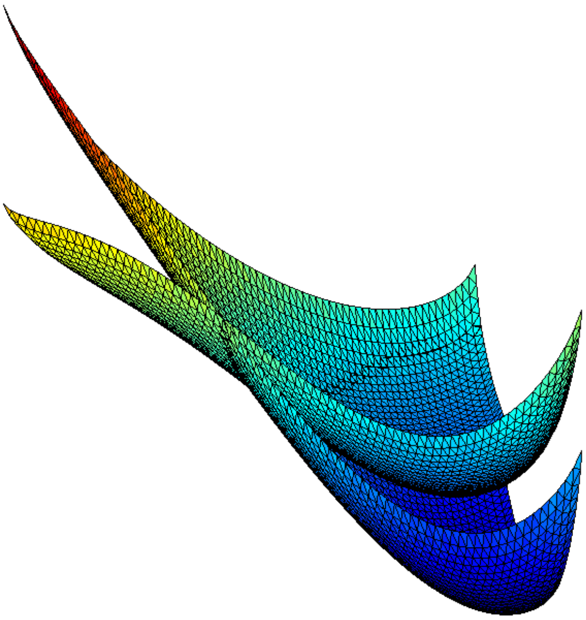
Computerized Thermodynamics for Materials Scientists and Engineers

by

Mats Hillert and Malin Selleby



SOLUTIONS TO BOOK EXERCISES

Computerized Thermodynamics for Materials Scientists and Engineers

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Contents

Chapter 1

Basic Thermodynamics

1.1 First law of thermodynamics

Exercise 1.1.1. Evaluate the heat of melting of 1 mole of pure fcc-Ni at 1 bar.
Hint 1) The melting point at 1 bar is 1728.25 K. 2) Integration of Eq. 1.4 yields $Q_{melting} = H^{liquid} - H^{fcc}$ because for a pure element the phases retain their properties during the whole melting process when P and T are kept constant.

Solution 1.1.1. Database: PURE
To perform the calculation at the exact melting point use two serially coupled equilibrium calculator activities. In the first, set the temperature to 1728 K. In the second, release the temperature condition and set the liquid phase as "fixed" to the system size. The molar enthalpies of fcc and liquid are obtained in a table renderer activity as 47458 and 64938 J/mol, respectively, i.e. the enthalpy of melting is 17480 J/mol.

1.2 Second law of thermodynamics

Exercise 1.2.1. Evaluate $\Delta_{ip}S$ for the solidification of 1 mole of liquid Ni in a system at 1720 K and 1 bar.
Hint Solidification of the liquid can be regarded as an internal process of the system. Liquid and fcc Ni are in equilibrium at 1728.25 K. At that temperature liquid Ni will not solidify spontaneously, $d_{ip}S = 0$. At 1720 K the liquid is supercooled and could solidify spontaneously, $d_{ip}S > 0$. The quantity $d_{ip}S$ could be evaluated from Eq. 1.6 in the integrated form, $\Delta_{ip}S = \Delta S - \Delta Q/T$. Eq. 1.4 then yields for one mole $\Delta_{ip}S_m = S_m^{fcc} - S_m^{liq} - \left(H_m^{fcc} - H_m^{liq}\right)/1720$. The molar quantities should here be taken from 1720 K.

Solution 1.2.1. Database: PURE
Do the equilibrium calculation at 1720 K. The status of phases (entered/dormant) doesn't matter as long as it is the molar quantities that are listed. The molar entropy and enthalpy of fcc are obtained as 85.5 and 47138 J/mol, respectively. The corresponding values for liquid are 95.6 and 64583 J/mol. This yields $\Delta_{ip}S_m = 0.048$ J/mol·K.

1.3 The combined law

Exercise 1.3.1. Evaluate $\Delta_{ip}S$ for the solidification of 1 mole of liquid Ni at 1720 K and 1 bar from information on ΔG for solidification.
Hint ΔG may be obtained from a table of G_m or from a computerized database.

Solution 1.3.1. Database: PURE
The same calculation as in 1.3.1 yields $G_m^\gamma = -99934$ and $G_m^L = -99851$ J/mol. We get $\Delta_{ip}S_m = -\Delta G_m/T = 0.048$ J/mol·K.

1.4 Driving force and dissipation

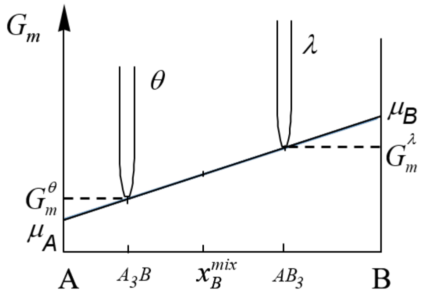
Exercise 1.4.1. Find the driving force for the formation of solid Ni from liquid Ni at 1720 K and 1 bar.
Hint The only quantity that changes during isobarothermal solidification of pure Ni is the amounts of solid and liquid Ni. It may thus be convenient to express the extent of solidification, ξ, by the amount of solid Ni, e.g. expressed as moles, N^{sol}. The driving force, D, will have the same value during the whole solidification of a pure substance and we obtain $D = -\Delta G/\Delta\xi = -\left(G^{sol} - G^{liq}\right)/\Delta N^{sol} = G_m^{liq} - G_m^{sol}$.

