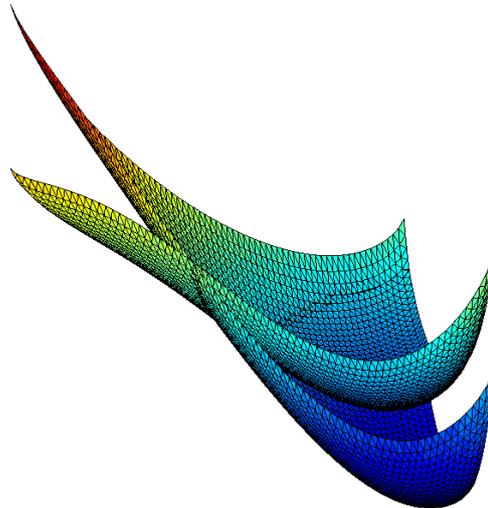




# Computerized Thermodynamics for Materials Scientists and Engineers

by

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## EXERCISES

## Exercises in Applied Thermodynamics Using Thermo-Calc 3.0

### List of the most common notations used in Thermo-Calc.

The <i>potentials</i> are	T	temperature
	P	pressure
	AC(comp)	chemical activity of component
	MU(comp)	chemical potential of component

In the following, Z stands for the *extensive* quantities G,H,S,U,V

Z is the value of Z of the whole system.

ZM is the molar value of the system

ZM(phase) is the molar value of the phase

N is total moles in the system

N(comp) is moles of component in the system

N(phase,comp) is moles of component in phase

NP(phase) is the moles of phase

B is total mass (*in gram*) in the system

B(comp) is the mass (*in gram*) of component in the system

B(phase,comp) is the mass (*in gram*) of component in phase

BP(phase) is mass (*in gram*) of phase

VP(phase) is volume  $m^3$  of phase

x(comp) is mole fraction of component

x(phase, comp) is mole fraction of component in phase

w(comp) is mass fraction of component

w(phase,comp) is mass fraction of component in phase

y(phase,species#sublattice) is site fraction of species in sublattice of phase

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## A. Thermodynamic Properties of Elements

**Ex. A1. Define the system “Co”. What phase is most stable at 1 bar and 1000 K in pure Co?. (CT compendium paragraphs: 1.4, 1.8, 1.15)**

**Background:** This exercise is for learning how to define a system in a database and how to fetch the thermodynamic information and how to define an equilibrium.

Duhem’s theorem is based on the fact that the conditions of a system as controlled by the surroundings can be defined by giving values of P and T if  $N_i$  of all the components are already fixed. The most straight-forward way to define the conditions is thus to give values of P, T and  $N_i$ . In the present case one could give  $N_{Co}=1$  (moles of cobalt equal to one) but could as well give  $N=1$  (moles in system equal to one) because there is no other component in the data fetched from the database.

### Instructions:

- Create a System Definer activity by right clicking on My Project
  - Select a suitable database, e.g. PURE5.
  - Select element Co, either in the alphabetical list over available elements or in the periodic table.
  - Under the tab “Phases and phase constitution” the phases that will participate in the calculation are selected by ticking the corresponding box. A phase that participates in the calculation can either be “entered” or “dormant”. A dormant phase will not be stable in an equilibrium calculation, but the driving force to precipitate the phase will be calculated. In this case you do not have to change anything.
- Create an Equilibrium Calculator activity as successor to the System Definer activity
  - Set the equilibrium conditions for temperature, pressure and system size
- Create a Table Renderer activity as successor to the Equilibrium Calculator activity
  - In the configuration window of the Table Renderer, click “perform”. Alternatively, select the System Definer activity, right-click and select “perform tree now” (selecting “Perform Now” would only trigger the action of the System Definer activity).
- The stable phase is shown in the results window under the corresponding Table Renderer tab. By ticking the box under “Columns” in the configuration window of the Table Renderer and selecting “Driving force/M/All phases” (M here means Molar) the driving forces for all phases are shown in the results window. The driving force is zero for the stable phase. The driving force is negative for the other phases. Then there is no tendency for them to form.

**Ex. A3. What is the driving force for transformation to the most stable phase in Co if it, for some reason, is not present initially? Consider 1 bar and 1000 K as in the previous exercise. (1.4)**

**Background:** You must stop the most stable phase from taking part in the equilibrium although it is included in the dataset.

**Instructions:** Follow the same procedure as in the previous example (you can use the same Project), but set the status of the most stable phase as “dormant”. Select the Table Renderer, right-click and select “Perform Now”. The system now consists of the hcp phase because it is

the one with zero driving force. The list gives a positive driving force for the dormant phase. Write down the value for use in next exercise.

**Ex. A4. Evaluate the difference in molar Gibbs energy of hcp and fcc of Co at 1000 K and 1 bar. (1.4)**

**Background:** It should be possible to recover all the thermodynamic properties of the state of equilibrium after it has been computed.

**Instructions:** The molar Gibbs energies are available after the equilibrium has been computed. By ticking the box under “Columns” in the configuration window of the Table Renderer and selecting “Gibbs energy/M/All phases” the molar Gibbs energy of all phases are shown in the results window. Then it is simple to calculate the difference by hand.

Alternatively it is possible to enter a function. This is done in the configuration window of the Equilibrium Calculator under the “Functions” tab. Tick the box under “Function Definitions”. The default name of the first function is simply “Function 1”. In the box to the right of the equality sign enter “GM(hcp)-GM(fcc)”. To enter multiple functions, press the small green “+” icon at the left end of the configuration window. To remove a function, press the red “-“ icon. Functions can also be entered in terms of “Quantities”. For the present case, select Q1 = Gibbs energy / M / HCP\_A3. Then press the “+” icon next to Q1 and select Q2 = Gibbs energy/M/FCC\_A1. The function “GM(hcp)-GM(fcc)” can then be entered as “Q1-Q2”.

