

## Chapter 5. Thermodynamics of processes

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### 5.1A. Thermodynamic treatment of kinetics of internal processes

Evaluate the thermodynamic force for the solidification of pure liquid Mo to bcc at 2800 K and 1 atm. The melting point of Mo is 2896 K. Suppose the reaction is so rapid that there is no heat exchange with the surroundings.

#### Hint

- 1) The first law gives  $dH=dQ+VdP=0$  in this case and the second law gives  $dS=dQ/T+d_{ip}S=d_{ip}S=(d_{ip}S/df)df=Xdf$  where  $X$  is the thermodynamic force. Suppose a small fraction,  $\Delta f$ , solidifies. Some heat of melting will be liberated and will heat the system to a temperature determined by the condition that  $H$  is constant. After finding that temperature you may evaluate  $X = d_{ip}S / df = dS / df \cong \Delta S / \Delta f$ .
- 2) The new temperature may be found by introducing  $\Delta f$  and guessing a value of the adiabatic  $T$  and evaluating  $\Delta H$  there. By extrapolation you can then find the correct temperature where  $\Delta H = 0$ . Then you can evaluate  $S$  at that temperature and obtain  $X \cong \Delta S / \Delta f$ .

#### Instruction for using T-C

Normally, POLY cannot give properties of a non-equilibrium state. However, if the non-equilibrium concerns the relation between two phases but does not concern the internal structure of the individual phases, then POLY can give the properties of each one of the phases and you can then add them.

#### 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 PURE4
Current database: SGTE Unary (Pure Elements) TDB v4

VA /- DEFINED
TDB_PURE4: def-el Mo
MO DEFINED
```

```

TDB_PURE4: rej p *
  BCC_A2                      FCC_A1                      HCP_A3
  LIQUID:L REJECTED
TDB_PURE4: rest p bcc liq
  BCC_A2                      LIQUID:L RESTORED
TDB_PURE4: get
  REINITIATING GES5 .....
  ELEMENTS .....
  SPECIES .....
  PHASES .....
  PARAMETERS ...
  Rewind to read functions          2
  FUNCTIONS ....

```

List of references for assessed data

'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.4), developed by SGTE (Scientific Group Thermodata Europe), 1991-2003, and provided by TCSAB (Aug. 2003). '

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

-OK-

```
TDB_PURE4: go pol
```

```

POLY version 3.32, Aug 2001
POLY_3: ch-st p bcc=dor
POLY_3: s-c P=101325 T=2800 N=1
POLY_3: c-e
  Using global minimization procedure
  Calculated          1 grid points in          0 s
POLY_3: ent-sym var S1=S;
POLY_3: ent-sym var H1=H;
POLY_3:
  *) Introduce the amount of liq in a two-phase state with 0.001 mole fraction solid.
POLY_3: s-c N=.999
POLY_3: c-e
  Using global minimization procedure
  Using already calculated grid
POLY_3:
  *) Save H for the liquid constituent at 2800 K and continue with the solid constituent.
POLY_3: ent-sym var HL2=H;
POLY_3: s-c N=.001
POLY_3: ch-st p bcc=ent 1
POLY_3: ch-st p liq=dor
POLY_3: c-e
  Using global minimization procedure
  Calculated          1 grid points in          0 s
POLY_3:
  *) Evaluate and save H for this two-phase state at 2800 K.
POLY_3: ent-sym var H2=H+HL2;
POLY_3:
  *) Guess the adiabatic temperature and evaluate H for the same state at that temperature,
  starting with the solid constituent.
POLY_3: s-c T=2801
POLY_3: c-e
  Using global minimization procedure
  Calculated          1 grid points in          0 s
POLY_3: ent-sym var HS3=H;

```

```

POLY_3: s-c N=0.999
POLY_3: ch-st p bcc=dor
POLY_3: ch-st p liq=ent 1
POLY_3: c-e
Using global minimization procedure
Calculated      1 grid points in          0 s
POLY_3: ent-sym var H3=H+HS3;
POLY_3:

```

\*) Now you could evaluate the difference in H between the pure liquid at 2800 K, H1, and the two-phase state at 2801 K. The difference should be zero for the actual adiabatic temperature. Your guess of 2801 K was thus good but not good enough. You find the real adiabatic temperature by interpolation.

```

POLY_3: ent-sym var T4=2800+1*(H2-H1)/(H2-H3);
POLY_3: sh T4
T4=2800.912
POLY_3:

```

\*) It remains to evaluate S for the two-phase non-equilibrium state at the adiabatic temperature. Again you have to find H for each constituent separately and add them.

