THE UNIVERSITY OF ILLINOIS AT CHICAGO

UIC

Advanced Thermodynamics

FINAL PROJECT

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Define the Binary System

Select a binary system of your interest. Please follow the instructions on how to select your system on the share Google document at `https://docs.google.com/document/d/1ss24XPn6V4550zzWmZHQDgdpuMHeejyXHgBCz6FcOgw/edit?usp=sharing`.
A sample project for Ni-Mn with the necessary calculation steps in ThermoCalc is available on the "ThermoCalc" tab on Blackboard.

In this project, the binary system of Cu-Ni has been selected:

Copper-nickel alloys find extensive application across various industries due to their unique blend of properties. These alloys offer exceptional attributes such as corrosion resistance, thermal stability, electrical conductivity, mechanical strength, and compatibility with diverse materials. Their versatility makes them indispensable in numerous sectors. For instance, their remarkable resistance to corrosion, especially in marine settings, is highly advantageous. Additionally, their ability to maintain mechanical integrity even under high temperatures makes them ideal for applications like heat exchangers and power generation equipment. Furthermore, their excellent electrical conductivity renders them crucial in electrical and electronic components. CuNi alloys offer several benefits, including tailorability to specific needs through composition adjustments, ease of fabrication using standard techniques like welding, and resistance to biofouling in marine environments. Their durability and recyclability contribute to their long service life and environmental friendliness. Overall, copper-nickel alloys stand out as valuable materials across a wide range of industries and applications. [1]

Calculation of the Phase Diagram (50 points)

Calculate the binary phase diagram for your system in the T-X space. A suggested temperature range is from room temperature to 2000-3000 K.

(a) (10 points) Illustrates the step-by-step calculation process in ThermoCalc in your report. Take screen snapshots of each step in the process (e.g., a snapshot of your system definition step)and embed them in your report. Please do not include separate files for this. You should explain each step with any specific assumption above each screenshot in a few sentences.

(b) (10 points) Finally, show the phase diagram plot. Use the label feature in ThermoCalc to specify all the single-phase regions and two-phase regions.

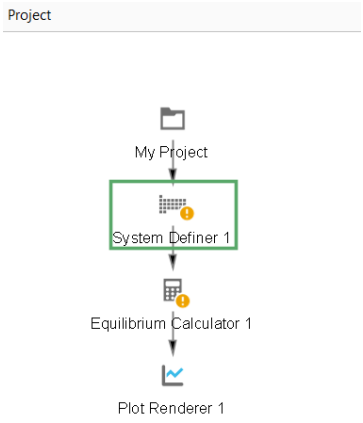
(c) (15 points) Specify 1) the highest melting point (in K) and the corresponding composition X (in mole% or mass%), 2) the lowest melting point (in K) and the corresponding composition X, 3) the melting point (in K) for unary systems. Show all of them over the phase diagram plot as well.

(d) (5 points) If there is any intermediate phase in your system, specify them.

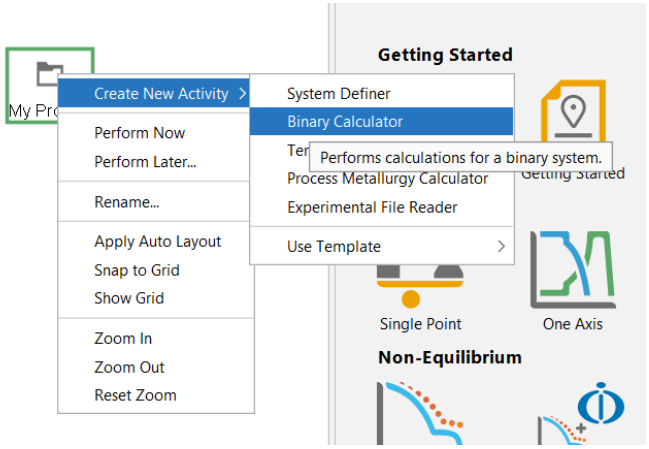
(e) (10 points) What is the stable phase for the corresponding unary systems (reference states) at room temperature?

Parts a and b)