To view the value of functions, 'do “Perform Now” in the last successor. Then select the functions in the configuration window of the Table Renderer, i.e. tick one or more boxes under “Columns” and select “Function / <function name>”. The definition of a function is then shown to the right of the function name. The function values are shown under “Quantities” in the results window.

The value differs from the driving force you obtained in the previous exercise. The reason is that the driving forces are given as dimensionless quantities by dividing them with  $RT$  where  $R$  is the gas constant  $8.3145 \text{ J/mol}\cdot\text{K}$ . Check this by entering a variable equal to the difference in Gibbs energy divided by  $RT$ . Do you get the same value as in A3?

**Ex. A5. Evaluate the heat of melting of pure Co at 1 bar, knowing that the melting temperature is 1767.99 K. (1.1)**

**Background:** You don't know what solid phase will appear at the melting temperature but you can trust that the Equilibrium Calculator will find it if you just ask for the equilibrium at the melting temperature when it is known.

**Instructions:** Follow the procedure in the previous example, but make sure that all phases are entered and that the temperature equilibrium condition is set to 1767.99 K. You can see that the computed equilibrium consists of 1 mole fcc. The driving force for the formation of liquid is negative but has a very low value. It should have been zero if the 1767.99 K was the exact melting point. Evidently, it is off by the third decimal. Accept the result and evaluate the heat of melting by entering a function. Either set the function to “HM(liq)-HM(fcc)” or define quantities Q1= Enthalpy/M/Liquid and Q2= Enthalpy/M/Fcc and a function “Q1-Q2”.

## B. Thermodynamic Properties of Compounds

**Ex. B1. Evaluate the molar Gibbs energy of the compound Fe<sub>3</sub>C at 1000°C. It may be called “cementite” in your database. (1.7,1.10)**

**Background:** Define the system with elements C and Fe check what phases in that system your database contains. Exclude all phases except Fe<sub>3</sub>C before you fetch the data.

**Instructions:** If you wish to reset the program you can press the “New” button in the upper left corner. You can also define multiple activity chains, e.g. one chain starting with a System Definer with only Co defined for the A exercises and another chain starting with another System Definer for the B exercises etc.

Create a System Definer and select a database containing Fe and C, for example the FEDEMO database. You need only the cementite phase for this exercise. Deselect all phases except for cementite. Create an Equilibrium Calculator. In the previous exercises all equilibrium conditions could be entered in the “simplified mode”, but now the “advanced mode” is necessary; press the “Switch to advanced mode” button. Enter the following Condition Definitions

Temperature/Celsius/1000.0  
Pressure/Bar/1.0  
Amount of component/None/Fe/Mole/3.0  
Amount of component/None/C/Mole/1.0

and check that the degrees of freedom is zero by verifying that “Number of missing conditions is 0”.

The check boxes determine if an equilibrium condition is active or not. Use the “+” and “-“ buttons to add and remove rows. In this case it is convenient to use the two “Amount of component” conditions because it corresponds to 1 mole of formula units of Fe<sub>3</sub>C. Create a Table Renderer. Do “Perform Now” in the last successor.

Ticking the check box under Columns in the Table Renderer configuration window and selecting “Gibbs energy / none / system” yields the Gibbs energy of **one mole of formula units** of cementite. Selecting “Gibbs energy / M / system” yields the **molar Gibbs energy** of the system, i.e. the Gibbs energy of one mole of atoms with the same average composition and constitution as the system. In this case it doesn’t matter if “system” or “cementite” is chosen since the system only consists of cementite.

**Ex. B2. Evaluate C<sub>P</sub> of Fe<sub>3</sub>C at 1000 K. (1.12)**

**Background:** This quantity is defined as  $\left(\frac{\partial H}{\partial T}\right)_P$ .

**Instructions:** Set the appropriate conditions. To enter a function containing a derivative a dot “.” syntax is used. Enter a function named “Cp” and set it equal to “H.T”. This is equal to C<sub>p</sub> if pressure has been entered as a condition. Note that quantities (Q1, Q2 etc) cannot be used to enter a derivative. Do “Perform Now” in the last successor and inspect the result.

**Ex. B3. Compute and plot the molar Gibbs energy of Fe<sub>3</sub>C and also its C<sub>p</sub> as functions of T from 300 to 1500 K. (1.12)**

**Background:** For this exercise you must calculate a number of equilibria over the temperature interval.

**Instructions:** Enable an “Axis definition” by ticking the appropriate box in the configuration window of the Equilibrium Calculator. For this axis you select “Temperature [Kelvin]/300.0/1500.0”. Leave the other options with their default values. When the Equilibrium Calculator is “performed”, calculations are made automatically over the specified range. You are only allowed to define axis quantities corresponding to equilibrium conditions, i.e. in order to have temperature as an axis variable temperature must be an equilibrium condition. Furthermore, the temperature selected in the equilibrium condition must be in the interval specified by the axis definition. Results can be viewed in the form of a table, using a Table Renderer activity, or as a plot.

For the latter, define a Plot Renderer activity as a successor to the Equilibrium Calculator. Note that you can have both Table Renderers and Plot Renderers simultaneously as successors to the Equilibrium Calculator. For the Plot Renderer, select temperature as X axis and “Gibbs energy / M / System” as Y axis. Do “Perform Now” in the last successor to obtain the plot. To plot C<sub>p</sub>, the corresponding function must be defined in the Equilibrium Calculator, as in the previous exercise. Then select as Y axis “Function / Cp”.

**Comment.** You may be surprised to see that C<sub>p</sub> has a constant value. The reason is that a rather simple description of cementite has been used in the database

$G - H^{SER} = A + BT + CT \ln T$  yielding  $C_p = \left( \frac{\partial H}{\partial T} \right)_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P = -C$  i.e. a constant value.

