Computerized Thermodynamics for Materials Scientists and Engineers

by

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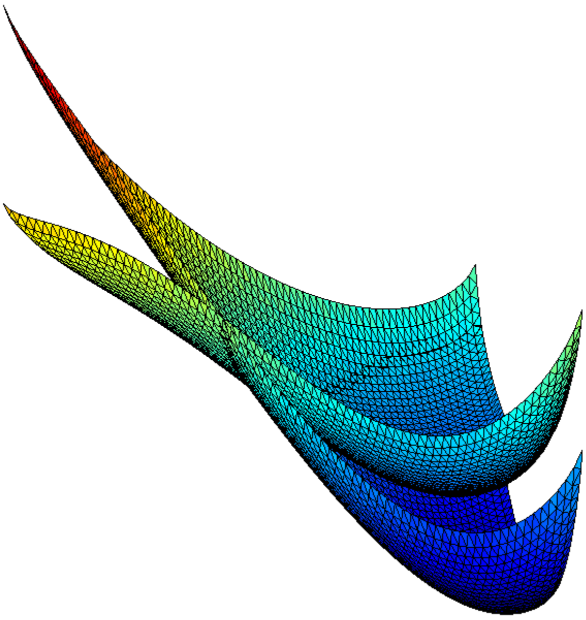


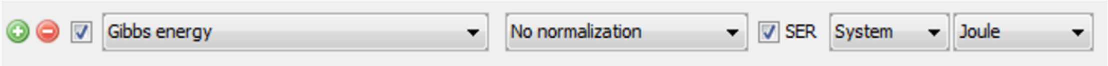
COMPUTER EXERCISES 2022

September 7, 2022

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:



☑ Gibbs energy ▾ | No normalization ▾ | ☑ SER | System ▾ | Joule ▾

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.
On Canvas, there are quizzes created for the exercises, in each quiz you should write the answers to the questions and/or upload 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 *potentials* 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(comp) is the mass fraction of component
w(phase,comp) is the mass fraction of component in phase
y(phase,species#sublattice) is the site fraction of species in sublattice of phase

Acknowledgements

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Thermodynamic Databases

There are many different thermodynamic databases available. Sometimes they have the same name but a different number e.g. SSUB5 and SSUB6 **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.
TCCU	Copper alloys, Cu with its most common alloying elements and impurities.
TCMG	Magnesium alloys, Mg with its most common alloying elements and impurities.
TCNI	Nickel alloys, Ni with its most common alloying elements and impurities.
TCTI	Titanium alloys, Ti with its most common alloying elements and impurities.
TCHEA	High entropy alloys
SSOL	Many systems with solution phase descriptions - but usually not good for multicomponent systems - check if a certain system is there.
SSUB	Stoichiometric compounds and ideal gas.
TCOX	Oxide systems using the ionic liquid model for the liquid and oxides modelled as solution phases.
TCBIN	Binary systems only!

and more specialized databases.

About phase names

Phase names used in databases often refer to the crystal structure e.g. FCC_A1 where the addition A1 is the so called strukturbericht designation where A mean pure elements and 1 mean the face centered cubic structure. In the same way we have BCC_A2, HCP_A3 etc. There are also strukturbericht designation for compounds and ordered structures. In the databases we can therefore find several phases with names starting with FCC, e.g. FCC_L12, and BCC e.g. BCC_B2, which means that it is an ordered phase based on the FCC and BCC lattice respectively. Such a phase can only exist in higher order systems. For the present exercises:

> when asked to select FCC – choose FCC_A1
>
> when asked to select BCC – select BCC_A2

Contents

A. Thermodynamic Properties of Elements and Compounds

Ex. A1 Define the system “Co”. What phase is the 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 (**Note: all databases have a number in addition to the name, the higher the number is, the more recent the database is.**)
    - 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 **Normalized 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.

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** by selecting the tab **Phases and Phase Constitution** under **System Definer**. Select **Table Renderer**, click **Perform**. The system now consists of the second most stable 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. A3 What is the change in Gibbs energy for the transformation from the second most stable phase to the most stable phase? Consider 1 bar and 1000 K as in the previous exercise.

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 the 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**. The function, here **GM(phase name 2)-GM(phase name 1)**, is entered in the box to the right of the equality sign.
  - You should replace **phase name 1** and **phase name 2** with the names of **the most stable** and **the second most stable** phases respectively.

  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, you can also select **Q2 = Gibbs energy/Per mole/**, then select the name of **the second most stable** phase. Then press the "+" icon next to Q1 and select **Q1 = Gibbs energy/Per mole/**, then select the name of **the most stable** phase. The function can be entered as **Q2-Q1**.

- To view the value of functions, **Perform**. Then select select **Function / <function name>** in the **Configuration** window of the Table Renderer. 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.