Solution 1.4.1. Database: PURE
In 1.4.1 we obtained $G_m^\gamma = -99934$ and $G_m^L = -99851$ J/mol. Thus $D = 83$ J/mol.

1.5 Variable Composition

Exercise 1.5.1. (Advanced) Use Eq. 1.17 to derive μ_A for a system composed of a mixture of two stoichiometric A-B phases.
Hint Remember that Gibbs energy is an additive quantity. How can one then keep N_B constant when one varies N_A?

Solution 1.5.1. The Gibbs energy curves of such a system can be plotted as:



We have $N_A = N_A^\theta + N_A^\lambda$, $N_B = N_B^\theta + N_B^\lambda$, and $G = N^\theta G_m^\theta + N^\lambda G_m^\lambda$.

$\mu_A = (\frac{\partial G}{\partial N_A})_{P,T,N_B} = \frac{\partial(N^\theta G_m^\theta + N^\lambda G_m^\lambda)}{\partial N_A} = \frac{\partial N^\theta}{\partial N_A} G_m^\theta + N^\theta \frac{\partial G_m^\theta}{\partial N_A} + \frac{\partial N^\lambda}{\partial N_A} G_m^\lambda + N^\lambda \frac{\partial G_m^\lambda}{\partial N_A}$

We need the derivatives, $\frac{\partial N^\theta}{\partial N_A}$ and $\frac{\partial N^\lambda}{\partial N_A}$.

$N_A = N^\theta x_A^\theta + N^\lambda x_A^\lambda$
$N_B = N^\theta x_B^\theta + N^\lambda x_B^\lambda$

Then take the first row times x_B^λ and the second row times $(-x_A^\lambda)$, and add then yielding: $x_B^\lambda N_A - x_A^\lambda N_B = (x_A^\theta x_B^\lambda - x_A^\lambda x_B^\theta)N^\theta + (x_A^\lambda x_B^\lambda - x_A^\lambda x_B^\lambda)N^\lambda$

Thus, $x_B^\lambda N_A - x_A^\lambda N_B = N^\theta(x_A^\theta - x_A^\lambda)$, which gives $N^\theta = \frac{1}{x_A^\theta - x_A^\lambda}(x_B^\lambda N_A - x_A^\lambda N_B)$

and the derivative $(\frac{\partial N^\theta}{\partial N_A})_{N_B} = \frac{x_B^\lambda}{x_A^\theta - x_A^\lambda}$

Similarly, $x_B^\theta N_A - x_A^\theta N_B = (x_A^\theta x_B^\theta - x_A^\theta x_B^\theta)N^\theta + (x_A^\lambda x_B^\theta - x_A^\theta x_B^\lambda)N^\lambda$

Thus, $x_B^\theta N_A - x_A^\theta N_B = N^\lambda(x_A^\lambda - x_A^\theta)$, which gives $N^\lambda = \frac{1}{x_A^\lambda - x_A^\theta}(x_B^\theta N_A - x_A^\theta N_B)$

and $(\frac{\partial N^\lambda}{\partial N_A})_{N_B} = \frac{x_B^\theta}{x_A^\lambda - x_A^\theta}$

The chemical potential of A can then be expressed as $\mu_A = \frac{x_B^\lambda}{x_A^\theta - x_A^\lambda} G_m^\theta + \frac{x_B^\theta}{x_A^\lambda - x_A^\theta} G_m^\lambda$

1.6 Expressing chemical potentials through the molar Gibbs energy

Exercise 1.6.1. Use Eq. 1.17 for evaluating the chemical potentials of Ag and Cu at equilibrium in an Ag-Cu melt of 40 mass-% Cu at 1200 K and 1 bar.
Hint When you can define the conditions for a state of equilibrium in your software then it should be possible to make your software evaluate most properties of the state. Find out if it can evaluate μ_{Ag} and μ_{Cu} as partial derivatives, i.e. as $(dG/dN_i)_{P,T,N_j}$.

Solution 1.6.1. Database: TCSLD
Note that partial differentiation may only be performed with respect to quantities that are equilibrium conditions. Therefore, first calculate the number of moles of each component in a system of total size 1 mole and 40 mass-% Cu, which yields 0.46911 moles Ag and 0.53089 moles Cu. Then set the number of moles of each component as equilibrium conditions instead of system size and composition. This allows the partial derivatives $\partial G/\partial N_{Cu}$ and $\partial G/\partial N_{Ag}$ to be entered as functions using “Thermo-Calc syntax”, i.e. “G.N(CU)” and “G.N(AG)”. As they should, these functions have the same values as the chemical potentials, viz. -75337 and -61767 J/mol, respectively.

1.7 Gibbs–Duhem relation

Exercise 1.7.1. Consider the equilibrium between an A-rich phase and a stoichiometric A_3B_2 compound. Use Eq. 1.34 to illustrate how μ_B can be obtained from a molar Gibbs energy diagram.
Hint Remember that the molar Gibbs energy of all phases is expressed per mole of atoms in the molar Gibbs energy diagram, not per formula unit.