**Ex. B4. Evaluate the standard Gibbs energy of formation of the compound Fe<sub>3</sub>C at 1000°C. (1.11)**

**Background:** This is the difference in Gibbs energy between 1 mole of formula units of cementite and its constituents in their most stable states at the current T and P, i.e. 3 moles of fcc-Fe and 1 mole of C as graphite. This is similar to the first exercise but you must now change the references to the elements in their stable states at the current T and P before computing equilibrium. In order to be able to do that you must retrieve also fcc and graphite from the database.

**Instructions:** Create a System Definer and select a suitable database. Select elements Fe and C. Under the “Phases and phase constitution” tab, select phases graphite, fcc\_a1 and cementite. Set the status of fcc and graphite as dormant since these phases only should act as references. Under the “Components” tab, un-tick the SER check-boxes. Then set graphite as reference phase for carbon and fcc for iron. Tick the Current temperature check-box (alternatively enter the fixed reference temperature 1000°C) and let the reference pressure be 1 bar. Create an Equilibrium Calculator and switch to Advanced mode. Set the following conditions: temperature 1000°C, pressure 1 bar, “Amount of component / none / Fe / mole /

3”, “Amount of component / none / C / mole / 1”. Create a Table Renderer to be able to view results. Perform all activities. The Gibbs energy of formation can now be obtained in a number of different ways

- In the configuration window of the Table Renderer, tick a check-box under “columns” and select “Gibbs energy / none / ‘tick’ / system”. Alternatively, enter Gibbs energy / none / “tick” / cementite. Since the system consists solely of cementite these yield the same value.
- In the configuration window of the Equilibrium Calculator under the functions tab, enter a function equal to “GR”, where R stands for selected reference (if no particular reference phase has been chosen the SER will be used). Alternatively, set quantity Q1= “Gibbs energy / none / ‘tick’ / system” and define a function equal to Q1. To display the value of functions, select “function / <function name>” in the configuration window of the Table Renderer.

Note that activities occasionally need to be re-performed when changes are made. When the icons of the activities in the project window are marked by a round green dot they are up to date. Also note that the standard Gibbs energy of formation refer to one mole of formula units, which in this case correspond to four moles of atoms. If a function GMR had been entered, the value would have been for one mole of atoms, or, equally, if normalization “M” instead of “none” had been selected. Finally, the most formal syntax for the standard Gibbs energy of formation would be  $GFR(\text{CEMENTITE})$ , where F stands for formula unit.

**Comment.** According to Gibbs phase rule we need to set  $c+2$  (= number of components + 2) conditions in order to define an equilibrium. In the case of cementite, a stoichiometric phase, we may use P, T, and  $N(\text{fe})=3$   $N(\text{c})=1$  or  $N=4$   $x(\text{c})=.25$  or  $N=4$  and an arbitrary value on the chemical potential or activity of any of the components as the fourth condition. For a stoichiometric phase  $\mu_i$  is not defined and that is why you could use an arbitrary value.

## C. Thermodynamic Properties of Solution Phases

**Ex. C1. Compute and plot the activity of Al and Si in the liquid phase of the Al-Si system at 1 bar and 800 K, assuming that no other phase forms. Try different reference states; liquid for both components or fcc for Al and diamond for Si. Plot the result. Use e.g. the TCAL1 database. (1.14)**

**Background:** You should here consider only the liquid phase. When considering a single phase it is often most convenient to choose the states of reference as the pure elements in the same phase as the solution and at the same P and T. It may even be more convenient to use a selected state of an element as reference independent of what solution phase is considered. That would help later comparisons between the activities in different phases. In the present case, first choose (as reference) the liquid phase for both Al and Si and then fcc for Al and diamond for Si.

**Instructions:** In the System Definer, select the liquid, fcc and diamond phases. Initially, set fcc and diamond as dormant and liquid as entered. Set the reference phase of Al and Si to be liquid at the current temperature and 1 bar pressure. In the Equilibrium Calculator, set conditions for temperature, pressure and mole fraction Si. Enable mole fraction Si between 0.0 and 1.0 as axis variable. In the Plot Renderer, set “activity of component / ‘tick’ / all” on the Y axis and “composition / Si / mole fraction” on the X axis. This first plot yields the activities of both Al and Si over the whole composition range with a pure Al-/Si-liquid phase at the same temperature and pressure as reference. Then set fcc and diamond as reference phases for Al and Si, respectively, and plot the result.

**Ex. C2. Use information on the activity of Mn in liquid Fe-Mn alloys at 1 bar and 1800 K to construct a dilute solution model based on mass-%. Examine how well it works at higher Mn contents. (2.5,2.7)**

**Background:** Steelmaking needs accurate information on alloying elements and impurities in liquid iron. Such information is collected in special databases that also cover oxidic slags.

**Instructions:** Use, for example, the FEDemo database. In the Equilibrium Calculator, choose a low value for the mass-% Mn as equilibrium condition, for example 0.001, where you would expect Henry’s law to hold. Set conditions for T, P and system size. After computing the equilibrium state, the activity of Mn (relative to the SER reference, let us here denote it ac-REF) is shown in the Table Renderer. The value in the dilute solution model should be equal to the mass-% value i.e. 0.001. For any other composition you will thus get the “dilute solution value” by multiplying the activity relative SER with 0.001 and dividing with ac-REF i.e.  $acMn = ac(Mn) \cdot 0.001 / ac-REF$ . Enter this function in the Equilibrium Calculator (enter the numerical value of ac-REF). In the configuration window of the Table Renderer, tick a check box under columns and select “Function / acMn” to display the function in the results window. You can now try different values for the mass-% Mn and if you like you can even plot acMn versus mass-% Mn and inspect how well your dilute solution model holds.