```

POLY_3: s-c T=T4
POLY_3: c-e
Using global minimization procedure
Calculated      1 grid points in          0 s
POLY_3: ent-sym var SL4=S;
POLY_3: s-c N=.001
POLY_3: ch-st p bcc=ent 1
POLY_3: ch-st p liq=dor
POLY_3: c-e
Using global minimization procedure
Calculated      1 grid points in          0 s
POLY_3: ent-sym var S4=S+SL4;
POLY_3:

```

\*) Finally, you can evaluate the thermodynamic force under adiabatic conditions, using the relation give in the hint.

```

POLY_3: ent-sym var TFad=(S4-S1)/.001;
POLY_3: sh S4 TFad
S4=109.41408
TFAD=0.44710169
POLY_3: exit
CPU time          0 seconds

```

## Comment

You should realize that the driving force is equal to T times the thermodynamic force under isothermal conditions. However, there is no such relation in the present case where the temperature is not fixed. The concept of driving force, as we have defined it, does not apply to non-isothermal cases. However, compare with Problem 5.1B that gives a different aspect.

## 5.1B. Thermodynamic treatment of kinetics of internal processes

Do the same under isothermal conditions. Compare the results and explain.

### Hint

For the isothermal case you can start by evaluating the driving force, DF, from the difference in Gibbs energy. Then you get the thermodynamic force  $TF=DF/T$ .

## Instructions for using T-C

Again you can get the properties of the individual phases by treating each of them as a separate system, considering its amount.

## 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 PURE4
Current database: SGTE Unary (Pure Elements) TDB v4

VA /- DEFINED
TDB_PURE4: def-el Mo
MO DEFINED
TDB_PURE4: rej p *
BCC_A2 FCC_A1 HCP_A3
LIQUID:L REJECTED
TDB_PURE4: rest p bcc liq
BCC_A2 LIQUID:L RESTORED
TDB_PURE4: get
REINITIATING GES5 .....
ELEMENTS .....
SPECIES .....
PHASES .....
PARAMETERS ...
Rewind to read functions 2
FUNCTIONS ....

List of references for assessed data

'PURE4 - SGTE Pure Elements (Unary) Database (Version 4.4), developed by
SGTE (Scientific Group Thermodata Europe), 1991-2003, and provided by
TCSAB (Aug. 2003). '

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

-OK-
TDB_PURE4: go pol

```

```

POLY version 3.32, Aug 2001
POLY_3:
*) Investigate the initial purely liquid state and store its G.
POLY_3: ch-st p bcc=dor
POLY_3: s-c P=101325 T=2800 N=1
POLY_3: c-e
Using global minimization procedure
Calculated 1 grid points in 0 s
POLY_3: ent-sym var G1=G;
POLY_3:

```

\*) Investigate a two-phase state and for convenience you may again choose a mole fraction of 0.001 solid constituent. This is a non-equilibrium state and the properties must be obtained by

adding the contributions from the individual phases. Start with the liquid because the solid is already dormant.

```
POLY_3: s-c N=.999
POLY_3: c-e
  Using global minimization procedure
  Using already calculated grid
POLY_3: ent-sym var GL2=G;
POLY_3:
  *) Continue with the solid constituent.
POLY_3: ch-st p bcc=ent 1
POLY_3: ch-st p liq=dor
POLY_3: s-c N=.001
POLY_3: c-e
  Using global minimization procedure
  Calculated          1 grid points in          0 s
POLY_3: ent-sym var GS2=G;
POLY_3: ent-sym var G2=GS2+GL2;
POLY_3:
  *) Finally, you can evaluate the driving force and the thermodynamic force.
POLY_3: ent-sym var DF=(G1-G2)/.001;
POLY_3: ent-sym var TFiso=DF/2800;
POLY_3: sh TFiso DF
  TFISO=0.44942638
  DF=1258.3939
POLY_3: exit
  CPU time          0 seconds
```

### Comment

- 1) Problem 5.1A gave a thermodynamic force of  $TF_{ad} = 0.44710169$  under adiabatic conditions. Within the accuracy expected when one takes the difference between quantities of almost the same magnitude, this is an excellent agreement with the thermodynamic force under isothermal conditions,  $TF_{iso}$ , obtained here. This is a confirmation of the arguments in Section 3.6 where it was claimed that the driving force for a change is a function of the state itself and not of how its conditions are controlled. Those conditions influence where the system is going but have no effect on the very first stage of the internal process when it cannot yet "feel" what external constraints (conditions) are applied on the system.
- 2) Even for a process that will change the temperature, it is thus possible to evaluate the thermodynamic force by first evaluating the driving force using the Gibbs energy at constant temperature and then just divide by the initial temperature.