Solution 1.7.1. We have $G_m^{A_3B_2} = x_A^{A_3B_2}\mu_A + x_B^{A_3B_2}\mu_B$
where $x_A^{A_3B_2} = 3/5$ and $x_B^{A_3B_2} = 2/5$
so $\mu_B = 5/2G_m^{A_3B_2} - 3/2\mu_A$

Exercise 1.7.2. The chemical potentials of A and B in an A-B solution phase can be changed by adding some B or by exchanging some A for the same amount of B. Check the validity of the Gibbs–Duhem relation at constant P and T for these two cases numerically on a solid Ag-Cu alloy with 5 atom-% Cu at 1 bar and 1100 K. *Hint* For these two cases the Gibbs-Duhem relation yields

$$N_{Cu}\left(\partial\mu_{Cu}/\partial N_{Cu}\right)_{N_{Ag},P,T}+N_{Ag}\left(\partial\mu_{Ag}/\partial N_{Cu}\right)_{N_{Ag},P,T}=0$$
$$N_{Cu}\left(\partial\mu_{Cu}/\partial N_{Cu}\right)_{N,P,T}+N_{Ag}\left(\partial\mu_{Ag}/\partial N_{Cu}\right)_{N,P,T}=0$$

An advanced thermodynamic program can give all these derivatives directly. If that is not available to you, consider 1 mole of the alloy, first evaluate the chemical potentials directly, then add a small amount of Cu, e.g. 0.01 mole, and evaluate the new chemical potentials, and apply Eq. 1.37 to the differences obtained and, finally, do the same after also removing the same amount of A.

Solution 1.7.2. Database: TCSLD
First, set conditions for P, T, N_{Cu} and N_{Ag}. Set, for example $N_{Cu}=0.05$ and $N_{Ag}=0.95$. Enter the functions $\partial\mu_{Cu}/\partial N_{Cu}$ and $\partial\mu_{Ag}/\partial N_{Cu}$ as "MUR(CU).N(CU)" and "MUR(AG).N(CU)", respectively.
We obtain $\partial\mu_{Cu}/\partial N_{Cu}=1.47237\cdot10^{5}$ and $\partial\mu_{Ag}/\partial N_{Cu}=-7749.3$
Then exchange the condition for N_{Ag} for a condition on the system size, for example $N=1$.
We then obtain $\partial\mu_{Cu}/\partial N_{Cu}=1.54986\cdot10^{5}$ and $\partial\mu_{Ag}/\partial N_{Cu}=-8157.2$ By incerting the values into the equations above we obtain:

$$N_{Cu}\left(\partial\mu_{Cu}/\partial N_{Cu}\right)_{N_{Ag},P,T}+N_{Ag}\left(\partial\mu_{Ag}/\partial N_{Cu}\right)_{N_{Ag},P,T}=$$
$$0.05\cdot1.47237\cdot10^{5}+0.95\cdot(-7749.3)=-1\cdot10^{-11}$$
$$N_{Cu}\left(\partial\mu_{Cu}/\partial N_{Cu}\right)_{N,P,T}+N_{Ag}\left(\partial\mu_{Ag}/\partial N_{Cu}\right)_{N,P,T}=$$
$$0.05\cdot1.54986e5+0.95\cdot-8157.2=4.5+\cdot10^{-12}$$

Since the resulting values are virtually zero, the relationship holds.

Exercise 1.7.3. It is common to express the chemical potential of oxygen in a gas through the partial pressure of the O_2 molecules. Of course, the value of this quantity is directly related to the chemical potential of O_2. Show that it is also related to the chemical potential of O. The result may seem absurd if there are no O atoms present. Some condition must be fulfilled. Which one?
Hint Apply Eq. 1.27.

Solution 1.7.3. Database: SSUB
Perform a calculation with hydrogen and oxygen at 1000 K and 1 bar. Set the mole fraction of oxygen to 0.5. Set the reference state of both elements to GAS at the current temperature and pressure of 1 bar (this is done under the components tab of the System definer activity). The chemical potential of oxygen is -4567 J/mol. The partial pressure of O_2 is 0.33333 (list the constitution of the gas).
The chemical potential of an element k is commonly written as

$$\mu_k = {}^\circ\mu_k + RT \ln a_k$$

However, the chemical potential listed by Thermo-Calc is actually

$$\mu'_k = (\mu_k - {}^\circ\mu_k) = RT \ln a_k$$

For the present case we obtain

$$\mu'_{O_2} = RT \ln a_{O_2} = RT \ln p_{O_2}$$

and

$$\mu'_O = \frac{1}{2}\mu'_{O_2} = \frac{1}{2} \cdot 8.314 \cdot 1000 \cdot \ln 0.3333 = -4567$$

This is based on eq. 1.27 which can only be applied for a real or assumed equilibrium.

1.8 Phases

Exercise 1.8.1. Find the total Gibbs energy of a system containing 0.5 kg of SiO_2 and 1 kg of CaO at 1 bar and 1500 K. Suppose the two substances have not reacted with each other. Check the law of additivity.
Hint The system is not really in internal equilibrium since the two oxides have a tendency to react with each other. To avoid that they react with each other, you could simply omit all other phases from the set of data fetched from the database. To check the law of additivity, evaluate the total G and G of the Al_2O_3 phase and G of the CaO phase separately and add them.