**Ex. C3. Compute and plot the molar Gibbs energy of fcc and liquid Ag-Cu alloys at 1 bar and 900 K using pure fcc Ag and Cu as references. (1.14, 2.2, 2.6)**

**Background:** You will find that the curve for fcc has two minima. Examine how that affects the activity of Cu by plotting  $ACR(Cu)$  (the activity of copper relative a selected reference state) without making any new computation.

**Instructions:** Choose a database, for example SLDEMO, and define a system with Ag and Cu and the liquid and fcc phases. Set the reference phase for both Ag and Cu as fcc at the current temperature and 1 bar pressure. Set conditions for T, P, system size and mole fraction Cu. Let mole fraction Cu over the whole composition range be an axis variable. First set the status of fcc as dormant and plot the Gibbs energy curve for liquid. Remember to tick the check box in the Equilibrium Calculator that indicates that you wish to use the selected reference state.

Now create a second activity chain with a System Definer, an Equilibrium Calculator and a Plot Renderer. In this chain, set liquid as dormant and fcc as entered and plot the molar Gibbs energy. You will find that there are two  $G_m$  curves for fcc with straight lines in the middle.

To create a new plot with results from both calculations, create another Plot Renderer from one of the Equilibrium Calculators. Then select the new Plot Renderer, right-click and select "Add predecessor / <the other Equilibrium Calculator>". The new Plot Renderer will then have two tabs in its configuration window, each corresponding to a specific Equilibrium Calculator. Make sure to select the correct quantities to plot in **both** tabs!

In order to avoid the decomposition into two fcc phases you should turn off the so called "global minimization". This is done in the configuration window of the Equilibrium Calculator under the options tab. Deselect global minimization for both single equilibrium and stepping. Re-performing should now yield a single Gibbs energy curve for fcc with two minima. An alloy with a composition in the middle of the system could thus decrease its Gibbs energy by decomposing into two phases, one low in Cu and one high. Plot the activity of Cu without making any new computation (set Y axis to "activity of component / 'tick' / Cu"). Notice that the Cu activity decreases with increased Cu content in the middle of the system for the fcc-calculation, which proves that the solution is unstable there and it explains why the solution decomposes into two phases.

**Ex. C4. The curve for fcc in the previous exercise had two minima and it affected the Cu activity. That phenomenon vanishes at higher temperatures. Estimate at what T it vanishes. (2.6)**

**Background:** You can find when it vanishes by repeated computations for increasingly higher temperatures. A rough but much simpler method would be to examine at what temperature the activity no longer decreases with the Cu content.

**Instructions:** First, observe at what value of the mole fraction of Cu,  $x(Cu)$ , the  $G_m$  curve is highest. That should be the approximate composition where the tendency for decomposition vanishes last. Set the observed value of  $x(Cu)$  as a condition. Enter a function, e.g. called dadx, for the derivative of the Cu activity with respect to the mole fraction of Cu, i.e.  $dadx = \frac{dacr(Cu)}{dx(Cu)}$  where  $acr(Cu)$  means that the activity is given relative our defined reference

state (i.e. here fcc and not SER). Set temperature as an axis variable, perform, plot and see where the derivative is no longer negative. Remember to turn off the global minimization.

**Ex. C5. Examine the phenomenon of two minima better by computing and plotting H and TS for fcc in Ag-Cu at 900 K and 1 bar. (1.2)**

**Background:** Since  $G=H-TS$  it is interesting to see how their values vary with T and how that affects the shape of the G curve. Plot G, H and TS for at least two different temperatures e.g. 900 and at the temperature where the derivative  $\text{acr}(\text{Cu}) \cdot x(\text{Cu})$  from the previous Exercise is zero.

**Instruction:** First do the plot at 900 K. In the System Definer, select only fcc and set it as reference for both Ag and Cu. Set all conditions in the Equilibrium Calculator and define an axis with mole fraction Cu as variable. Turn off the global minimization. Then select the Equilibrium Calculator in the project window, right-click and select clone. You now have two Equilibrium Calculators originating from the same System Definer with identical settings. In the second of these, enter a function equal to “ $T \cdot \text{SMR}$ ”. From the first Equilibrium Calculator, create a Plot Renderer. Then select the Plot Renderer, right click and select “Add predecessor / <the other Equilibrium Calculator>”. In the first tab of the configuration window of the Plot Renderer, set “Enthalpy / M / ‘tick’ / system” as Y-axis. Under the second tab, set the function as Y-axis. Under both tabs, set “composition / Cu / mole fraction” as X axis. Do “Perform Now” on the last successor. Adjust the scaling manually under both plot tabs so that they are the same. The activity tree should now consist of one System Definer, two Equilibrium Calculators and one Plot Renderer. To plot also G add another Equilibrium Calculator and add also that to the Plot Renderer. Don’t forget to adjust the scaling.

For the calculation at the higher temperature, start by selecting the System Definer, right-click and select “clone tree”. You now have two copies of the same activity tree. In the three newly created Equilibrium Calculators, set the temperature condition. “Perform Now” in the last successor. Adjust the scaling in the plot for the higher temperature.

**Comment.** You know that  $G=H-TS$ . Both are highest around the middle of the system. Since S is multiplied by T its effect will increase at increasing T and it will soon make the two minima merge into one.

To understand the above we may calculate the binary phase diagram Ag-Cu, see Exercises H1 and H2.

## D. Computing Phase Equilibria

### Ex. D1. Compute the melting point for Al at 1 bar. (1.16)

**Background:** You are looking for the equilibrium between liquid and the first solid phase to precipitate. Suppose you don't know which phase that is.