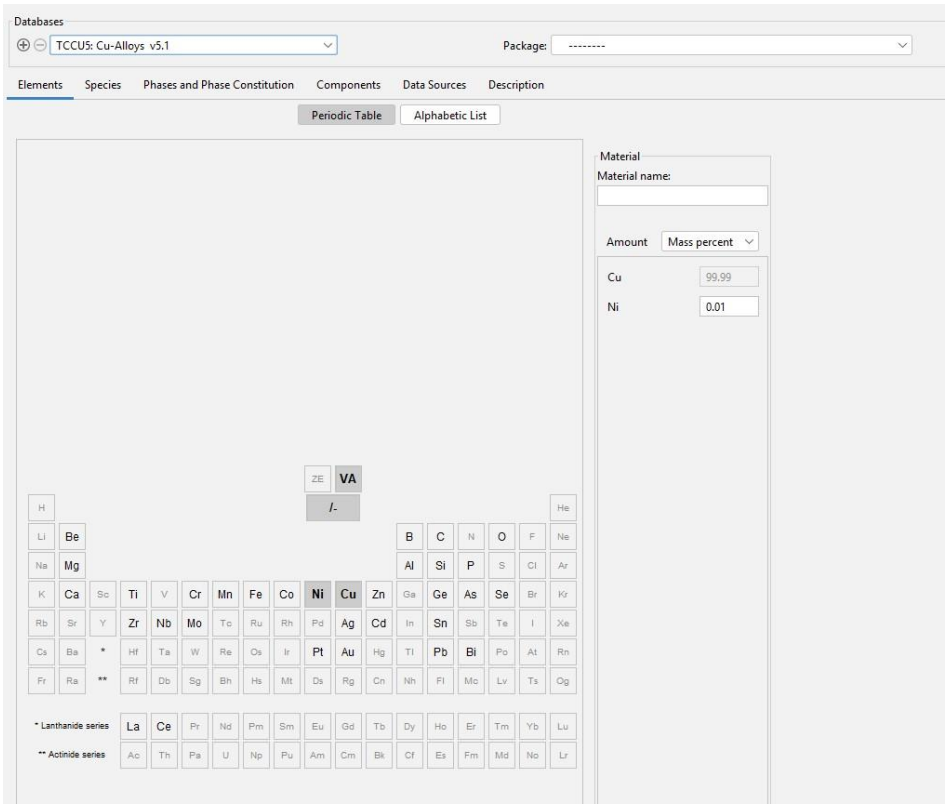
Basically, there are two ways to start a Thermocalc project for generating binary phase diagrams (PDs). One way is to use the standard ready-to-use templates, which can be accessed from the "Phase Diagram" section in the "Graphical Mode." After clicking on the "Phase Diagram" button, a template including a "System Definer," an "Equilibrium Calculator," and a "Plot Renderer" will be created as shown below:



The second way is to open a “Binary Calculator” from “Create New Activity” under the project name as shown below:

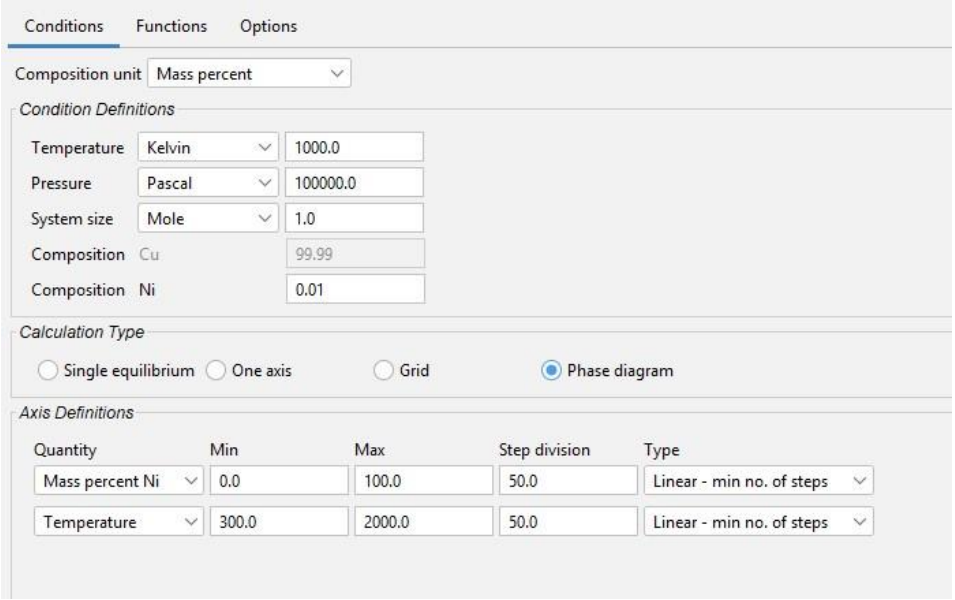


In this project, the first method was chosen to generate the Cu-Ni PD. Upon opening the binary PD template, the setting in each section (i.e., system definer, equilibrium calculator, and plot renderer) must be adjusted based on the desired PD. System definer is the first place to start with. In this section, the choice of database is the necessary step, and it depends on the binary system being studied. The TCCU5: Cu-Alloys v5.1 database was chosen that contains information about the Cu-Ni binary system. Subsequently, the Cu and Ni elements were chosen from the periodic table.

