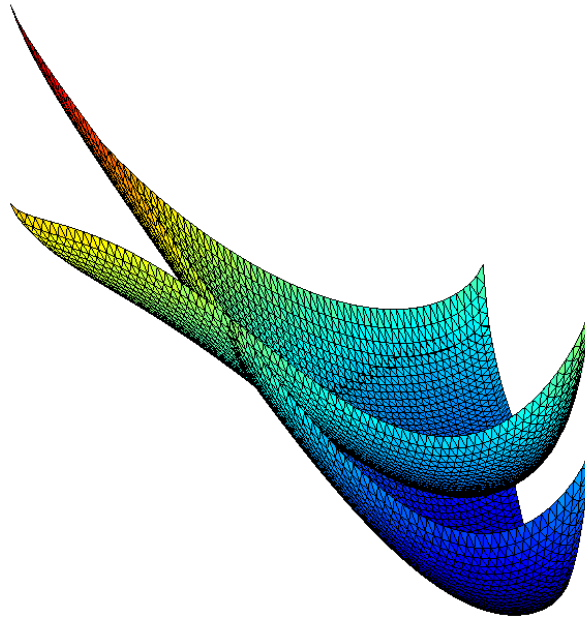


Computerized Thermodynamics for Materials Scientists and Engineers

by

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COMPUTER EXERCISES 2018

2018-03-07

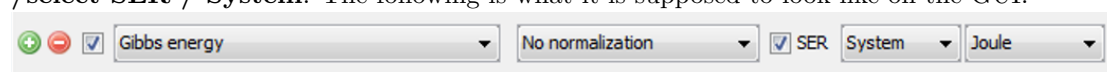
Preface

Instructions to the exercises

When performing these exercises make sure to read the instructions carefully, the questions which should be answered are always in the title of the exercise.

It is recommended that you save your projects and to go back and look at them at a later stage. In some exercises you need to adjust settings on a Configuration window (e.g. the Plot Renderer or Table Renderer). This is an example of these settings.

For the check boxes, either select or deselect as indicated. **Gibbs energy / No normalization /select SER / System.** The following is what it is supposed to look like on the GUI.



You can also search the help in Thermo-Calc for information about terminology and settings. From the main menu choose **Help > Online Help**.

Make sure not to have too many activities in your project tree, it is confusing both for yourself and the software and can therefore make the program crash.

A document should be handed in after each lab session, in that document you should write the answers to the questions and insert the required images/plots. Images can be saved from Thermo-Calc by right-clicking the image/plot and selecting "Save As..."

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, " μ_i "

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) of the system

B(comp) is the mass (in grams) of a 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 in m^3 of phase

x(comp) is the mole fraction of component

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

$w(\text{comp})$ is the mass fraction of component

$w(\text{phase}, \text{comp})$ is the mass fraction of component in phase

$y(\text{phase}, \text{species} \# \text{sublattice})$ is the site fraction of species in sublattice of phase

Acknowledgements

This course material has evolved over the years starting with Mats and me and continued with hard work of many colleagues, mainly when they were still PhD students: Bonnie Lindahl, Sedi Bigdeli, David Dilner, Bartek Kaplan, Yang Yang, Carl-Magnus Arvhult, Fredrik Haglöf.. thank you all. Thanks also go to Henrik Larsson for valuable feedback and to Amanda Wood for correction of the English.

Thermodynamic Databases

There are many different thermodynamic databases available. Sometimes they have the same name but a different number e.g. SSUB4 and SSUB5 where the highest number indicates the most recent version of the database.

- PURE** Pure elements
- TCFE** Steel database, Fe with its most common alloying elements and impurities.
- TCAL** Aluminium alloys, Al with its most common alloying elements and impurities.
- COST** A database for light alloys, mainly Al and Ti alloys.
- TCBIN** Binary systems only!
- SLAG** A database for steel making covering liquid Fe with alloying elements and impurities and oxidic slags.
- SSUB** Stoichiometric compounds and ideal gas.
- SSOL** Many systems with solution phase descriptions - but usually not good for multicomponent systems - check if a certain system is there.
- TCOX** Oxide systems using the ionic liquid model for the liquid and oxides modelled as solution phases.

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A. Thermodynamic Properties of Elements and Compounds

Ex. A1 Define the system “Co”. What phase is most stable at 1 bar and 1000 K?