**Instructions:** Create a System Definer activity. Use, for example, the ALDEMO database and select only Al. Create an Equilibrium Calculator activity as successor to the System Definer activity. Switch to advanced mode. Set the pressure to 1 bar and the system size to 1 mole. We want to first calculate an equilibrium where the system consist of liquid only. Try setting the temperature to 1000 K. Create a Table Renderer activity as successor to the Equilibrium Calculator. "Perform Now" on the last successor and check that the stable phase is liquid. Now create a second Equilibrium Calculator activity as successor to the first. The second Equilibrium Calculator will use the equilibrium state calculated by the first as a starting point. This procedure will aid the program when more advanced equilibrium conditions are used. In the second Equilibrium Calculator, instead of the temperature condition set "Fix phase / LIQUID / 0.0". This means that at the calculated equilibrium liquid should just be stable, but the system should consist of some other phase. Create a Table Renderer activity as successor to the second Equilibrium Calculator. Perform Now. The melting point of Al at 1 bar has been calculated by the second Equilibrium Calculator and you can also see what solid phase that would precipitate.

**Comment:** When an equilibrium calculation fails to converge it often helps to calculate a similar equilibrium, but with simpler conditions, just before. Simple conditions are typically temperature, pressure and overall composition. Conditions that may be difficult to satisfy without a good starting point could be, for example, fixed phases and composition of phases.

### Ex. D2. Compute the temperature where liquid is in equilibrium with Al(fcc) and Si(diamond structure) at a pressure of 1 bar in the Al-Si system. Check also the composition of the liquid. (1.9;1.15)

**Background:** In exercise A2 the number of conditions was discussed with reference to Duhem's theorem but it does not apply to the present case. That will be discussed in the comments.

**Instructions:** Fetch data for fcc, diamond and liquid for the Al-Si system from the ALDEMO database. As in the previous example, this type of calculation in general needs to be performed in several steps to ensure convergence. Create an equilibrium calculator and switch to advanced mode. Set the conditions that pressure is 1 bar, temperature is 1000 K and amount of Al and Si is 1 mole each. Create a table renderer, click perform, and check that liquid is stable. Now create a second equilibrium calculator as successor to the first. In the second equilibrium calculator, replace the temperature equilibrium condition with the condition "Fix phase / LIQUID / 0.0". Create a second table renderer as successor to the second equilibrium calculator, click perform, and inspect the results. Finally, create a third equilibrium calculator where the conditions are that pressure is 1 bar and that fcc, diamond and liquid are "fixed" to 1 mole each. Create a table renderer and inspect the final results.

**Comments:** Here you have set only one condition,  $P=1e5$  and normally four conditions are required for a binary system according to Duhem's theorem. The difference is explained by three phases being fixed.

**Ex. D3. At what temperature will an Al alloy with 1 mass-% Si start to precipitate fcc at 1 bar? (1.16)**

**Background:** You know the phases in the equilibrium but one of them is not yet present.

**Instructions:** Use the same data, and a similar procedure, as in the previous exercise. In the first equilibrium calculator, set conditions for temperature, pressure, system size and composition. Set the temperature such that liquid is stable. In the second equilibrium calculator, release the temperature condition and set a condition "Fix phase / fcc / 0.0".

**Ex. D4. What is the solubility of Si in the Al-rich fcc phase at 1 bar and 400°C? (1.16)**

**Background:** The system can have any composition as long as it falls outside the one-phase field for fcc-Al. You can either define where the system should fall in the phase diagram by giving a Si content, or what phases it should have at given P and T.

**Instructions:** There are (at least) two options. The first is to simply set conditions for temperature, pressure, system size and then a condition for the silicon content such that the Al-rich fcc phase and another phase (the diamond phase) are simultaneously stable. The second option is to set "Fix phase / diamond / 0.0" instead of the condition for the Si content. The second option may require that the calculation is performed in two steps as in the previous exercise.

**Ex. D5. What is the solubility of Cu in solid Al at 1 bar and 400°C? (1.16)**

**Background.** This is similar to the previous exercise but this time you should learn to inspect all the aspects of the results.

**Instructions:** You don't know what Cu-rich phase will first precipitate from the Al-rich fcc phase. After you have selected the two elements you should therefore retain all the phases that are obtained automatically. Set conditions for temperature, pressure, system size and then guess that a condition for 2 mass-% Cu will be above the solubility limit. Perform the calculation and inspect the result. You find an equilibrium between two phases, fcc and  $Al_2Cu$ , and you can read their compositions. The solubility of Cu is the Cu content of the fcc phase.

**Ex. D6. In the Al-Si-Cu system, at what temperature is an Al-rich liquid in equilibrium with solid diamond-Si, solid fcc-Cu and  $Al_2Cu$  at 1 bar? (1.16)**

**Background:** This exercise show how to progressively replace "simple" equilibrium conditions with "advanced".

**Instructions:** Choose the ALDEMO database and define the Al-Si-Cu system. Use the same procedure as in exercise D2. Start with conditions for temperature, pressure, and the number of moles of each component, e.g. "Amount of component / None / Al / Mole / 1.0". In each successive equilibrium calculator, replace one of the original conditions with a "fix phase 1.0

mole” type of condition. In the end there will only be conditions for pressure and “fix phase”. You may need to adjust the number of moles of components to come closer to the final equilibrium.

**Comments:** This kind of equilibrium is often called a ternary eutectic or a class I four-phase equilibrium.

## E. Properties of Equilibrium States

**Ex. E1. Compute and plot the molar Gibbs energy and enthalpy of pure Fe between 300 and 2300 K at 1 bar. (1.12;4.3)**

**Background:** In this exercise there is no reason to change the reference. Compare with next exercise.

**Instruction:** Select, for example, the FEDEMO database. In the Equilibrium Calculator set the pressure to 1 bar, system size to 1 mole and the temperature to any value between 300 and 2300 K. Define temperature as an axis variable in the range 300 to 2300 K. It may be convenient to use two Plot Renderers, one for plotting Gibbs energy and one for enthalpy. If “Gibbs energy / M / all phases” is chosen as Y axis the curve is coloured differently in different phase regions, contrary to what is obtained if “system” is chosen instead of “all phases”. Also try this for the enthalpy plot.