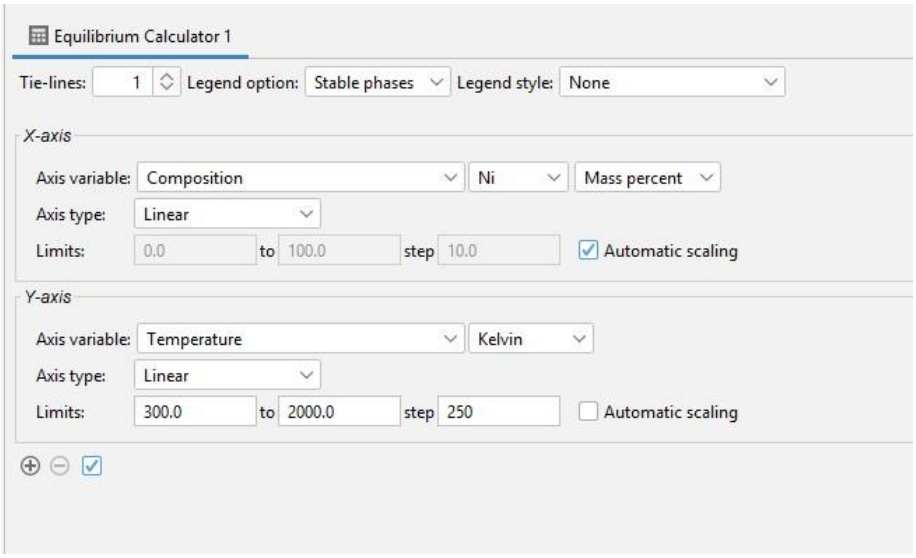


In the system definer section, additional settings are available for modification. For example, under "Phases and Phase Constitution," users have the option to exclude certain phases from calculations. For the purposes of this project, we will retain these settings at their default values.

The “Equilibrium Calculator” section defines important conditions, such as the temperature and composition range. Mass percent was chosen to be the composition unit, and then the temperature range was chosen to be from 300 to 2000 K.

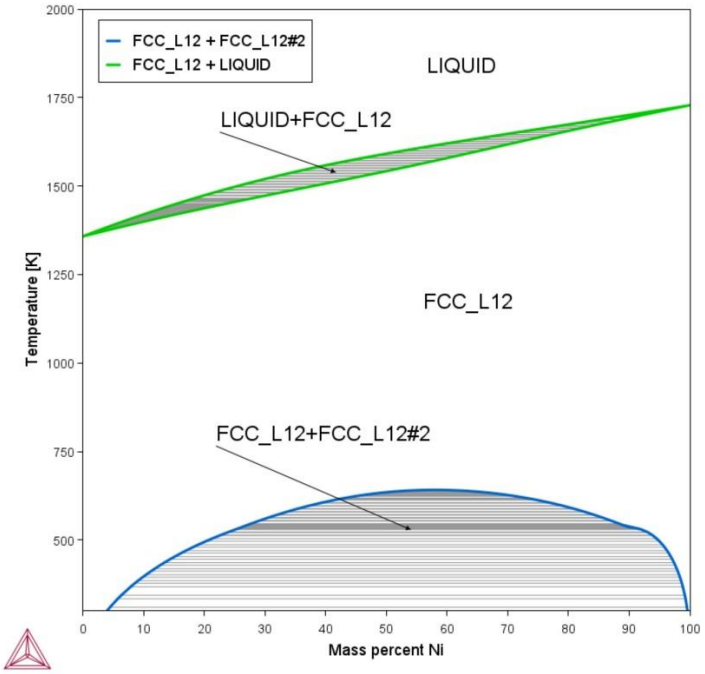


In the “Plot Renderer” section, the temperature range can be adjusted according to the changes made in the previous step.



Subsequently, by utilizing the "Perform Tree" button within the system definer, calculations will commence, leading to the generation of the binary phase diagram. ThermoCalc provides numerous options for enhancing visualization, including phase labeling, adjusting line width, color

customization, and more. In the Cu-Ni PD and the range specified, the liquid, liquid+FCC_L12, FCC_L12, and FCC_L12+FCC_L12#2 single- and two-phase regions can be observed as below. Furthermore, a miscibility gap can be observed; additional information will be provided in the next sections.

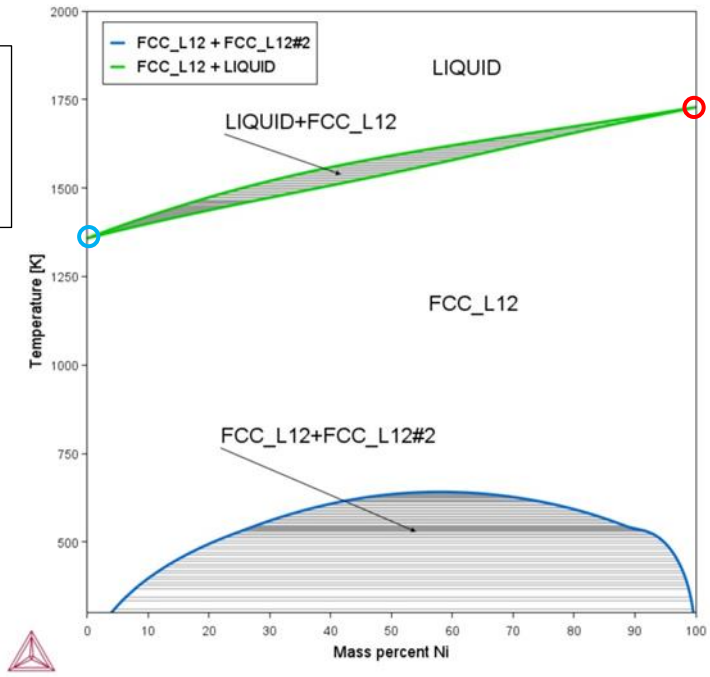


Part C)

The highest melting point is located at (100, 1730), while the lowest melting point is located at (0, 1363). These numbers also indicate the melting point of the unary systems of Cu and Ni at Mass Percent Ni = [0, 100]. According to SGTE [2], the melting points of Cu (FCC_A1) and Ni (FCC_A1) are 1357 K and 1728 K, respectively.