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** and selecting *Create new activity*
 - Select a suitable database in the drop-down menu at the top of the **System Definer**, e.g. PURE.
 - Select element Co, either in the alphabetical list over available elements or in the periodic table.
 - On the tab “Phases and phase constitution” the phases that will participate in the calculation are selected by clicking to select the corresponding box. A phase that participates in the calculation can either be “entered” or “dormant”. A dormant phase will not be allowed to participate in the equilibrium, but the driving force to precipitate the phase will be calculated. In the present exercise, you do not have to change anything.
- Create an **Equilibrium Calculator** activity as successor to the System Definer activity. This can be done either by right-clicking the System Definer icon in the “activity chain” or by clicking the button called “Create New Successor” at the bottom of the System Definer
 - 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 selecting the box under “Columns” in the Configuration window of the Table Renderer and selecting “Driving force/Per mole/All phases” 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.

Answer: FCC

Ex. A2 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.

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, click “Perform Tree”. 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.

Answer: Driving force of FCC_A1 = 0.02257

Ex. A3 Evaluate the difference in molar Gibbs energy between hcp and fcc Co at 1000 K and 1 bar.

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 selecting the box under “Columns” in the Configuration window of the Table Renderer and selecting “Gibbs energy/Per mole/All phases” the molar Gibbs energy of all phases is 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. Select the checkbox 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, click the small green “+” icon at the left end of the Configuration window. To remove a function, click the red “-” icon. Functions can also be entered in terms of “Quantities”. For the present case, select Q1 = Gibbs energy/Per mole/HCP_A3. Then press the “+” icon next to Q1 and select Q2 = Gibbs energy/Per mole/FCC_A1. The function “GM(hcp)-GM(fcc)” can then be entered as “Q1-Q2”.

To view the value of functions, do “Perform Tree”. Then select the functions in the Configuration window of the Table Renderer, i.e. click 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 J/mol,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 [Ex. A2](#)?

Answers:

Q1 = Gibbs energy of HCP_A3 = -44254.68798 [J/mol]

Q2 = Gibbs energy of FCC_A1 = -44442.34498 [J/mol]

Driving force = Q1-Q2 = 187.657 [J/mol]

Driving force = 0.02257 [dimensionless]

Ex. A4 Evaluate the melting temperature of pure Co at 1 bar

Background: You are looking for the equilibrium between liquid and the solid phase. In order to find the melting temperature of pure Co we must use the “fixed phase” condition, this condition makes the equilibrium a bit harder to find and therefore we must calculate a simple equilibrium, e.g. using P, T and N as conditions in a first step.

Instructions: First remember to set fcc as “entered” again. Then create a second Equilibrium Calculator as a successor to the first one. In the Configuration window of the Equilibrium Calculator, click **Switch to advanced mode** and enter conditions for P , N and “Fix phase/LIQUID/1.0”. Create a Table Renderer, Perform and view the results.

Comments: We remove the condition for the temperature, since that is the quantity we want to find out. The Fix phase condition varies the condition that has been removed until the conditions are satisfied.

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.

Answer: $T_{\text{melt}} = 1767.99 \text{ K}$

Ex. A5 Evaluate the heat of melting of pure Co at 1 bar

Background: After the previous exercise you know the melting temperature and which two phases are in equilibrium, this means that the heat of melting can now be evaluated.

Instructions: Evaluate the heat of melting by entering a function. Either set the function to “HM(liq)-HM(fcc)” or define quantities $Q1 = \text{Enthalpy/Per mole/LIQUID}$ and $Q2 = \text{Enthalpy/Per mole/FCC_A1}$ and a function “ $Q1-Q2$ ”.

Answer: 16200.00274 [J/mol] (TCFE8)

Answer: 16174.527 [J/mol] (TCFE9)

Ex. A6 Evaluate the molar Gibbs energy of the compound Fe_3C at 1000 °C. It may be called “cementite” in your database.

Background: Define the system with elements C and Fe check what phases in that system your database contains. Exclude all phases except Fe_3C 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 TCFE9 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; click “Switch to advanced mode”. Enter the following Conditions:

Temperature/Celsius/1000.0

Pressure/Bar/1.0

Amount of component/No normalization/Fe/Mole/3.0

Amount of component/No normalization/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_3C . Create a Table Renderer and click “Perform Tree”.