## 5.5. Chemical reactions

Evaluate the driving force for the formation of more  $H_2O$  molecules in a gas with the constitution 5 mol%  $H_2O$ , 40 mol%  $H_2$  and 55 mol%  $O_2$  at 1 atm and 2000 K.

### Hint

The driving force for the formation per mole of more  $H_2O$  is  $\mu_{H_2} + 0.5 \cdot \mu_{O_2} - \mu_{H_2O}$  according to Eq. 5.62. The question is how your data bank system can give you values for the chemical potentials of a non-equilibrium gas.

## Instructions for using T-C

POLY can only give properties for states of equilibrium. The database for the gas treats it as an ideal gas where the chemical potential of a species is given by its partial pressure, i.e., as if it were a pure gas of a pressure equal to its partial pressure. You can thus evaluate the chemical potential of a species by requiring that it is the only species present and give its partial pressure as the value to the total pressure.

## 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-el H O
H O DEFINED
TDB_PSUB: rej p *
GAS:G H2O_L H2O2_L
REJECTED
TDB_PSUB: rest p gas
GAS:G RESTORED
TDB_PSUB: rej sp *
VA H O
H1O1 H1O2 H2
H2O1 H2O2 O2
O3 REJECTED
TDB_PSUB: rest sp H2 O2 H2O1
H2 O2 H2O1
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 tab
TAB: tab-sub gas
FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /1/: 1
H2O1 /1/: 0

```

\*) This will thus be pure H<sub>2</sub>. It is not necessary to give the fraction of the last constituent. Give its partial pressure as the total pressure.

Pressure /100000/: **40000**  
 Low temperature limit /298.15/: **2000**  
 High temperature limit /2000/:  
 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. 5.11 22.27.19

Phase : GAS Pressure : 40000.00  
 Specie: \*

```
*****
  T      Cp      H      S      G
  (K)    (Joule/K) (Joule) (Joule/K) (Joule)
  *****
2000.00  3.43045E+01  5.29300E+04  1.96016E+02  -3.39103E+05
  *****
```

TAB:

\*) Go to POLY and save the value of G in the last column as the chemical potential for the H<sub>2</sub> constituent. Then, go back to TAB and do the same for O<sub>2</sub>.

TAB: **go pol**

POLY version 3.32, Aug 2001  
 POLY\_3: **ent-sym var muH2=-3.39103E+05;**  
 POLY\_3: **b**  
 TAB: **tab-sub gas**  
 FRACTION OF CONSTITUENT (RETURN FOR PROMPT):  
 H2 /1/: **0**  
 H2O1 /0/: **0**

\*) This gas has no H<sub>2</sub> and no H<sub>2</sub>O. It is thus pure O<sub>2</sub>. Give its partial pressure as the total pressure.

Pressure /40000/: **55000**  
 Low temperature limit /2000/:  
 High temperature limit /2000/:  
 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. 5.11 22.27.19

Phase : GAS Pressure : 55000.00  
 Specie: \*

```
*****
  T      Cp      H      S      G
  (K)    (Joule/K) (Joule) (Joule/K) (Joule)
  *****
2000.00  3.78262E+01  5.91909E+04  2.73724E+02  -4.88258E+05
  *****
```

TAB: **b**

POLY\_3: **ent-sym var muO2=-4.88258E+05;**  
 POLY\_3:

\*) This was the chemical potential of O<sub>2</sub>. Finally, do the same for the H<sub>2</sub>O constituent.

POLY\_3: **b**  
 TAB: **tab-sub gas**

```

FRACTION OF CONSTITUENT (RETURN FOR PROMPT):
H2 /0/: 0
H2O1 /0/: 1
Pressure /55000/: 5000
Low temperature limit /2000/:
High temperature limit /2000/:
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. 5.11                                22.27.20

```

```

Phase : GAS                                Pressure : 5000.00
Specie: *

```

```

*****
T      Cp      H      S      G
(K)    (Joule/K) (Joule) (Joule/K) (Joule)
*****
2000.00  5.16962E+01  -1.68705E+05  2.89916E+02  -7.48537E+05

```

TAB: **b**

POLY\_3:

\*) Now you can directly evaluate and store the difference in chemical potentials as the driving force.

POLY\_3: **ent-sym var D=muH2+.5\*muO2-(-7.48537E+05);**

POLY\_3: **sh D**

D=165305

POLY\_3: **exit**

CPU time 0 seconds

## Comment

The positive driving force means that the reaction actually goes in the direction of forming more H<sub>2</sub>O, which is not self-evident because the dissociation of H<sub>2</sub>O into H<sub>2</sub> and O<sub>2</sub> is not negligible at such a high temperature.