Mass percent Ni: 0%

Melting Point: 1363 K



Mass percent Ni: 100%

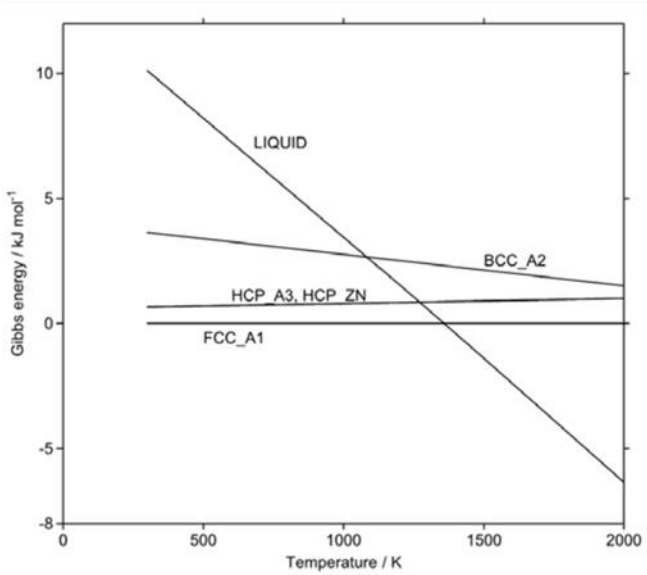
Melting Point: 1730 K

Part d)

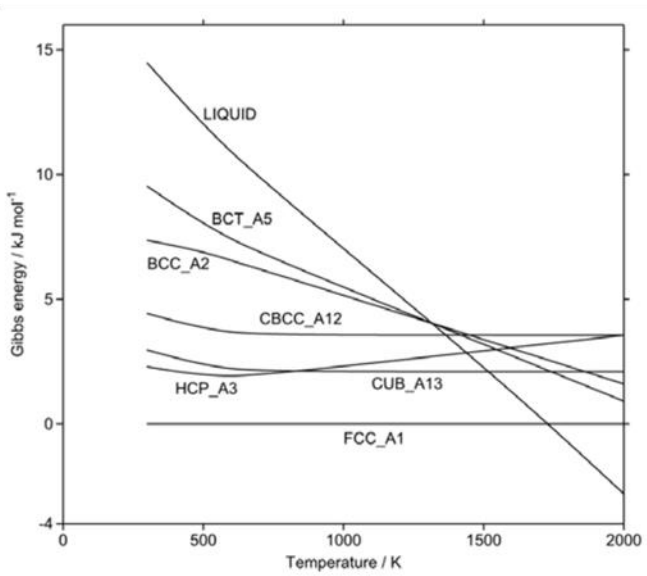
There is no intermediate phase present in the binary PD of Cu-Ni.

Part e)

At room temperature, the stable phase of the corresponding unary components is FCC_L12, according to the PD. Besides, SGTE confirms the fact that the most stable phase of pure Cu and Ni is the FCC phase. Therefore, both elements share the same structure. SGTE plots:



Gibbs energy of phases of Cu relative to FCC_A1



Gibbs energy of phases of Ni relative to FCC_A1

Calculation of the Gibbs energy (50 points)

Calculate the Gibbs energy curves for your system (G-X curves).

(a) Illustrates the step-by-step calculation process in ThermoCalc in your report for the following.

(b) (10 points) Show the G-X curves at the highest melting point (T=highest melting point). Show the lowest Gibbs curve on the plot and the corresponding phases. Make sure to specify the phases associated with the common tangents to the curves (if any).

(c) (10 points) Show the G-X curves at the lowest melting point. (T=lowest melting point). Show the lowest Gibbs curve on the plot and the corresponding phases. Make sure to specify the phases associated with the common tangents to the curves (if any).

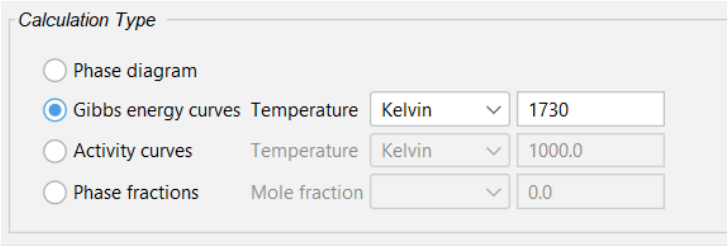
(d) (10 points) Show the G-X curves at 200 K above the room temperature. (T=498 K). Show the lowest Gibbs curve on the plot and the corresponding phases. Make sure to specify the phases associated with the common tangents to the curves (if any).

(e) (10 points) Show the G-X curves at room temperature. (T=298 K). Show the lowest Gibbs curve on the plot and the corresponding phases. Make sure to specify the phases associated with the common tangents to the curves (if any).