Comment: The rate of decrease of Gibbs energy may be regarded as the driving force, D, i.e. $D = -(\partial G/\partial \xi)_{P,T}$. For a calculation like the present case, $D = -\Delta G$. However, you may notice that the value differs from the driving force you obtained in the previous exercise. The reason is that 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 change in Gibbs energy divided by RT. Do you get the same value as in Ex. A2?

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 can calculate a simple equilibrium, e.g. using P, T and N as conditions in a first step.

Instructions: Set all phases as **entered**. 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.

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 solid phase is in equilibrium with liquid, this means that the heat of melting, $\Delta H = H_m^{liq} - H_m^{solid}$, can now be evaluated.

Instructions: Evaluate the heat of melting by entering a function. Either set the function to **HM(liq)-HM(the solid phase)** or define quantities **Q1= Enthalpy/Per mole/LIQUID** and **Q2= Enthalpy/Per mole/the solid phase** and a function **Q1-Q2**.

Ex. A6 Evaluate the Gibbs energy of the compound Fe$_3$C at 1300 K. It may be called "cementite" in your database.

Background: The Gibbs energy is always given relative to a reference. This exercise is to learn to calculate the Gibbs energy relative to different reference states.

We need references for both H and S. In the databases, the **Standard Reference State (SER reference state)** is used, i.e. $\Delta^o G_i = {}^o G_i(T) - [{}^o H_i(298) - T {}^o S_i(0)]$, where ${}^o H_i(298)$ is the enthalpy for the element in its most stable state at 298 K and 1 bar. This quantity is denoted as H_i^{SER}. ${}^o S_i(0)$ is the entropy at 0 K which by convention is set to zero. Since S_i^{SER} is zero, the expression can be rewritten as $\Delta^o G = {}^o G_i(T) - H_i^{SER}$. In the case of cementite, the Gibbs energy is therefore given as $\Delta^o G_{Fe_3C} = {}^o G_{Fe_3C}(T) - 3H_{Fe}^{SER} - H_C^{SER}$. The SER reference state is never used for experimental or industrial practice, one uses pure elements at the actual temperature and pressure.

Instructions 1:

- Create a **System Definer** and select a database containing Fe and C, for example the TCFE database. You only need the cementite phase for this exercise and deselect all the other phases. Create an Equilibrium Calculator.
- In the advanced mode, enter the following Conditions:

  Temperature/Kelvin/1300.0
  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 checkboxes 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 checkbox in the **Table Renderer** and selecting **Gibbs energy /No normalization / Select SER / 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.

Question 1: What is the Gibbs energy of the compound Fe_3C per formula unit you calculated at 1300 K with SER as the reference state?

Comment 1: The Gibbs energy per formula unit is four times that of the molar Gibbs energy.

In this case for cementite, it is more useful to know the **standard Gibbs energy of formation** which states 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, i.e. $\Delta^o G_{Fe_3C} = {}^oG_{Fe_3C}(T) - 3{}^oG_{Fe}(T) - {}^oG_C(T)$.

Instructions 2:

- Go back to **System Definer** and make the following changes:
  - Under the **Phases and phase constitution** tab, 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** checkbox and let the reference pressure be 1 bar (alternatively enter the fixed reference temperature 1300 K).
- In **Table Renderer**, click the green button "+" to add one result column. Selecting **Gibbs energy /No normalization / Deselect SER / system** yields the Gibbs energy of cementite calculated with the reference state you have selected, i.e. fcc-Fe and graphite-C at 1300 K.

Question 2: What is the standard Gibbs energy of formation of the compound Fe_3C you calculated at 1300 K?

Comment 2: 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 $N_{Fe} = 3$ $N_C = 1$, or $N = 4$ and $x_C = 0.25$, 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.

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

Background: Stoichiometric compounds are modelled similarly to the pure elements, since their composition is fixed.

The heat capacity under constant pressure, C_P, is defined as $\left(\frac{\partial H}{\partial T}\right)_P$. Use the setup from the previous exercise A6 and set the appropriate conditions. In order to calculate C_P, a function $\left(\frac{\partial H}{\partial T}\right)_P$ needs to be entered. A derivative is defined by using a dot syntax.

Instructions: There are two methods to define the function:

- 1st method: in **Equilibrium Calculator**, under the **Functions** tab, enter a function **Cp** and set it equal to H.T which is equal to C_P if pressure has been entered as a condition.
- 2nd method: set quantity **Q1= Enthalpy / No normalisation / Select SER / System** and set quantity **Q2=Temperature / Kelvin**. Enter a function **Cp** and set it to **Q1.Q2**.

Go to **Table Renderer**, click the green button "+" to add one result column, Function / C_P. **Perform** and inspect the result.