Solution 1.8.1. Database: TCOX
First calculate the Gibbs energy of 0.5 kg SiO_2. Select only the QUARTZ phase. It can be convenient to set the site fraction of the SiO_2 species to one as an equilibrium condition. $G^{QUARTZ} = -8.71326 \cdot 10^6$
Then calculate the Gibbs energy of 1 kg CaO. Select only the HALITE phase. $G^{HALITE} = -1.34116 \cdot 10^7$
Finally calculate the Gibbs energy of the joint system. The number of moles of Ca, Si and O can be obtained from the previous two calculations. $G^{HALITE+QUARTZ} = -2.06027 \cdot 10^7$

1.9 Gibbs phase rule

Exercise 1.9.1. Sometimes one plots the phase diagram for a system with different sets of axes in order to illustrate different aspects. Fig. 1.5 shows the Ag-Cu phase diagram at a pressure of 1 bar, plotted in two ways. Locate the fcc+L phase field in both diagrams and try to apply the Gibbs phase rule. Explain the results.
Hint In this system there are two fcc phases. Choose one of them. Remember under what conditions the rule was derived.

Solution 1.9.1. According to Gibbs phase rule the variance is given by $v = c + 2 - p = 2 + 2 - 2 = 2$ for two-phase equilibria in a binary system. In these plots the pressure is fixed to 1 bar, which reduces the variance by one i.e. $v = 1$. A variance of one corresponds to a line, as can be observed in the left hand figure. In the right hand figure however we have two-phase equilibria that are two dimensional which would correspond to a variance of two i.e. be in disagreement with Gibbs phase rule. Gibbs phase rule is only valid for potentials and therefor does not apply to the right hand figure.

Exercise 1.9.2. Eq. 1.16 has some terms with a potential as variable and some with an extensive quantity. Which one is intensive and which one is extensive in the term $Dd\xi$?
Hint You may for instance consider the solidification of a pure metal as the internal process.

Solution 1.9.2. If we consider the solidification of pure metal, then the extent of the process, ξ, is the number of moles of solid metal, which is an extensive property.

1.10 Introduction of new components

Exercise 1.10.1. For the Ca-O-Si system it may be natural to use the three elements as components. However, suppose you are only interested in the reactions between the two primary oxides, CaO and SiO_2, and you like to compute the CaO-SiO_2 phase diagram, which is really a quasibinary section of the ternary one. Should you expect any problem? If so, try to solve it.
Hint A thermodynamic program normally treats the elements as components and for a ternary system they are three. In the present case it may seem natural to define CaO and SiO_2 as the components but the program may still require a third component. You have to introduce a third component that is not situated on the CaO-SiO_2 line. It may seem most logical to select O as the third component. To avoid that other phases in the CaO-O-SiO_2 system appear in the calculation it may be convenient to use a very low O activity, e.g. $1 \cdot 10^{-10}$.

Solution 1.10.1. Database: TCOX
Set CA1O1, SIO2 and O as components. Set the reference state of O as GAS at ambient temperature. Remove the phases fcc, bcc, hcp, diamond, cbcc and cub and set the gas phase dormant. Set N=1, P=1e5, ACR(O)=1e-10, T and x(SIO2) as conditions. Let T and x(SIO2) be axis variables.

1.11 Gibbs energy of formation

Exercise 1.11.1. Evaluate the standard Gibbs energy of formation of $Cr_{23}C_6$ at 1 bar and 1000 K from your data bank system.
Hint Find the Gibbs energy for 1 mole of formula units of $Cr_{23}C_6$. Start by changing the references of Cr and C to bcc-Cr and graphite at 1 bar and 1000 K.

Solution 1.11.1. Database: TCFE
Set the reference states of Cr and C to BCC and GRAPHITE at current temperature and 1 bar pressure, respectively. Separate calculations of the Gibbs energy of 1 mole each of bcc-Cr, graphite and $Cr_{23}C_6$ yields -36694, -12659 and -1315648 [J]. The standard Gibbs energy of formation of $Cr_{23}C_6$ at 1000 K and 1 bar is then $-1315648 + 23 \cdot 36694 + 6 \cdot 12659 = -395723$ [J/mol formula unit]. So $Cr_{23}C_6$ may form spontaneously.
Alternatively, a calculation can be made where bcc and graphite are entered and where the status of $Cr_{23}C_6$ is set to dormant. The driving force D for $Cr_{23}C_6$ is then equal to 1.6409. We have that $1.6409 \cdot 29 \cdot R \cdot T = 395656$, which is almost the same absolute value, but not exactly the same since the bcc is not pure bcc-Cr.

1.12 Properties of the Gibbs energy function

Exercise 1.12.1. Evaluate the enthalpy of pure Mo at 2000 K relative 25°C and 1 bar.
Hint You may not need to use Eq. 1.50 because most kinds of thermodynamic software have special procedures for the evaluation of the properties based on the first derivatives of G.

Solution 1.12.1. Database: PURE
Since the reference state is by default 25 °C the correct answer is obtained by simply making an equilibrium calculation at 2000 K and checking the molar enthalpy (50445 J/mol).

Exercise 1.12.2. Evaluate the thermal expansion of an alloy of Fe with 0.5 mass-% C at 1300 K and 1 bar from stored information on G for the fcc phase, which is the stable phase under those conditions.
Hint Again you need the kind of software that can evaluate partial derivatives.

Solution 1.12.2. Database: TCFE For partial derivatives a dot, ".", syntax is used, for example "V.T" for $\frac{\partial V}{\partial T}$. Enter a function "V.T/V", compute the equilibrium and list the value of the function ($6.4 \cdot 10^{-5}$ K^{-1}).