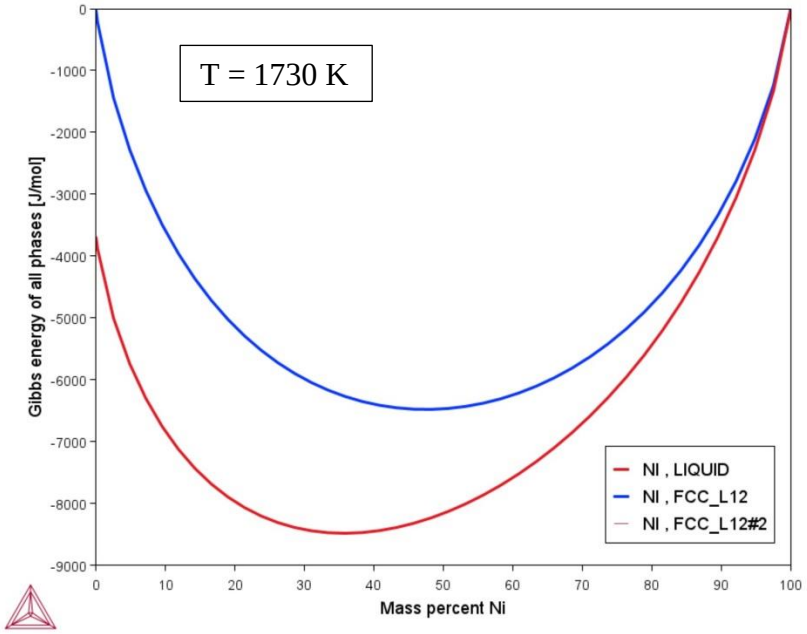
(f) (10 points) Show the G-X curves at a temperature at which there exists either an intermediate phase or a two-phase coexistence. Show the lowest Gibbs curve on the plot and the corresponding phases. Make sure to specify the phases associated with the common tangents to the curves (if any).

Part a and b)

In order to plot G-X curves, one can follow the second method mentioned in the previous question. In this method, a new activity is created under the project name, and the binary calculator is selected. For G-X curves, the calculation type should be “Gibbs energy curves” as shown below:

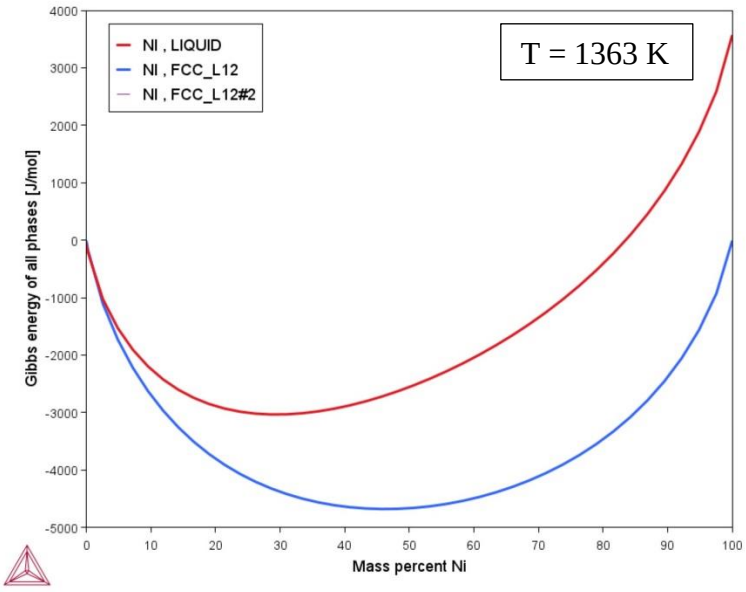


For visualization, a plot renderer can be created under the binary calculator as a new successor. The resulting G-X plot at the highest melting point (1730 K) is as below. From the PD, we know that the liquid phase must be the stable phase throughout the composition space at T = 1730 K. At mass percent Ni = 100% the Gibbs curves of the liquid phase and the solid phase will coincide. It should be emphasized that FCC_L12 and FCC_L12#2 share the same Gibbs curve. The reason for defining FCC_L12#2 is probably the spinodal decomposition that can be observed in the PD.


T = 1730 K
Gibbs energy of all phases [J/mol]
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
-8000
-9000
0
10
20
30
40
50
60
70
80
90
100
Mass percent Ni
NI , LIQUID
NI , FCC_L12
NI , FCC_L12#2