Select the check box under Columns in the Table Renderer Configuration window and selecting “Gibbs energy /No normalization / system” yields the Gibbs energy of **one mole of formula units** of cementite. Selecting “Gibbs energy/Per mole/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.

Answer: $G_m(\text{Fe}_3\text{C}, 1000 \text{ C}) = \text{Gibbs energy of the system} = -2.095662\text{E}5 \text{ [J]}$

Ex. A7 Evaluate C_P of cementite, Fe_3C , at 1000 K.

Background: Compounds are modeled similar to the pure elements, since their composition is fixed. Define the system with elements C and Fe and check what phases in that system your database contains. Exclude all phases except Fe_3C before you fetch the data.

Instructions: Create a System Definer and select a database containing Fe and C, for example the TCFE 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; click “Switch to advanced mode”. Enter the following Conditions:

Temperature/Kelvin/1000.0

Pressure/Bar/1.0

Amount of component/No normalization/Fe/Mole/3.0

Amount of component/No normalization/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 giving 3 moles of Fe and 1 mole of C, because it corresponds to 1 mole of formula unit of Fe_3C . Create a Table Renderer and click “Perform Tree”.

The heat capacity under constant pressure, c_P is defined as $(\frac{\partial H}{\partial T})_P$. 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_p if pressure has been entered as a condition. Note that quantities (Q1, Q2 etc) cannot be used to enter a derivative. “Perform Tree” and inspect the result.

Answer: $C_p = 120.60000 \text{ [J/mol*K]} \text{ (TCFE8)}$

Answer: $C_p = 118.828156 \text{ [J/mol*K]} \text{ (TCFE9)}$

Ex. A8 Compute and plot the molar Gibbs energy of Fe_3C and also its heat capacity as functions of T from 300 to 1500 K at constant pressure.

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

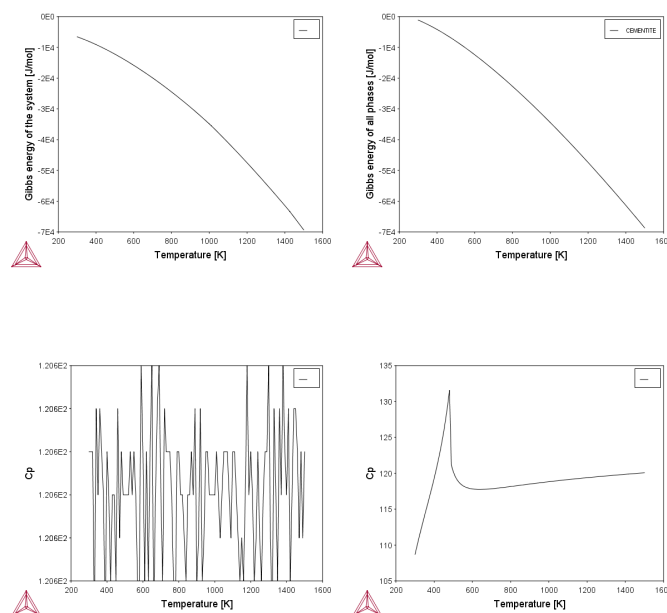
Instructions: Enable an “Axis definition” by selecting the appropriate box in the Configuration window of the Equilibrium Calculator, in this case **Property diagram**. For this axis you select “Temperature /300.0/1500.0”. Leave the other options with their default values. When the Equilibrium Calculator 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 / Per mole / System” as Y axis. Do “Perform” in the last successor to obtain the plot. To plot C_P , the corresponding function must be defined in the Equilibrium Calculator, as in the previous exercise. Then select as Y axis “Function / Cp”. Make sure that the scaling on the Y axis is appropriate by deselecting the “Automatic scaling” box and manually setting the limits to e.g. “100/150/10”.

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.

Comment: If you used an older TCFE database, you may be surprised to see that C_P has a constant value. The reason is that a rather simple description of cementite has been used in this 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. For a newer TCFE database, this description has been improved and the value is no longer constant when varying the temperature.

Answer:



Make sure they only have selected the Cementite phase for the calculations.

Ex. A9 Evaluate the standard Gibbs energy of formation of the compound Fe_3C at 1000 °C.