**Comments.** The G curve is continuous but has a kink between bcc and liquid. The H curve has an evident discontinuity there because  $H=dG/dT$ . That discontinuity is the difference in H of the liquid and bcc and is thus the heat of melting. There is also some heat of transition between bcc and fcc and between fcc and bcc. It is so small that you should magnify that region in order to see it. This is why it is not possible to see the corresponding kinks in the G curve.

**Ex. E2. Compare the molar Gibbs energy for pure Fe as liquid, fcc and bcc.**

**Background:** The most accurate way to compare a property between two phases in a range of temperatures is to compute and plot the difference directly. Then you can use a high magnification for a wide range of T. A convenient way would be to change the reference to fcc at all temperatures.

**Instructions:** Follow the same procedure as in the preceding example except that you should i) set fcc at the current temperature and 1 bar pressure as reference and ii) change the right-most option for the temperature axis definition from “normal” to “separate phases”. The latter change will ensure that the properties of all phases are evaluated at all temperatures, and not just where the phase is stable. Remember to tick the check-box in the Plot Renderer indicating that the chosen reference should be used.

**Comments:** The curve for the difference between liquid and fcc looks simple but the one for bcc and fcc has a peculiar shape. It passes through zero twice, which reflects the two transition points obtained in the previous exercise. Crystallographically, bcc is a high temperature phase which is also manifested for Fe. However, at low temperatures bcc turns ferromagnetic which lowers its Gibbs energy and that stabilizes bcc.

**Ex. E3. Compute and plot the fractions of various phases for an Fe alloy with 0.3 mole-% C between 300 and 2000 K at 1 bar. (1.9;4.3)**

**Background:** This is similar to exercise E1 but here it is a binary system. However, the procedure is almost identical. In addition you should plot the fractions of phases but that does not affect the computations. That is done in the Plot Renderer.

**Instructions:** In the Plot Renderer, set temperature as X axis and “Amount of phase / M / All phases / Mole” as Y axis.

**Comments:** At about 1000 K there are abrupt changes in the fractions. Evidently, there is a transformation that occurs at a well defined temperature. The legend helps you to identify the transformation  $bcc + graphite \rightarrow bcc + fcc$ , although the amount of graphite is very low. Three phases are thus involved and the Gibbs phase rule tells you that the variance is  $v=c+2-p=2+2-3=1$ . That degree of freedom has been used to choose a value of P. The three-phase equilibrium is thus *invariant*. It is hard to see all the details in this diagram. You may like to magnify some interesting ranges of T.

**Ex. E4. Compute and plot the fractions of various phases for an Fe-C alloy between 0 and 1.5 mole-% C at 1 bar and 1100 K. (4.3)**

**Background:** This is similar to the previous exercise but now you should have composition as axis variable.

**Instructions:** In the Equilibrium Calculator, set “Mole percent C” as axis variable. Note that only the equilibrium conditions are available as axis variables. In the Plot Renderer, set “composition / C / mole percent” as X-axis and “amount of phase / M / all phases / mole” as Y-axis.

**Comments:** It is well demonstrated that the fractions vary linearly in the two-phase fields, which is in agreement with the lever rule. That was not the case in the previous exercise where you stepped in T.

**Ex. E5. Compute and plot the fractions of various phases for an Fe alloy with 3 mass-% Mn and 1 mass-% C between 500 and 2000 K at 1 bar. (1.9;4.3)**

**Background:** Similar to exercise E3 but concerns a ternary system and there could be a four-phase equilibrium, which would here be an invariant equilibrium.

**Instructions:** Use, for example, the FEDemo database. Set the same axes in the Plot Renderer as in exercise E3. If you want a smoother curve you can try to increase the minimum number of steps, alternatively decrease the maximum step size. These are options for the axis definition in the Equilibrium Calculator.

**Comments:** Parts of the diagram are confusing and need higher magnification. However, the legend helps you to identify the reactions. At low temperatures there is a three-phase reaction that is not invariant in the present ternary system. Check with the Gibbs phase rule. The three-phase reaction can be identified by observing in what direction the fractions increase. Increasing T gives the reaction  $bcc + graphite \rightarrow cementite$ . It is finished around 900 K where the last of the graphite has been consumed. Another third phase, fcc, appears at about 950 K but there will never be an invariant four-phase equilibrium because bcc and cementite have disappeared long before the liquid appears.

**Ex. E6. Compute and plot the fractions of various phases for an Fe-Mn-C alloy with 3 mass-% Mn between 0 and 1 mass-% C at 900 K and 1 bar. (4.3)**

**Background:** This is similar to the previous exercise but involves having composition instead of temperature as axis variable.

**Instructions:** Follow the same procedure as in the previous exercise but use carbon content as axis variable. Plot mole-% carbon versus number of moles of the different phases.

**Comments:** In exercise E4 the fractions varied linearly with composition in a two-phase field but not here. The lever rule cannot be applied because the change in composition is not along a tie-line. That could be seen in an isothermal section of the ternary phase diagram to be presented later.

**Ex. E7. Compute and plot the fractions of phases over the whole Fe-C system at 1000 K. Check if the lever rule is applicable. (1.15;4.3)**

**Background:** It should be interesting first to plot the fractions versus the mass-% C and then using mole-%.

**Instructions:** Use the same procedure as before.

**Comments:** You should have found linear variations in one of the diagrams. The conclusion is that the lever rule only holds if the axis variables are related in the correct way! In fact, the lever rule applies to diagrams with two molar axes where the mole is defined in the same way. The fraction “amount of phase / M / <phase> / mole” is actually the number of moles of a phase per mole of the system. The mole fraction of C is also expressed per mole of the whole system. The lever rule can thus be applied to that diagram. If you would like to use mass-% of C then you should plot the mass fraction of the phases!