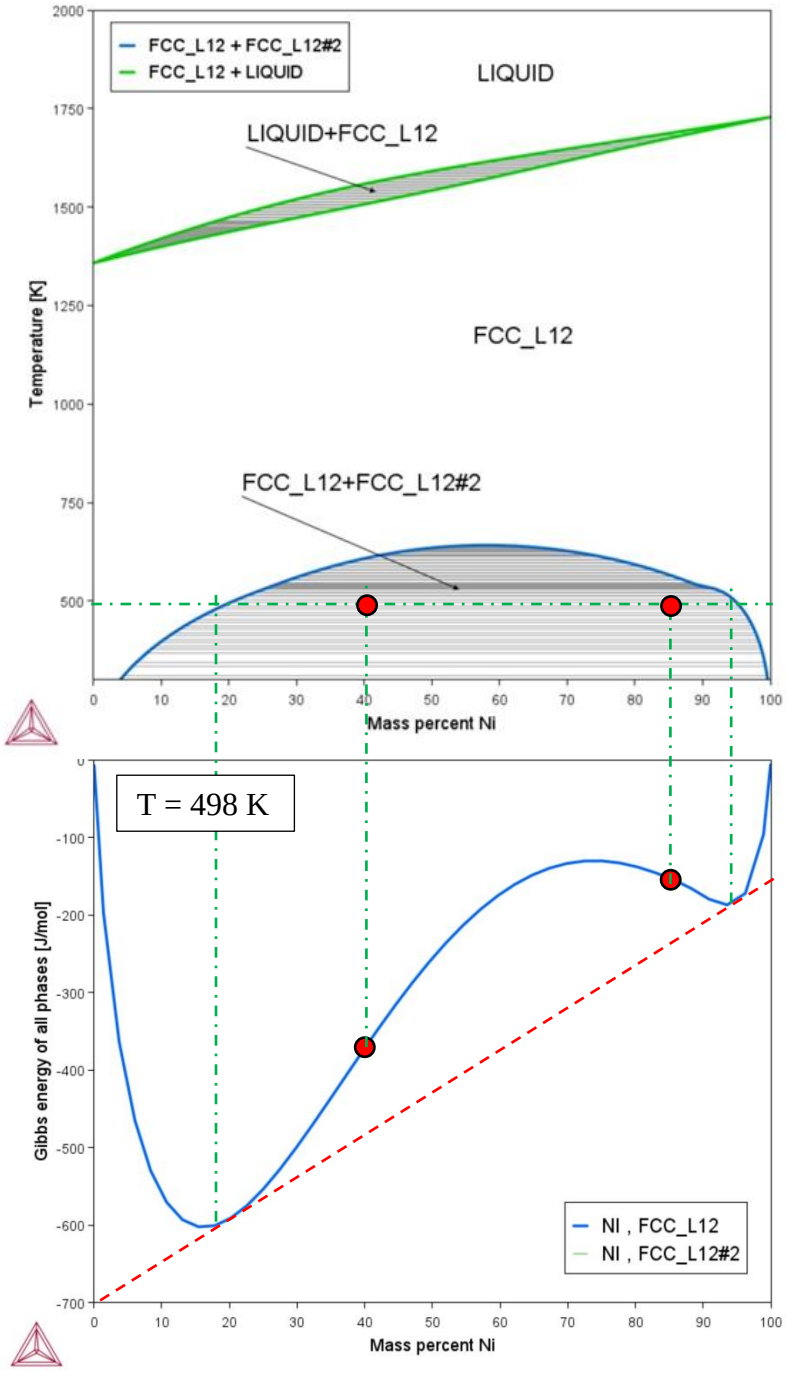
Part c)

The G-X plot at the lowest melting point (T = 1363 K) is somehow similar to the G-X plot at the highest melting point, with the difference that at this temperature, the solid phase is stable throughout the composition space. This time, the liquid and solid Gibbs curves coincide at mass percent Ni = 0%.



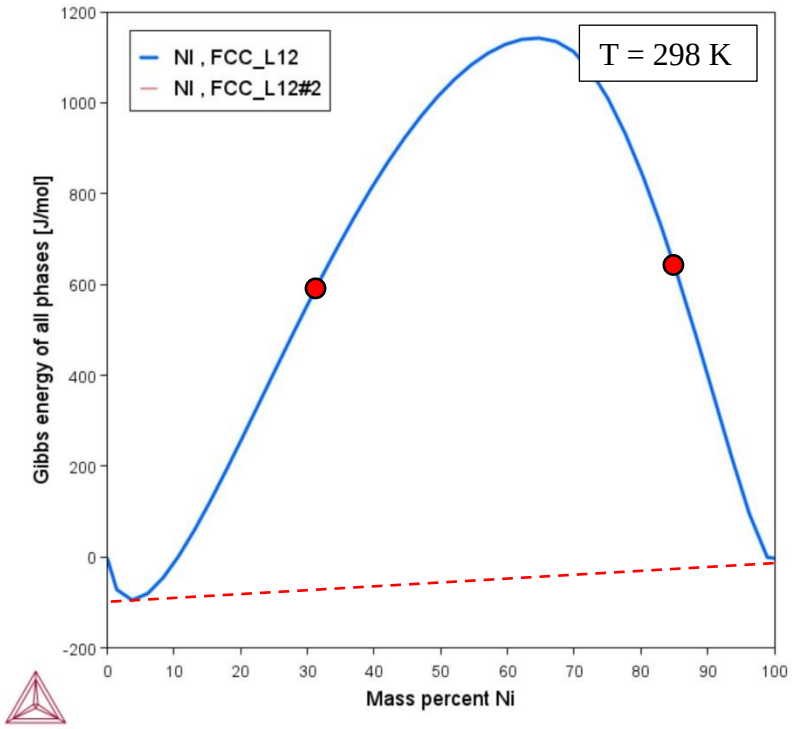
Part d)

At T = 498 K, one can observe important details about the spinodal decomposition process. Spinodal decomposition is a phase separation mechanism within the miscibility gap. A miscibility gap is a range of temperature and composition on the phase diagram where a phase that is stable at higher temperatures decomposes into two or more phases. Between the inflection points, the Gibbs energy curve has a negative curvature, which indicates a tendency to decrease the free energy. This region defines the spinodal region (illustrated in the figure).