Ex. A8 Compute and plot the heat capacity of cementite Fe_3C as a function 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:

- To define an axis for your plot:
  - In **Equilibrium Calculator** select **One axis**, this is to enable an "Axis definition" in this case one axis.
  - In **Axis Definitions**, set **Temperature /300.0/1500.0** and 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.

- To plot C_P:
  - Define C_P function in the **Equilibrium Calculator** as you did in A7.
  - 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 then select **Function / Cp** as **Y axis**.
  - Make sure that the scaling on the Y axis is appropriate, you may need to **deselect the Automatic scaling"**box and manually set 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.

The C_P curve plotted with the newer TCFE database has a λ shape with a sharp peak. The peak is due to the magnetism of cementite and appears at the Curie temperature of cementite.

Question: At which temperature can you see the sharp peak?

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:** 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. However, it needs to be stressed that it is better to have fewer chains under one single project.

- 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.
- Select **Phase diagram** to enable two Axis Definitions, choose Mole Fraction Al and Temperature. Note that 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. You may also notice that the labels are automatically plotted but that you can delete them.

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 can enter labels for the different phase regions by right-clicking in the plot. The labels can be moved by clicking and dragging. There are other options popping up when you right-click:

Copy - copy the plot
Save As - Save the plot
Print - Print out the plot
Properties - Edit the plot

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", e.g. AL2FE, are also one-phase regions although only at a single composition, i.e. 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 TCCC1 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 in the configuration of the Plot Render 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 activity. 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 unwanted. Find and mark out the region where we only have Liquid and MC.

Ex. B5 Compute the P-T phase diagram for pure Fe between T = 300 - 3000 K and P = 1 - 50 GPa

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: Select the SSOL2 database and define a system with only Fe and the phases BCC_A2, FCC_A1, HCP_A3 and liquid. According to the Gibbs phase rule, a maximum of three phases can in this case be in equilibrium. Select Phase diagram on the Equilibrium Calculator Configuration window and set Pressure and Temperature as the axis variables. In the Plot Renderer, set Pressure as X and Temperature as Y axis. 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**.

Try also to plot Volume (Per mole, All phases) instead of Pressure - what happens to the invariant lines?

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:

- In **System Definer**, select the **SSUB database** and define a system with **H, O and C**.
- In **Equilibrium Calculator**, 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 / No normalization / C / mole / 1.0" etc. Select **Single equilibrium**.
- In **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.

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 Py_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. 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 H2, O2 and H2O1 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:

- In **System Definer**, define a system with H and O. On the Phases and Phase Constitution tab, make sure that you only have the gas phase. 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 in the first Plot Renderer, set molar entropy (**Entropy / Per mole / deselect / System**). For the Y-axis in 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 H2O1, O2 and H2.

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

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 the SSUB database. Select the gas and graphite phases. You may notice that in the SSUB database, graphite is called "C_S" instead. 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.

Comments: you may find that the activity you obtained is rather high.

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 using at least two different methods.

Instructions:

- 1st method: using the Graphical mode
    - Define a system 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.
    - Define K^P from $P_{CO_2}/(P_{CO}P_{O_2}^{0.5}) = K^P$ where all pressures are in bar. Unfortunately, partial pressures may not be accepted as thermodynamic quantities. However, you can use one of the methods given as follows to obtain partial pressures:
        - If you have set P=1 bar (1E5 Pa) as a condition, you then have: $P_j = Py_J$ etc. and $K^P = P_{CO_2}/(P_{CO}P_{O_2}^{0.5}) = y_{CO_2}/(y_{CO}y_{O_2}^{0.5})$. 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) (you have to use "**" instead of "^").

- 2nd method: using the Tabulation module in the Console mode, you can evaluate $\Delta^\circ G_m^{\text{reaction}} = {}^\circ G_{CO_2} - {}^\circ G_{CO} - 0.5{}^\circ G_{O_2}$ and obtain $K^P = \exp\left(-\Delta^\circ G_m^{\text{reaction}}/RT\right)$.
  - 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.

Ex. C6 Evaluate the carbon solubility in iron in equilibrium with a gas initially consisting of 80% CO and 20% CO_2 at 1300 K and 1 bar.

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

Instruction:

- Evaluate the carbon solubility in iron in equilibrium with gas (80% CO and 20% CO_2):
  - In 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.
  - In the Equilibrium Calculator, 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 CO_2 in the gas to 0.2. The last condition is to ensure that we get the gas constitution 80% CO / 20% CO_2.
  - Calculate the equilibrium, change to Constitution for the Gas in the Table Renderer, inspect the result.
  - Plot how the solubility varies with temperature, for example between 1100 and 1500 K.
- Evaluate the carbon solubility in iron in equilibrium with gas (10% CH_4 and 90% H_2):
  - Define a new System Definer and change O to H.

