you can use the special operator for partial derivatives.

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
CR DEFINED
TDB_DFECRC: rej p *
LIQUID:L          FCC_A1          BCC_A2
HCP_A3 REJECTED
TDB_DFECRC: rest p bcc
BCC_A2 RESTORED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions          11
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'
```

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:

*) As always, you must start setting the conditions with the set of variables for which you know the values.

POLY_3: **s-c P=101325 T=1500 N=1**

POLY_3: **c-e**

Using global minimization procedure

Calculated 1 grid points in 0 s

POLY_3:

*) There are two partial derivatives using this set of variables.

POLY_3: **ent-sym var VKT=-V.P;**

POLY_3: **ent-sym var CP=H.T;**

POLY_3:

*) Change the set of variables for the next partial derivative.

POLY_3: **s-c P=none V=**

Value /7.527872324E-06/:

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 CV=U.T;**

POLY_3:

*) Again, change the set of variables for the fourth partial derivative.

POLY_3: **s-c V=none P=101325**

POLY_3: **s-c T=none S=**

Value /70.56209834/:

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 VKS=-V.P;**

POLY_3:

*) Time to test the relation.

POLY_3: **ent-sym var LHS=CV*VKT;**

POLY_3: **ent-sym var RHS=CP*VKS;**

POLY_3: **sh LHS RHS**

LHS=1.4375568E-15

RHS=1.4375568E-15

POLY_3: CPU time 0 seconds

Comments

As expected, you have found that LHS = RHS.

2.9. Maxwell relation

Prove numerically that $(\partial S / \partial V)_T = (\partial P / \partial T)_V$. Use an Fe alloy with 10 mass% Cr at 900 and 700°C under 1 atm.

Hint

- 1) These partial derivatives use the same three independent variables, including N that is omitted.
- 2) This alloy is bcc at those temperatures.

Instructions for using T-C

This is a simple case for the special "." operator.

Prompts, commands and responses

```

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

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

VA DEFINED
TDB_DFECRC: def-el Cr Fe
CR FE DEFINED
TDB_DFECRC: rej p *
LIQUID:L FCC_A1 BCC_A2
HCP_A3 SIGMA REJECTED
TDB_DFECRC: rest p bcc
BCC_A2 RESTORED
TDB_DFECRC: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 22
FUNCTIONS ....

```

List of references for assessed data

```

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

```

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

-OK-

```
TDB_DFECRC: go pol
```

```

POLY version 3.32, Aug 2001
POLY_3: s-c P=101325 T=1173 N=1 w(Fe)=.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:

```

*) Only one variable must be changed.

```

POLY_3: s-c P=none V=
Value /7.421121642E-06/:

```

```
POLY_3: c-e
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated          137 grid points in          0 s
  6 ITS, CPU TIME USED  0 SECONDS
```

POLY_3:

*) Use functions because you will soon repeat the evaluation.

```
POLY_3: ent-sym fun SV=S.V;
```

```
POLY_3: ent-sym fun PT=P.T;
```

```
POLY_3: eval
```

Name(s):

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

SV=7583868.5

PT=7583868.5

POLY_3:

*) The values are the same and Maxwell's relation was confirmed. Do it for the other temperature also.

When changing to the new temperature, you must take back the known pressure and compute equilibrium. Then change again to the wanted set of variables.

```
POLY_3: s-c V=none P=101325 T=973
```

```
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: s-c P=none V=
```

Value /7.364757305E-06/:

```
POLY_3: c-e
```

```
Normal POLY minimization, not global
Testing POLY result by global minimization procedure
Calculated          137 grid points in          0 s
  6 ITS, CPU TIME USED  0 SECONDS
```

POLY_3:

*) Because you used functions, you can now evaluate them for the new temperature directly.

```
POLY_3: eval
```

Name(s):

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

SV=6862135.8

PT=6862135.8

```
POLY_3: exit
```

```
CPU time          0 seconds
```

Comments

For both temperatures you have confirmed Maxwell's relation.