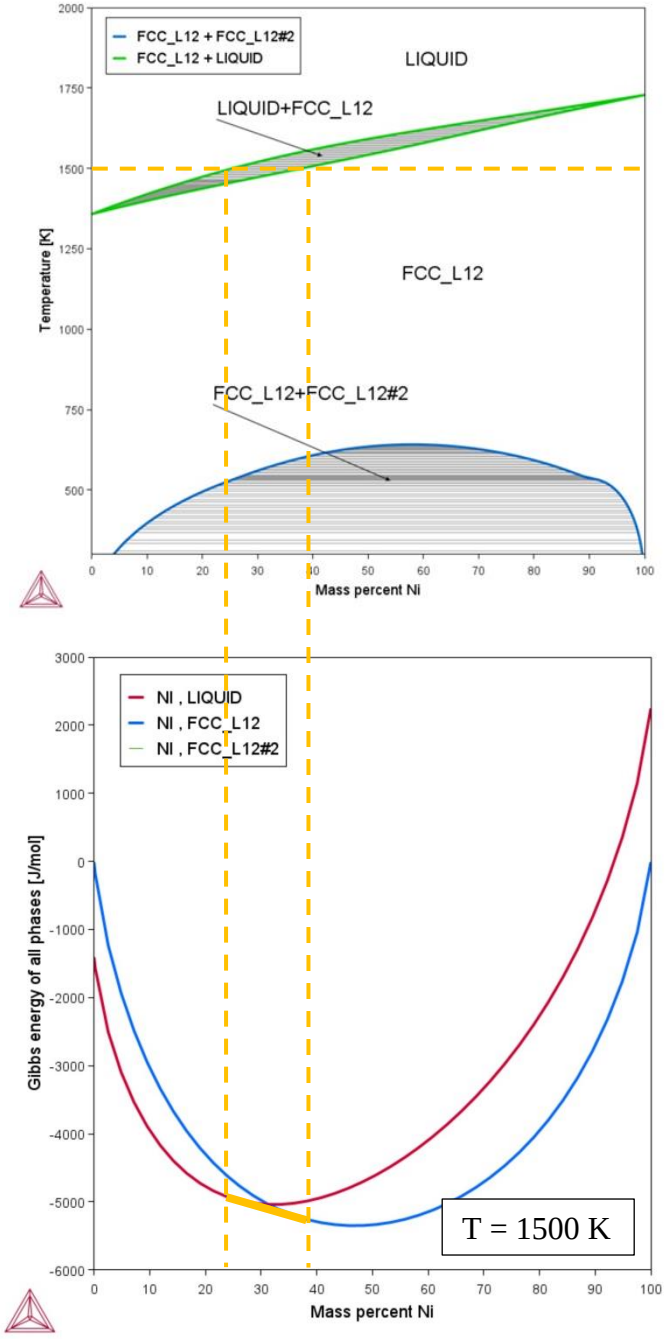
Part e)

At T = 298 K, the Gibbs energy plot is similar to the Gibbs energy plot at T = 498 K, providing details about the spinodal region. The details are illustrated in the plot below.



Part f)

The temperature chosen for this part is T = 1500 K. Initially, at this temperature, the liquid phase exhibits greater stability. By plotting the common tangent of the two phases, it becomes evident that a mixture of liquid and solid (FCC) will form within an intermediate region. As the mass percent of Ni increases, the solid phase becomes stable.



Calculation of the Activity (20 points)

Calculate your system's activity (for a given phase) (a-X curves).

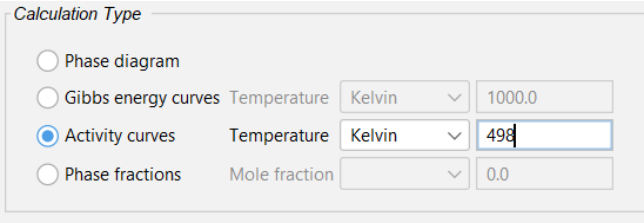
(a) Illustrates the step-by-step calculation process in ThermoCalc in your report for the following.

(b) (10 points) Show the a-X curves for the activity of both components at 200 K above the room temperature and for all the relevant phases at that temperature. Specify whether the system exhibits a negative or a positive departure from the ideal behavior at each phase.