1.13 Adiabatic changes

Exercise 1.13.1. Consider a shock wave traveling through a plate of iron, which initially is at 20°C. Evaluate dT/dP.
Hint A shock wave is very fast and there is very little time for heat conduction. It may happen that there is time for some dislocation movements and the wave may leave the material slightly deformed. Neglecting such effects one can approximate the compression and the release of pressure on the back side of the wave as isentropic. One could then obtain dT/dP when the wave is approaching as $(\partial T/\partial P)_S$. It is directly obtainable from an advanced data bank system for thermodynamics. If such a system is not available one must express the partial derivative in terms of the properties available in tables, i.e. C_P, α and κ_T, which are second derivatives of G with respect to P and T. In that case you should thus transform $(\partial T/\partial P)_S$ to derivatives where P and T are the variables. Since S is also involved you should consider a function $S\,(T, P)$.

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

For $dS = 0$

$$0 = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S + \left(\frac{\partial S}{\partial P}\right)_T$$

and using Eqs. 1.51 and 1.53

$$\left(\frac{\partial T}{\partial P}\right)_S = -\left(\frac{\partial S}{\partial P}\right)_T \Big/ \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{-\partial^2 G}{\partial P \partial T}\right) \Big/ \left(\frac{-\partial^2 G}{\partial T^2}\right) = \frac{V\alpha}{C_P/T}$$

It should be emphasized that V, α and C_P vary with P and T and detailed information is required in order to integrate this result to higher pressures. That can be obtained from a database but integration is still laborious. Much can be gained by using an advanced data bank system.

Solution 1.13.1. Database: TCFE
First make an equilibrium calculation at 293 K to evaluate the entropy. Then replace the temperature equilibrium condition with an entropy condition and compute the equilibrium again. Enter a function “T.P” and evaluate it ($3 \cdot 10^{-9}$ K/Pa).

1.15 Duhem’s theorem

Exercise 1.15.1. Using a thermodynamic data bank system, determine the state of equilibrium of an alloy with 20 mole-% Cu in Ag at 800°C and 1 bar.
Hint The size is not prescribed and you can choose any size, e.g. $N = 1$. With that choice $N_{Cu} = 0.2$ and $N_{Ag} = 0.8$. Or you could enter the condition as $N = 1$ and $x_{Cu} = 0.2$ or even $N_{Cu} = 0.2$ and $x_{Ag} = 0.8$.

Solution 1.15.1. Database: TCSLD
A simple calculation yields the stable phases, fcc and liquid.

Exercise 1.15.2. From the previous exercise you know that there will be two phases, fcc and liquid (L). You will also know the amounts and compositions of the phases. Omit the condition on the value of the temperature and accept the value of the Cu content in L as a new condition for an attempt to determine the temperature.
Hint Of course, you should expect to recreate the same state of equilibrium, i.e. to find $T = 1073\,\mathrm{K}$.

Solution 1.15.2. Database: TCSLD
Of course, the same equilibrium state is obtained.

1.16 Characteristic state function and Gibbs energy model

Exercise 1.16.1. For the Ag-Cu system, try to use the condition that fcc and L must be present in an equilibrium at 800°C and 1 bar.
Hint A way to define that both phases are present would be to require a certain amount of each one, e.g. 1 mole. According to Duhem's theorem it then remains to define $2 + c - 2 = c = 2$ conditions, which should be the values of P and T.

Solution 1.16.1. Database: TCSLD
There are many ways to do this. For example by setting the status of the liquid and fcc phases as "fixed". Alternatively, the number of moles of each phase can be used directly as equilibrium conditions.

Chapter 2

Solution Models

2.1 Constitution and constituents

Exercise 2.1.1. The mole fractions of the components in a phase can be evaluated from the site fractions if one considers the stoichiometric coefficients. Evaluate the mole fraction of component B in the phase $(\mathrm{A,B})_1(\mathrm{B,C,D})_2$ if $y'_B = 0.2$ and $y''_B = 0.05$.
Hint Apply the definition $x_B = N_B/\sum N_i$ to one formula unit.

Solution 2.1.1. For a phase with the constitution $(\mathrm{A,B})_1(\mathrm{B,C,D})_2$, evaluate the mole fraction of B if the site fraction of B on the first sublattice is 0.2 and 0.05 on the second sublattice.

$$x_B = \frac{1y'_B + 2y''_B}{1+2} = \frac{0.2+0.1}{3} = 0.1$$

Exercise 2.1.2. Give the formula showing the constitution of an $\mathrm{A_1B_2}$ phase if one has been able to decrease the mole fraction of B to 0.5 by some A atoms entering as a second constituent of the second sublattice.
Hint Express the formula in a general way as $\mathrm{A}_1(\mathrm{A}_{1-z}\mathrm{B}_z)_2$ and apply $x_B = N_B/\sum N_i$.

Solution 2.1.2. Write the constitution as $\mathrm{A_1(A,B)_2}$

$$x_B = \frac{2y''_B}{1+2} = 0.5$$
$$y''_B = 0.75$$

Thus, $\mathrm{A_1(A_{0.25},B_{0.75})_2}$

2.2 Ideal solutions and related non-ideal solutions

Exercise 2.2.1. In the regular solution model of a binary A-B system one assumes that ${}^{E}G_m = x_A x_B L_{AB}$. Evaluate the partial excess Gibbs energy of component B. *Hint* You can apply Eq. 1.32 directly by neglecting the other terms in G_m or Eq. 1.33 by identifying A_m with ${}^{E}G_m$.