## F. Potential Phase Diagrams

**Ex. F1. Compute the P,T phase diagram for pure Fe between 300 and 2300 K and 1E5 and 20E9 Pascal.**

**Background:** Here you are introduced to using two axis variables which helps you to produce phase diagrams, which are quite different from property diagrams. In phase diagrams each point in the entire diagram represents a possible equilibrium state, not only the points that fall on lines as in property diagrams.

**Instructions:** Select the FEDEMO database and define a system with only Fe. You will probably see that there are many possible phases even in a unary system. However some of them are so called end-members that would never be stable in the pure Fe system and those phases you may deselect. According to the Gibbs phase rule, a maximum of three phases can be in equilibrium with each other. You should thus expect more than one such equilibrium. Tick two axis definitions in the Equilibrium Calculator and set temperature and pressure as axis variables. In the Plot Renderer, set temperature and pressure as X and Y axis, respectively. The legend option “stable phases” will help you identify the different phase regions.

To label the phase fields, note that you may right click in the area of interest and select “Add Label”.

**Ex. F2. Produce a phase diagram for pure Fe with the P and  $\mu_{Fe}$  axes.**

**Background:** For pure Fe there are three potentials, T, P and  $\mu_{Fe}$ . However, according to the Gibbs-Duhem relation, there is a relation between them. Only two are independent. The diagram from the previous exercise shows all the possible equilibrium states of pure Fe within the limits defined by the axes. However, one could as well describe these states in another coordinate system, e.g. P,  $\mu_{Fe}$  and plot the result in the P,  $\mu_{Fe}$  coordinate system. You may compute that diagram as you computed the P, T diagram. On the other hand, since the states are really the same as before you can use the previous computations and simply choose a new pair of axes when plotting.

## G. Molar Phase Diagrams

### Ex. G.1. Produce a molar phase diagram for pure Fe. (4.4)

**Background:** For a pure element there are no mole fractions to use as axes. However, you could produce a  $V_m, S_m$  phase diagram.

**Instructions:** After having computed a potential phase diagram as before, you can in principle plot the results with any pair of axes. Repeat the computation of the Fe system (Exercise F1) and plot the results as a molar phase diagram with  $V_m, S_m$  axes (molar volume, molar entropy).

## H. Mixed Phase Diagrams

**Ex. H1. Calculate the binary phase diagram Ag-Cu at constant pressure. Perform the calculation by varying the mole fraction of Cu and the temperature (which will be in Kelvin). Plot the diagram also using mass-% Cu and temperature in Celsius**

**Background:** Previously we have only used one axis variable, but now we will use two.

**Instructions:** In the System Definer, choose for example the SLDEMO database and select Ag and Cu. In the Equilibrium Calculator, define a starting point for your calculation using conditions on pressure, temperature, system size and mole fraction Cu. Enable two Axis Definitions for Mole Fraction Cu and Temperature [Kelvin]. The variables of the Axis Definitions must be equilibrium conditions. In the plot renderer, try both mass-% and mole fraction Cu as X axis variable and both Kelvin and Celsius as temperature unit on the Y axis.

**Comment:** Note that you can plot other quantities than those that you used in the calculation without reperforming the calculation.

**Ex. H2. Calculate the binary phase diagram Ag-Cu at constant pressure. Perform the calculation using a Binary Calculator activity.**

**Background:** For simple binary phase diagram calculations it is possible to use the Binary Calculator activity. Use the TCBIN database and select Ag and Cu. You must still create a plot renderer activity.

**Ex. H3. Calculate the ternary phase diagram Fe-Cr-Ni at constant pressure and 1000 K. Perform the calculation by varying the mole fraction of Cr and Ni.**

**Background:** You can only choose axis variables that have been used as conditions .

**Instructions:** Use, for example, the FEDEMO database. Set conditions for pressure, temperature, system size and composition expressed in mole fraction Cr and Ni. Select mole fraction Ni and Cr as axis variables. To toggle between a square and triangular diagram, use the “Show Triangular” button. Try also to vary the number of tie-lines shown.

**Ex. H4. Calculate the ternary phase diagram Fe-Cr-Ni at constant pressure and 1000 K. Perform the calculation by using a Ternary Calculator activity.**

**Instructions:** Similarly to the Binary Calculator there is also a Ternary Calculator.

## J. Equilibria in Gases

**Ex. J1. Evaluate the equilibrium fractions of the different molecules that appear in a gas with the initial amounts 1 mole each of H<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> at 1 bar and 1000 K. (2.10)**

**Background.** One can find the answer using the equilibrium constants for a number of reactions but then one must select a set of “independent reactions” and not use the equilibrium constants for any other reactions. Otherwise, the system of equations will be overdetermined. There will be no such problem when one uses a computer program.

**Instructions.** Use, for example, the SUB4A database and define a system with H, O and C. In the Equilibrium Calculator, enter conditions in the advanced mode (press the button “switch to advanced mode” if the current view is the simplified mode). Set conditions for temperature and pressure. Set the number of moles of C, O and H to 1, 4 and 2, respectively, by using conditions “Amount of component / None / C / mole / 1.0” etc. In the Table Renderer results window, choose “composition and constitution” from the drop-down menu to view the site fractions, i.e. partial pressures, of the various species.

**Ex. J2. Consider pure hydrogen gas at 2000 K and 1 bar. Compute equilibrium and evaluate the partial pressure of the monatomic H species. (2.10)**

**Background:** It may be interesting to check what species a system, defined by the single component H, has according to your database.