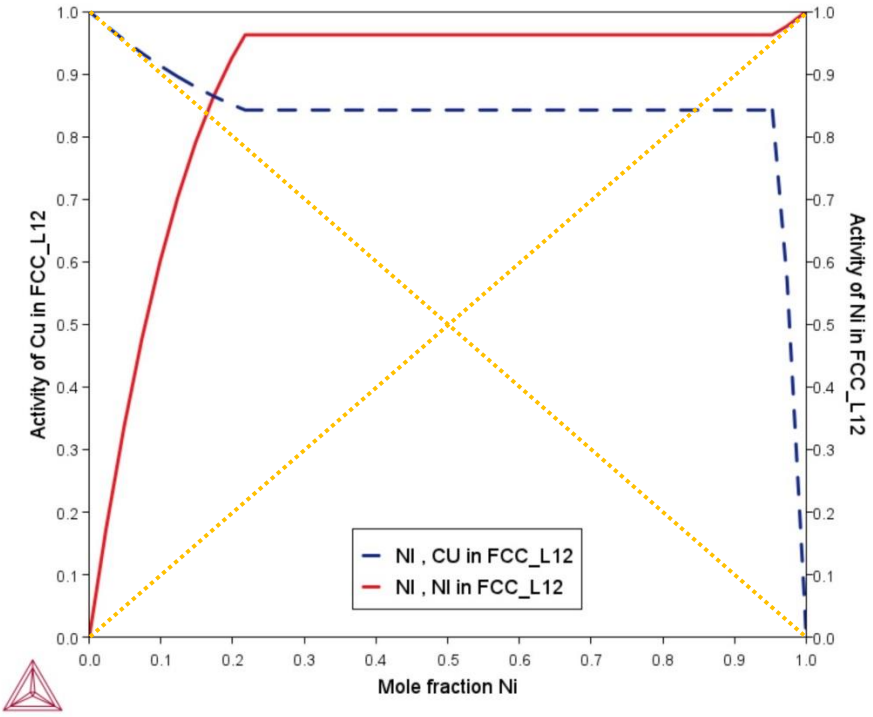
(c) (10 points) Show the a-X curves for the activity of both components at the lowest melting point and for all the relevant phases at that temperature. Specify whether the system exhibits a negative or a positive departure from the ideal behavior at each phase.

Part a and b)

At T = 498 K, the changes in the activity of Cu and Ni in the FCC_L12 solid phase can be studied. In order to generate a-X plots, a procedure similar to generating G-X plots can be implemented. In this procedure, a new activity is created under the project name, and the binary calculator is selected. For a-X curves, the calculation type should be "Activity curves" as shown below:



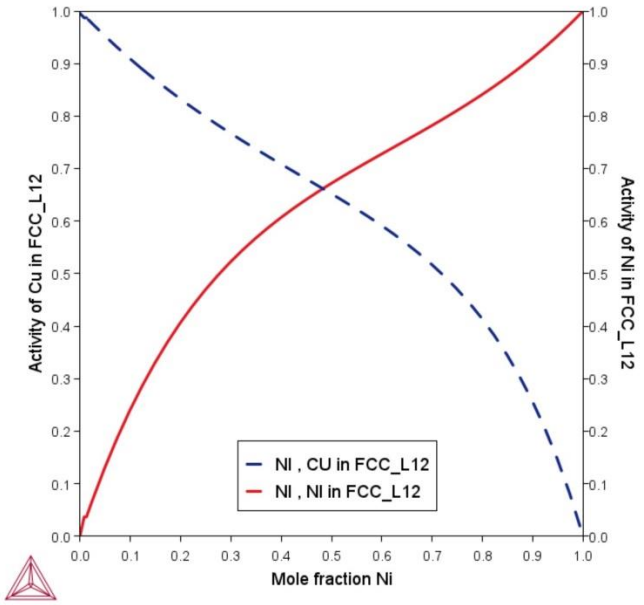
For visualization, a plot renderer can be created under the binary calculator as a new successor. The resulting a-X plot at T = 498 K is as below. Both Cu, and Ni display a huge positive departure from the ideal behavior, indicating a low tendency to mix together. This is another proper representation of the miscibility gap and spinodal region.

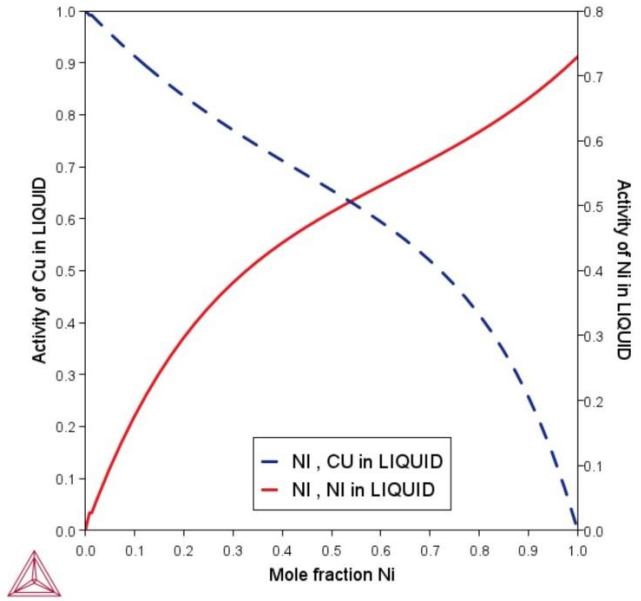


$\gamma_k > 1 \rightarrow \Delta\overline{G}_k^{xs} > 0$ Positive departure from the ideal behavior

Part c)

At the lowest melting point, two phases are present and the changes in the activity of Cu and Ni in these phases can be studied. In both plots, both components manifest a positive departure from the ideal behavior; however, the departure extent is smaller than what was observed in the previous section.





References

1- Xometry, Team. “Copper Nickel Alloys (CuNi): Definition, Applications, Advantages, and Disadvantages.” Xometry, 13 July 2023, www.xometry.com/resources/materials/copper-nickel-alloys.
2- A.T. Dinsdale, “SGTE data for pure elements,” Calphad, Volume 15, Issue 4, 1991.