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 the 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, deselect the SER checkboxes. Then set graphite as the reference phase for carbon and fcc for iron. Select 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 / no normalization / Fe / mole / 3”, “Amount of component / no normalization / 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, select a checkbox under “Columns” and select “Gibbs energy / No normalization / deselect / keep the default System”. Alternatively, enter Gibbs energy / No normalisation / deselect / CEMENTITE. Since the system consists solely of cementite these yield the same value.
- In the Configuration window of the Equilibrium Calculator on 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 / No normalisation / deselect / keep the default 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 the standard Gibbs energy of formation refers to one mole of formula units, which in this case corresponds 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 $\text{GFR}(\text{CEMENTITE})$, 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 $N = 4$ and $x_{\text{C}} = 0.25$, 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 μ_i is not defined and that is why you could use an arbitrary value.

Answer: Gibbs energy of the system -2573.199858 [J]

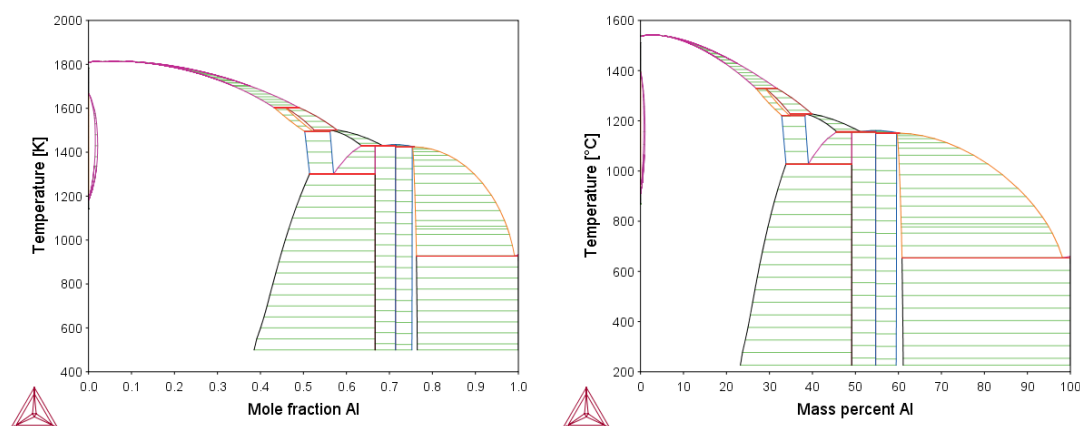
B. Phase Diagrams

Ex. B1 Calculate the binary phase diagram Fe-Al at constant pressure. Perform the calculation by varying the mole fraction of Al and the temperature. Plot the diagram also using mass-% Al 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 SSOL database and select Fe and Al. In the Equilibrium Calculator, define a starting point for your calculation using conditions on pressure, temperature, system size and mole fraction Al. Enable two Axis Definitions by choosing the “Phase diagram” option under “Calculation Type” in the Configuration, chose Mole Fraction Al and Temperature. The variables of the Axis Definitions must be equilibrium conditions. In the Plot Renderer, try both mass-% and mole fraction Al as X axis variable and both Kelvin and Celsius as temperature units on the Y axis.

Comment: Note that you can plot other quantities than those that you used in the calculation without re-performing the calculation.