**Instructions:** Use, for example, the SUB4A database and define the system H. The partial pressure of a species  $j$  is equal to  $P y_j$  (where  $y_j$  is the so-called site fraction) and, since  $P=1$  bar,  $y_j$  will directly give the partial pressure in units of bar.

**Ex. J3. Compute the equilibrium of the H-O gas system across the whole system at 2000 K and 1 bar. Plot the molar entropy of mixing in one diagram and the fractions of species H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O in another. (2.10)**

**Background.** From information on metallic binary solutions you have the experience that the entropy is highest around the middle of the system. This is not necessarily so for solutions with associates. Gases may serve as good examples.

**Instructions.** Define a system with H and O. Check that you only have the gas phase. If there is another phase, you should deselect it. Change the reference of H and O to gas, i.e. pure H<sub>2</sub> and O<sub>2</sub>, at the same T and P. In the Equilibrium Calculator, set conditions for temperature, pressure, system size and mole fraction oxygen. Set mole fraction oxygen as axis variable. Create two Plot Renderers as successors to the Equilibrium Calculator. In both Plot Renderers, set “composition / O / mole fraction” as X-axis. Set molar entropy (“entropy / M / ‘tick’ / system”) as Y-axis in one of them and site fractions of all species in the gas phase in the other (“site fraction / gas / all / all”). Tie-lines may appear in the plot although they shouldn’t be there; just set “tie-lines: 0” if that is the case. You may see that there are also some additional species with small amounts apart from H<sub>2</sub>O, O<sub>2</sub> and H<sub>2</sub>.

**Comments:** You should find that the entropy diagram shows a deep minimum. The explanation is given by the second diagram.

**Ex. J4. Compute the carbon activity of a gas made by mixing 1 mole of H<sub>2</sub> and 1 mole of CH<sub>4</sub> at 1 bar and 1200 K. (2.10)**

**Background:** You would probably like to get the resulting carbon activities given with graphite as the reference. Make sure that your dataset will contain information on graphite. If it does not, then you must get that information from another database and add that to your dataset.

**Instructions:** Use, for example, the SUB4A database. Select the gas and graphite phases. Set graphite as dormant. Set graphite at ambient temperature and pressure as the reference phase of carbon. In the advanced mode of the Equilibrium Calculator, set conditions for temperature, pressure and amount of components.

**Ex. J5. Evaluate the equilibrium constant  $K^P$  for the reaction  $CO + 0.5O_2 = CO_2$  at 1500 K. (2.10)**

**Background:** One can find the answer in at least two ways.

1) One can start with a gas containing the species C1O1, C1O2 and O2. Use any amounts of C and O and the fixed value of T as conditions. Remember that  $K^P$  is defined from  $P_{CO_2} / P_{CO} P_{O_2}^{0.5} = K^P$  where all pressures are in bar. Unfortunately, your computer system may not accept partial pressures as thermodynamic quantities. On the other hand,  $P_j = P y_j$  etc. and  $K^P = P_{CO_2} / P_{CO} P_{O_2}^{0.5} = y_{CO_2} / y_{CO} y_{O_2}^{0.5}$  if you have set P=1 bar (1E5 Pa) as a condition. Use for example the SUB4A database. In the Equilibrium Calculator, enter a function Kp equal to “y(gas,c1o2)/(y(gas,c1o1)\*y(gas,o2)\*\*0.5)”. Alternatively, define three quantities Q1, Q2 and Q3 equal to the site fraction of C1O2, C1O1 and O2 in the gas phase, respectively, and enter a function equal to “Q1/(Q2\*Q3\*\*0.5)” (instead of “\*\*” you can use “^”).

2) Evaluate  $\Delta^o G_m^{reaction} = ^o G_{CO_2} - ^o G_{CO} - 0.5^o G_{O_2}$  and obtain  $K^P = \exp(-\Delta^o G_m^{reaction} / RT)$ . This can be done in the tabulation module which is not available in the Graphical mode.

- Click the “Switch to Console Mode” button. You are now using Thermo-Calc Classic. The prompt says “SYS”, meaning that you are in the SYSTEM\_UTILITIES module
- Write “go tab” and press enter. This takes you to the ancient TABULATION\_REACTION module (the prompt becomes “TAB”). In this module you must use CAPITAL LETTERS.
- Enter a function. Write “ENT-FUN KP” and press enter. Write “EXP(-G/R/T);” and press enter.
- Write “TAB-REA” (short for TABULATE\_REACTION) and press enter.
- Write “C1O1+0.5O2=C1O2;” and press enter.
- Select a SSUB database
- Set pressure to 100000 Pa
- Select the low and the high temperature limit and the step in temperature, e.g. 1400, 1600 and 100. The value for  $K^P$  is listed in the rightmost column.

Compare the two different ways of calculation.

**Ex. J6. Evaluate the carbon solubility in iron in equilibrium with a gas initially consisting of 80% CO and 20% CO<sub>2</sub> at 1300 K and 1 bar.**

**Background:** For this exercise you should use the SUB4A database for the gas and the FEDEMO database for the iron.

**Instruction:** Create a System Definer activity and select the SUB4A database. Define C, O and Fe and select the gas phase only. Then create a second System Definer as successor to the first. The default name will be “Appended system”. In this System Definer activity, select the FEDEMO database. Select C, O and Fe and the bcc, fcc and graphite phases. Set the reference phase of carbon as graphite at ambient temperature and pressure. Set graphite as dormant. As a successor to the second System Definer activity, create an Equilibrium Calculator activity. Switch to advanced mode. As an approximation of the gas being an inexhaustible source, set the input number of formula units of the gas species to 100 moles and the number of moles of iron to 0.01.

Try also to plot how the solubility varies with temperature.

If you make a similar calculation, but instead have a gas composed of 10% methane and 90% hydrogen the variation with temperature will be different. Why?