Solution 2.2.1.

$$
\begin{aligned}
&{}^{E}G_m = x_A x_B L_{AB} \\
&{}^{E}G_B = {}^{E}G_m + \frac{\partial {}^{E}G_m}{\partial x_B} - x_A \frac{\partial {}^{E}G_m}{\partial x_A} - x_B \frac{\partial {}^{E}G_m}{\partial x_B} \\
&{}^{E}G_B = x_A x_B L_{AB} + x_A L_{AB} - x_A x_B L_{AB} - x_A x_B L_{AB} = x_A(1 - x_B) L_{AB} = x_A^2 L_{AB}
\end{aligned}
$$

2.3 Chemical activity and activity coefficient

Exercise 2.3.1. One has studied solutions of Mn in fcc Fe-Ni and bcc Fe-Cr alloys at 1200 K and has expressed the Mn activity using pure fcc-Mn and pure bcc-Mn, respectively, as references. For both alloys, Fe-Mn-Ni and Fe-Mn-Cr, one obtained $a_{Mn} = 0.03$. What alloy had the highest activity?
Hint To answer this question you must use a common reference and you may use any state as the common reference, say fcc-Mn. With a data bank system you can simply ask for the activity relative fcc-Mn instead of bcc-Mn as long as you have kept data for the fcc phase. Of course, you could just as well solve the problem analytically by changing to the fcc reference using $a_{Mn}^{fcc-ref} = a_{Mn}^{bcc-ref} \cdot \exp\left[\left({}^{\circ}G_{Mn}^{bcc} - {}^{\circ}G_{Mn}^{fcc}\right)/RT\right]$ but then you must first evaluate the difference for Mn in the two states at 1200 K.

Solution 2.3.1. Database: TCFE
For the unary system Mn, compute the equilibrium at 1200 K and 1 bar for 1 mole and list the Gibbs energy of the system for the cases i) only fcc entered and ii) only bcc entered. These values (-62363 and -62129 [J/mol]) are of course the Gibbs energies of pure fcc-Mn and bcc-Mn. Evaluating the activity of Mn in the Fe-Cr-Mn alloy with fcc as reference we obtain

$$
a_{Mn}^{fcc} = a_{Mn}^{bcc} \cdot \exp\left(\frac{{}^{\circ}G_{Mn}^{bcc} - {}^{\circ}G_{Mn}^{fcc}}{RT}\right) = 0.0307
$$

The activity is highest in the Fe-Cr-Mn alloy.
Note: The chemical potential given by Thermo-Calc for a species k (MU(k) or MUR(k)) is

$$
\mu_k' = \mu_k - {}^{\circ}\mu_k^{REF} = RT \ln a_k
$$

2.4 Excess Gibbs energy

Exercise 2.4.1. An A-B solution phase can be approximated as a regular solution with $L_{AB} = 20$ kJ/mol at 800°C. Evaluate the activity coefficient for B at $x_B = 0.40$. *Hint* You must solve this exercise analytically if you cannot create your own database. Having evaluated the activity coefficient, f_B, you should also evaluate a_B.

Solution 2.4.1. We have

$$RT \ln f_B = L_{AB} x_A^2$$

Thus

$$f_B = exp\left(\frac{L_{AB} x_A^2}{RT}\right) = 2.24$$

and

$$a_B = f_B x_B = 0.8964$$

2.5 Dilute solutions

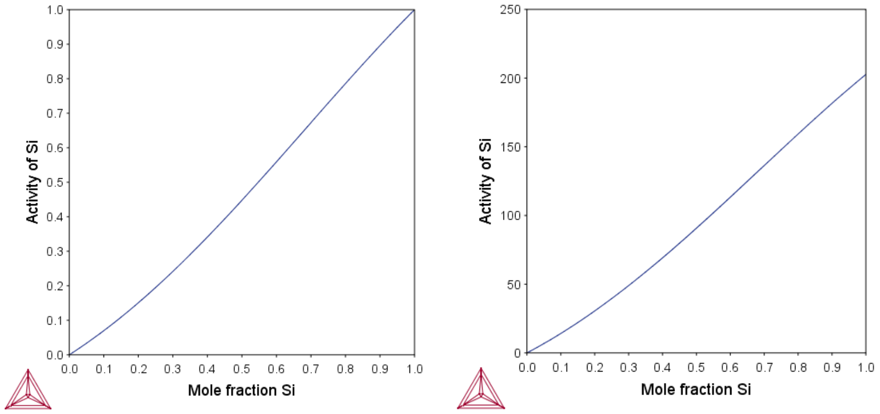
Exercise 2.5.1. The experimental information on many terminal solutions is very limited and often one only gives an ideal solution description based on the Gibbs energy of the solute element in a hypothetical state with the same structure as the solvent. On the other hand, there are methods to estimate that energy relative to the stable state of the solute element in pure form. Study the description of the solution of Si in fcc-Al in your data bank.

1. Plot the activity of Si in the fcc solution (suspend all other phases) at 500°C all the way to pure Si using fcc-Si as reference.
2. Change the reference state to the stable state of Si at the current T and plot the diagram again.
3. From the activity of pure Si obtained from the first diagram compared to the second one, you may calculate the difference in Gibbs energy between the two reference states.