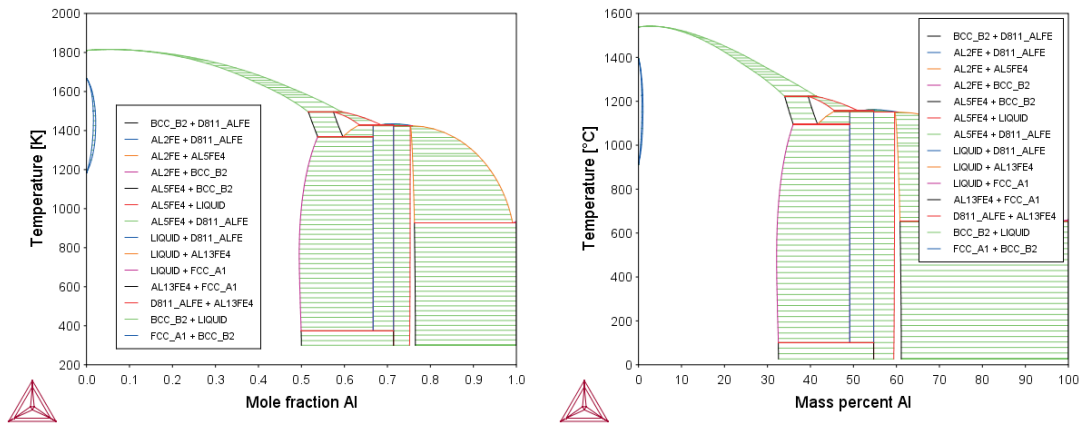


Ex. B2 Calculate the binary phase diagram Fe-Al at constant pressure. Perform the calculation using a Binary Calculator activity. Label all the phase regions and invariant reactions.

Background: For simple binary phase diagram calculations it is possible to use the Binary Calculator activity. Use the TCBIN database and select Fe and Al. You must still create a Plot Renderer activity. You can enter labels for the different phase regions by right-clicking in the plot. The labels can be moved by clicking and dragging.

Comment: Notice that the one-phase regions are always followed by a two-phase region and

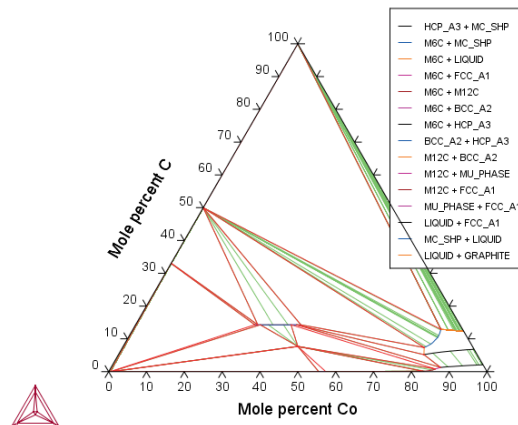
vice-versa if composition is varied. Note also that the “lines” for e.g. AL2FE is also one-phase region although only at a single composition. This is called a stoichiometric phase.



Ex. B3 Calculate the ternary phase diagram W-Co-C at 1 bar and 1400 °C. Perform the calculation by varying the mole percent of Co and C.

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

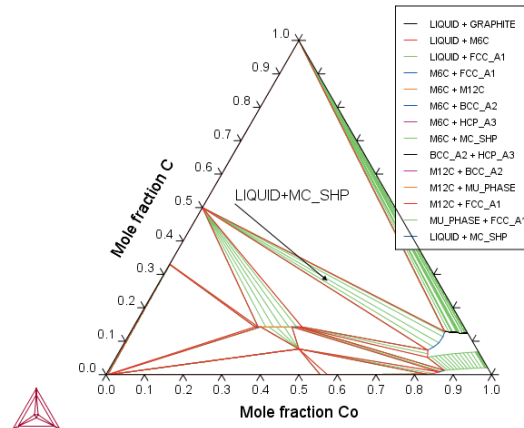
Instructions: Use the TCCC database (Cemented Carbide database). Set conditions for pressure, temperature, system size and composition of Co and C. Select mole percent Co and C as axis variables. To toggle between a square and triangular diagram, click the “Show Triangular” button and Perform. Try also to vary the number of tie-lines shown.



Ex. B4 Calculate the ternary phase diagram W-Co-C at 1 bar and 1400 °C. Perform the calculation by using a Ternary Calculator activity.

Instructions: Similarly to the Binary Calculator there is also a Ternary Calculator. 1400 °C is a typical sintering temperature for cemented carbides. At the sintering temperature the binder phase (Co) is melted but not the carbide grains (MC, where M=W,Co)) All other phases, e.g.

M6C and Graphite, are not wanted. Find and mark out the region where we only have Liquid and MC.