  - Make sure you still have the same phases as before but now with a gas of 10% methane (CH_4) and 90% hydrogen gas (H_2).
  - Following the steps listed before to make a new calculation. Remember to set the site fraction of H_2 to 0.9.

Questions: What are the solubilities of C in iron in the two equilibria above respectively?

Comment: If you also plot how the solubility varies with temperature you will see different trends. Since the C activity has to be the same in the gas as in Fe, the solubility will increase with increasing C activity in the gas:
- CO is more stable than CO_2 when temperature increases → C activity decreases → Less carburizing
- H_2 is more stable than CH_4 when temperature increases → C activity increases → More carburizing

Ex. C7 Calculate the furnace nitrogen pressure (in Bar) to avoid gradient formation in a cemented carbide during sintering

Background: For some cutting applications, mainly turning, it is often beneficial to use a cemented carbide grade with a gradient zone near the surface. This gradient zone is almost free from carbonitrides, (Ti,W)(C,N), and has a higher binder content (Co) than the bulk. If the gas atmosphere in the sintering furnace is nitrogen free (which it is normally), carbonitrides near the surface of the material will dissolve and nitrogen will leave the material as N_2. This will create a surface zone free from carbonitrides, i.e a gradient. In some cases though, this gradient formation is not desired. One way to prevent this is to add nitrogen to the atmosphere in the sintering furnace. With the right partial pressure of nitrogen there is no driving force for the carbonitrides to dissolve.

Instructions: Study patent *US 4277283 A* (http://www.google.com/patents/US4277283) and calculate the nitrogen pressure (in Bar) to avoid gradient formation in the material described in *Example 1*. As you will realize patents are often not written to be easy to read. In this case for example the composition of the material in example 1 is not given for each element, but as weight percentage of raw material compounds. This means we have to do some calculations on the side before we use Thermo-Calc. Here are some corrections of the misprints in the patent:

Misprints in the patent	Correction
$(Ti_0.75W_0.25)(C_0.68N_0.32)$	$(Ti_{0.75}W_{0.25})(C_{0.68}N_{0.32})$
5.0% by weight of $Ta_0.75Nb_0.25$	5.0% by weight of $Ta_{0.75}Nb_{0.25}$
5.5% by weight of C_0	5.5% by weight of Co

Follow the instructions below to obtain the nitrogen pressure and also answer the additional questions at the end.

1. Use Excel, MATLAB or any other software (or by hand) and calculate the mass percent (with four digits) of each element in the material described in *Example 1*.

   Hint: $w(Ta) = 0.05 \cdot \frac{0.75 \cdot M_{Ta}}{M_{Ta_{0.75}Nb_{0.25}C}}$

2. Now create a single Equilibrium Calculator and select the database suitable for cemented carbides, i.e. CCC1. Define the elements (it should be seven). In the Equilibrium Calculator click Switch to advanced mode and enter the sintering temperature and pressure given

in the patent and also your calculated compositions, as mass percent with four digits, for all elements except W (tungsten).

3. Perform and check that one of the stable phases is Gas. The other three should be Liquid ("the melted Co"), MC_SHP ("WC") and FCC_A1 (a mixed carbonitride). If you don't get these phases only (a very small amount of M6C is ok), you probably have made something wrong in step 1.
4. As you can see the given pressure will give denitrification since we get the gas phase. Now create a new Equilibrium Calculator as successor to the first one. Remove the Pressure condition and enter a new condition Fix phase / Gas / 0.0. Create a new Table Renderer and choose to show Pressure in Bar and click Perform. This will give you the pressure needed to avoid the gas phase to form.

5. Compare your results with the needed N_2 pressure given in the patent. Your calculated pressure is much higher. One reason for this is probably that the material will loose nitrogen in the vacuum step of the sintering process, before the liquid state sintering starts. This means that the actual nitrogen content is lower than the initial amount, but this is not mentioned in the patent.
6. Assume that the needed N_2 pressure given in the patent is correct and calculate the nitrogen content in the material that corresponds to this pressure. You can do this by again creating a new Equilibrium Calculator, now as successor to the second one. Then remove the nitrogen condition, and enter the pressure given in the patent, for avoiding denitrification.

Question 1: One of the used raw materials is a $(Ti_aW_b)(C_cN_d)$ (titanium tungsten carbonitride) with a given composition. What is the:

a) Mole fraction of C in that compound, x(C)?
b) Site fraction of C in that compound, y(C)?

Comment: There can be one more reason (at least) that we get another nitrogen pressure than in the patent description. For instance, Thermo-Calc calculates the equilibrium state and one hour sintering time might not be enough to reach equilibrium. Besides, as you can see it might not always be so easy to use information from a patent for calculations, and it can be even harder to try to reproduce the experiments or materials described.