Hint

2. To find the stable state of Si you may for instance calculate the binary phase diagram.
3. Applying the definition of the chemical potential for the two cases you get $\mu_{Si} = {}^{\circ}G_{Si}^{(1)} + RT\ln a_{Si}^{(1)} = {}^{\circ}G_{Si}^{(2)} + RT\ln a_{Si}^{(2)}$.

Solution 2.5.1. The left image shows the activity of Si in fcc-Al relative fcc and in the right image the reference for Si is diamond.



For the difference in Gibbs energy of the two reference states we have

$$
{}^{\circ}G_{Si}^{diamond} - {}^{\circ}G_{Si}^{fcc} = RT\ln\frac{a_{Si}^{fcc}}{a_{Si}^{diamond}} = -34000
$$

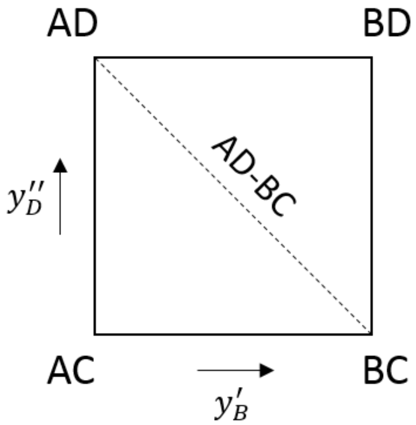
2.6 Phases with sublattices

Exercise 2.6.1. Suppose $a = b = 1$ and $^\circ G_{AC} = 10$, $^\circ G_{AD} = 8$, $^\circ G_{BC} = 2$, $^\circ G_{BD} = 20$ (kJ/mol) in Eq. 2.27. Derive an equation for the line of reference along the AD-BC diagonal using y'_B as the variable.
Hint Start by expressing y'_A, y''_C and y'_D as functions of y'_B along the diagonal.

Solution 2.6.1. for $(A,B)_1(C,D)_1$ we have

$$^\circ G_m = y'_A y''_C {}^\circ G_{AC} + y'_A y''_D {}^\circ G_{AD} + y'_B y''_C {}^\circ G_{BC} + y'_B y''_D {}^\circ G_{BD}$$

For AD-BC we get the following relationships between the site fractions



$$y'_A = 1 - y'_B$$
$$y''_C = y'_B$$
$$y''_D = 1 - y'_B$$

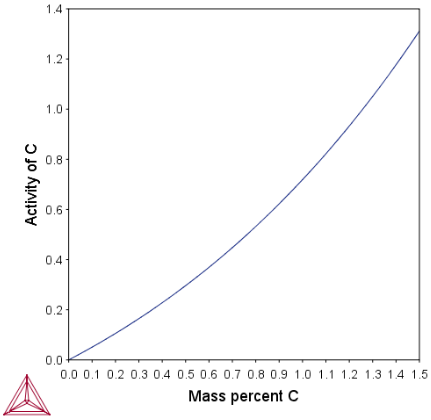
Inserting these relationships gives

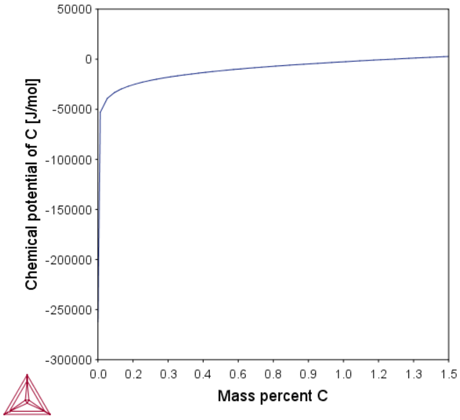
$$\begin{aligned} {}^\circ G_m^{AD-BC} &= (1 - y'_B) y'_B {}^\circ G_{AC} + (1 - y'_B)^2 \, {}^\circ G_{AD} + (y'_B)^2 \, {}^\circ G_{BC} + (1 - y'_B) y'_B {}^\circ G_{BD} \\ &= 10(y'_B - (y'_B)^2) + 8(1 - 2y'_B + (y'_B)^2) + 2(y'_B)^2 + 20(y'_B - (y'_B)^2) \\ &= 8 + 14y'_B - 20(y'_B)^2 \text{ [kJ/mol]} \end{aligned}$$

2.7 Interstitial solutions

Exercise 2.7.1. The interstitial solution of C in fcc-Fe can be represented by the formula $Fe_1\left(Va, C\right)_1$. Using a database compute and plot μ_C and a_C as functions of the C content at 1200 K and 1 bar from 0 to 1.5 mass-% C, using graphite as reference. Use the mole fraction of C, not y''_C.
Hint Of course, the computer can directly evaluate x_C and plot the diagram.

Solution 2.7.1. Database: TCFE
The left image shows a_C vs mass-% C and the right μ_C vs mass-% C





2.8 The ideal gas model

Exercise 2.8.1. What is the partial pressure of monatomic H in a hydrogen gas when in internal equilibrium at 1 bar and 2000 K?

Solution 2.8.1. Database: SSUB
Since, $p_H = y_H$, this can be obtained directly after computing the equilibrium by listing the site fractions/constitution of the gas phase ($=1.6 \cdot 10^{-3}$).