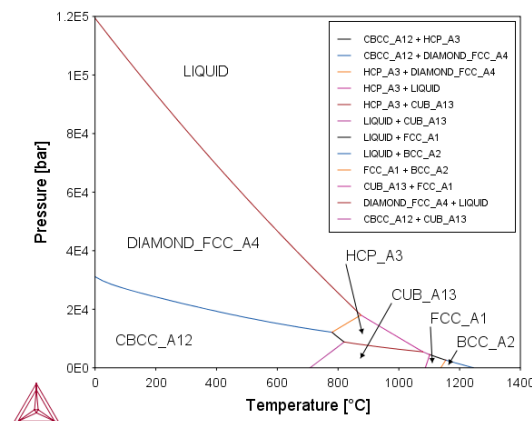
Ex. B5 Compute the P,T phase diagram for pure Mn for $T = 0 - 1400$ °C and $P = 1 - 120000$ Bar

Background: Unary (pure elements) phase diagrams, as opposed to binary are often potential diagrams. In a true phase diagram each point is a uniquely defined equilibrium.

Instructions: If you wish to reset the program you can click 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.

Select the TCFE database and define a system with only Mn. You will probably see that there are many possible phases even in a unary system. However some of them are so called end-members of other phases that would never be stable in the pure Mn system. According to the Gibbs phase rule, a maximum of three phases can in this case be in equilibrium with each other. You should thus expect more than one such equilibrium. Select “Phase diagram” on the Equilibrium Calculator Configuration window and set Temperature and Pressure as the 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.

Once the plot displays in the Results window, you can label the phase fields. Right-click the area of interest and select “Add Label”.



C. Equilibria in Gases

Ex. C1 Evaluate the equilibrium fractions of the different molecules that appear in a gas with the initial amounts 1 mole each of H_2 , O_2 and CO at 1 bar and 1000 K.

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 the SSUB database and define a system with H, O and C. In the Equilibrium Calculator, enter conditions in the advanced mode (click “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, 3 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 list to view the site fractions, i.e. partial pressures, of the various species.

Answer:

$$P_{\text{CO}_2} = y_{\text{CO}_2} = 0.50000 \text{ Bar}$$

$$P_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}} = 0.50000 \text{ Bar}$$

Ex. C2 Consider pure hydrogen gas at 2000 K and 1 bar. Compute equilibrium and evaluate the partial pressure of the monoatomic H species.

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

Instructions: Use the SSUB 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.

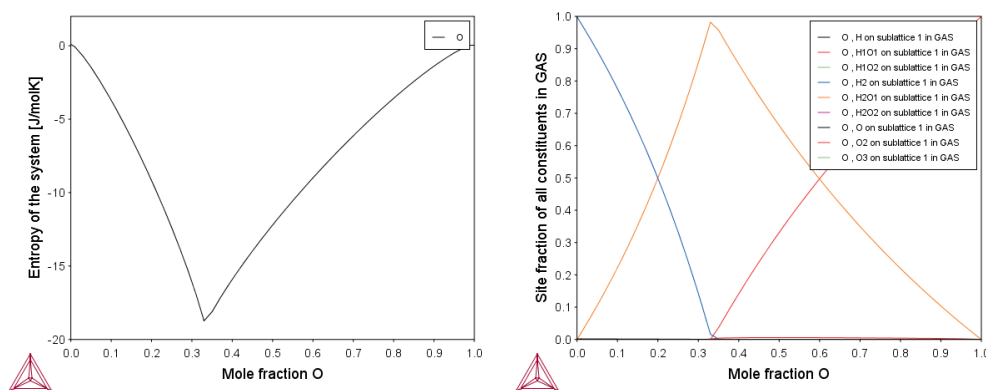
$$\text{Answer: } P_{\text{H}} = y_{\text{H}} = 0.00163 \text{ Bar}$$

Ex. C3 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_2 , O_2 and H_2O in another.

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. On the Phases and Phase Constitution tab, confirm 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_2 and O_2 , 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 for the X-axis variable, set “Composition / O / Mole fraction”. For the Y-axis variable on one Plot Renderer, set molar entropy (“Entropy / Per mole / deselect / System”). For the second Plot Renderer, set site fractions of all species in the gas phase (“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_2O , O_2 and H_2 .

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



Answer: The entropy has a minimum where we only have H_2O .

Ex. C4 Compute the carbon activity of a gas made by mixing 1 mole of H_2 and 1 mole of CH_4 at 1 bar and 1200 K.

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 SSUB 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.

Answer: Activity of C, $a_C=48.24211$ (Graphite is ref. for C)

Ex. C5 Evaluate the equilibrium constant K^P for the reaction $CO + 0.5O_2 = CO_2$ at 1500 K.

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

Instructions:

1. One can start with a gas containing the species CO , CO_2 and O_2 . 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, $P_j = Py_j$ 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 SSUB 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 $\Delta^\circ G_m^{reaction} = \Delta^\circ G_{CO_2} - \Delta^\circ G_{CO} - 0.5\Delta^\circ G_{O_2}$ and obtain $K^P = \exp(-\Delta^\circ G_m^{reaction}/RT)$. This can be done in the Tabulation module only available in Console Mode.

- On the toolbar, click “Switch to Console Mode”. The prompt says “SYS”, meaning that you are in the SYSTEM_UTILITIES module of Thermo-Calc.
- Write “go tab” and press enter. The prompt is TAB, which is the short name for the TABULATION_REACTION module. In this module you must use CAPITAL LETTERS.
- Enter a function. You can use the short names of commands. 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.

Answers:

Method 1: Kp 2,06285E5

Method 2: KP 2.06285E+05

Ex. C6 Evaluate the carbon solubility in iron in equilibrium with a gas initially consisting of 80% CO and 20% CO₂ at 1300 K and 1 bar.

Background: For this exercise you should use the SSUB database for the gas and the TCFE database for the iron.

Instruction: Add an Equilibrium Calculator to a System Definer. On the System Definer, select the SSUB database and then add on another database by clicking on the green plus sign. Select TCFE as the second database. Now you should have two databases (SSUB and TCFE). Define the elements C, O and Fe. For SSUB select the gas phase only and for TCFE select the bcc, fcc and graphite phases. Set graphite as Dormant. On the Equilibrium Calculator click Switch to advanced mode. To approximate that the gas is an inexhaustible source we should here put in much more of the gas components than Fe. Set the System size to 100 mole, the amount of Fe to 0.01 mole and the Site fraction of CO₂ in the gas to 0.2. The last condition is to ensure that we get the gas constitution 80% CO / 20% CO₂ (After calculating the equilibrium you can check this by changing to Constitution for the Gas in the Table Renderer)

Plot how the solubility varies with temperature, for example between 1100 and 1500 K.

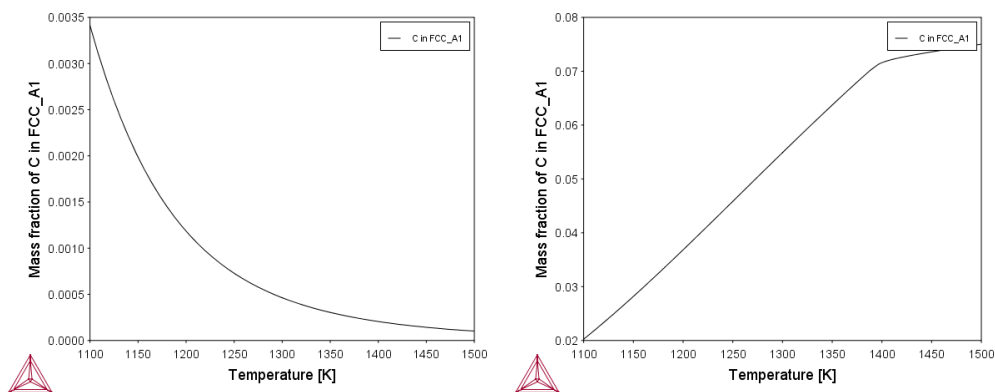
Make a new calculation, but now with a gas of 10% methane (CH₄) and 90% hydrogen gas (H₂) (change O to H and set the Site fraction of H₂ to 0.9). Make sure you still have the same phases as before. What is the solubility of C in Fe now? If you also plot how it varies with temperature

it will now be different. Why?

Answers:

$$CO/CO_2 : w(C, f_{cc}) = 0.000463 \quad \text{or} \quad x(C, f_{cc}) = 0.00215$$

$$H_2/CH_4 : w(C, f_{cc}) = 0.054892 \quad \text{or} \quad x(C, f_{cc}) = 0.2126$$



Comment: Since the C activity has to be the same in the gas as in the Fe, the solubility will increase with increasing C activity in the gas:

- CO is more stable than CO₂ when temperature increases → C activity decreases → Less carburizing
- H₂ is more stable than CH₄ when temperature increases → C activity increases → More carburizing