Exercise 2.8.2. Evaluate $\mu_O - H_O^{SER}$ and $\mu_O - 0.5{}^{\circ}G_{O_2}\left(T\right)$ for air with 20% O_2 at 1 bar and 1000 K.

Solution 2.8.2. Database: SSUB
Read only oxygen from the database and set the pressure to 0.2 bar. Set the reference state of oxygen to GAS at current T and 1 bar pressure. Both quantities are given by the chemical potential as listed by Thermo-Calc. The former with the default SER reference (=-117074 J/mol) and the latter with the user defined reference (=-6691 J/mol).

Exercise 2.8.3. Find the value of the standard Gibbs energy of formation of monatomic O from O_2 at 1000 K.

Solution 2.8.3. Database: SSUB
Try the TABULATION module in the classic console version of Thermo-Calc:
Note: In the ancient tabulation module it is sometimes necessary to use upper case letters.

```
SYS: GO TAB
TAB: SWITCH SSUB6
TAB: TABULATE-REACTION
Reaction: 0.5O2=O;
Pressure /100000/: 100000
Low temperature limit /298.15/: 1000
High temperature limit /2000/: 1000
Step in temperature /100/: 100
Output file /SCREEN/: SCREEN
```

Giving the result: $1.87685 \cdot 10^5$

2.9 Vapour pressure

Exercise 2.9.1. Find the partial pressures of Fe_1 and Fe_2, respectively, in equilibrium with solid fcc-Fe and bcc-Fe, respectively, at 1750 K. Suppose the solid phase is under a pressure of 1 bar caused by an inert atmosphere. From the results, decide whether bcc or fcc Fe is most stable.

Solution 2.9.1. Database: SSUB and TCFE
Read the gas phase from SSUB and the solid phases from TCFE.
Do equilibrium calculations with one of the solid phases at a time. The partial pressures are obtained from "AC(FE,GAS)" and "AC(FE2,GAS)", respectively. The partial pressures are slightly higher over fcc-Fe, which therefore is less stable than bcc-Fe.

2.10 Thermal vacancies

Exercise 2.10.1. Suppose the fraction of vacancies in a pure solid metal is $1 \cdot 10^{-3}$ at the melting point. What should be the fraction at half the melting point?
Hint Of course, half the melting point means half of the absolute melting temperature.

Solution 2.10.1.

$$\begin{aligned}
\text{Equation 2.57: } y_{Va}^{eq} &= \exp\left(\frac{-{}^{\circ}G_{Va}}{RT}\right) \\
y_{Va}^{eq}(T_m) &= 0.001 \\
\ln y_{Va}^{eq}(T_m) &= \frac{-{}^{\circ}G_{Va}}{RT_m} = -6.91 \\
y_{Va}^{eq}\left(\frac{T_m}{2}\right) &= \exp\left(2 \cdot \frac{-{}^{\circ}G_{Va}}{RT_m}\right) = \exp(-6.91 \cdot 2) = 10^{-6}
\end{aligned}$$

Exercise 2.10.2. Suppose a specimen of pure solid A is equilibrated at the melting point and then quenched to half that temperature. What is the driving force for decreasing the vacancy content at the new temperature? Use the value of $^{\circ}G_{Va}$ obtained from the preceding exercise.

Solution 2.10.2. We know that:

$$D = -\frac{\Delta G}{\Delta \xi}$$

From the previous exercise we have that

$$^{\circ}G_{Va} = -RT_m \ln y_{Va}^{frozen}$$

Consider one mole of lattice sites

$$D_m = -\frac{\Delta G_m}{\Delta \xi}$$

The molar Gibbs energy change can be expressed as:

$$\begin{aligned} -\Delta G_m &= -(y_{Va}^{eq}\mu_{Va}^{eq} - y_{Va}^{frozen}\mu_{Va}^{frozen}) \cong y_{Va}^{frozen}\mu_{Va}^{frozen} \\ &= \{\mu_{Va} = {^{\circ}G_{Va}} + RT\ln y_{Va}\} \\ &= y_{Va}^{frozen}({^{\circ}G_{Va}} + R\frac{T_m}{2}\ln y_{Va}^{frozen}) \\ &= -y_{Va}^{frozen}R\frac{T_m}{2}\ln y_{Va}^{frozen} \end{aligned}$$

The internal variable in this case would be the change in fraction of vacancies

$$\Delta \xi = \Delta y_{Va} \cong y_{Va}^{frozen}$$

The driving force then becomes

$$D_m = -\frac{\Delta G_m}{\Delta \xi} = -R\frac{T_m}{2}\ln y_{Va}^{frozen}$$

2.11 Solutions with associates

Exercise 2.11.1. Analytical expressions for equilibrium constants are usually given through Eq. 2.69 with $\Delta^\circ G_{AB} = \alpha + \beta T$ but more exact descriptions could easily be used in computerized databases. Use such a database to check the temperature dependence of $\Delta^\circ_f G_{H_2O}$. Make the examination from 0 to 1000°C.
Hint Plot $\Delta^\circ G_{H_2O}$ as function of T using the standard states of H_2 and O_2 as references.

Solution 2.11.1. Database: SSUB
The Gibbs energy of formation, $\Delta^\circ_f G_{H_2O}$, can be calculated by setting the standard states of O and H to GAS and calculating the Gibbs energy for one formula unit, i.e. 1 mol O and 2 moles H.