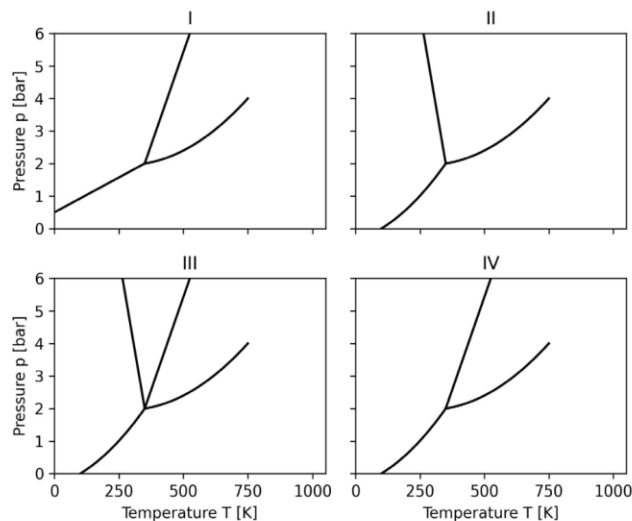


Exercise 1

Four hypothetical phase diagrams of different pure substances are shown below. Note that at least one gas, one liquid, and one solid phases are present in the diagrams below.



- a. Are all of the diagrams possible according to the laws of thermodynamics? For each one, explain whether their form is likely or unlikely to occur. Which phase diagram is the most common?

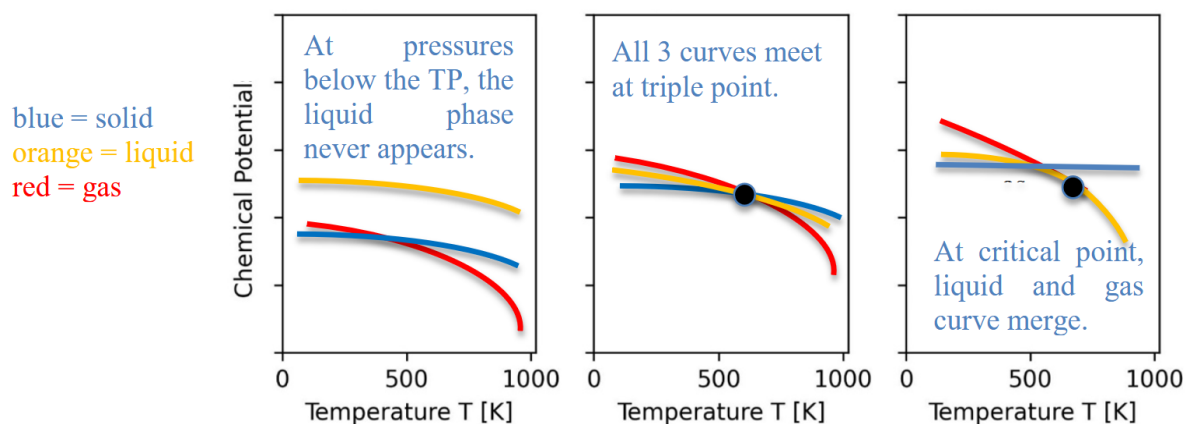
Diagram I: This diagram looks similar to IV with one difference: at low temperatures $T \rightarrow 0\text{K}$, the material stays in the gas phase. While this might be possible in principle, it is highly unlikely.

Diagram II: This is the phase diagram of materials like water, for which the liquid phase is denser than the solid phase.

Diagram III: This diagram is impossible, since there are four phase equilibrium lines starting at the “triple point”. This would mean that 4 phases would coexist at this temperature and pressure, contradicting the Gibbs phase rule: the number of degrees of freedom (for a point: zero) $0 = F = 2 + c - n = 3 - n$ which would be -1 for $n=4$. Only three phases can coexist at a point.

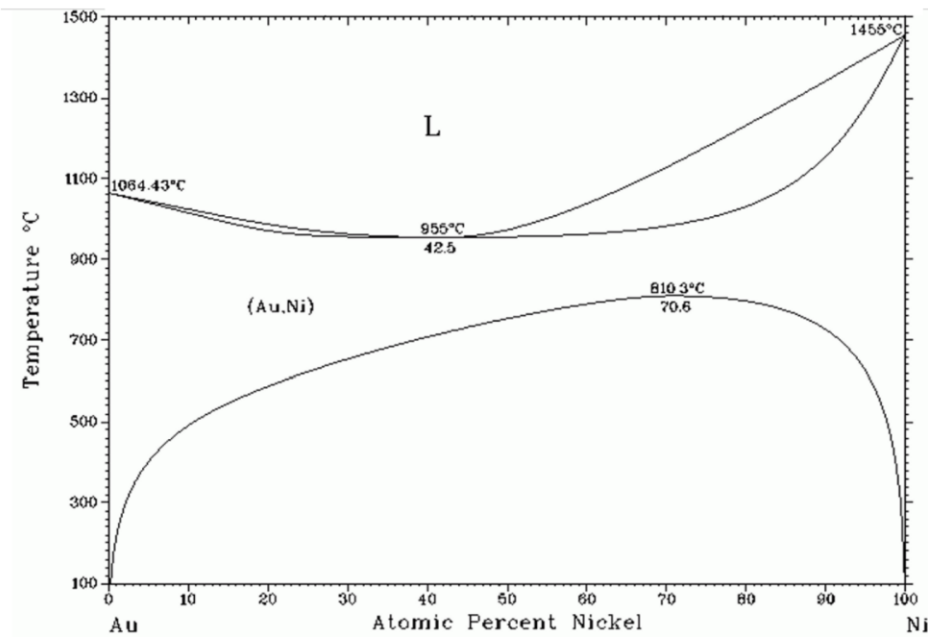
Diagram IV: This is the most standard phase diagram of a material, e.g. CO_2 . See also diagram I.

- b. For the phase diagram IV shown above, draw the behavior of the chemical potentials as a function of the temperature for all three phases at the constant pressures: $p_1 = 1\text{ bar}$, $p_2 = p_{TP} = 2\text{ bar}$ and $p_3 = p_{CP} = 4\text{ bar}$.



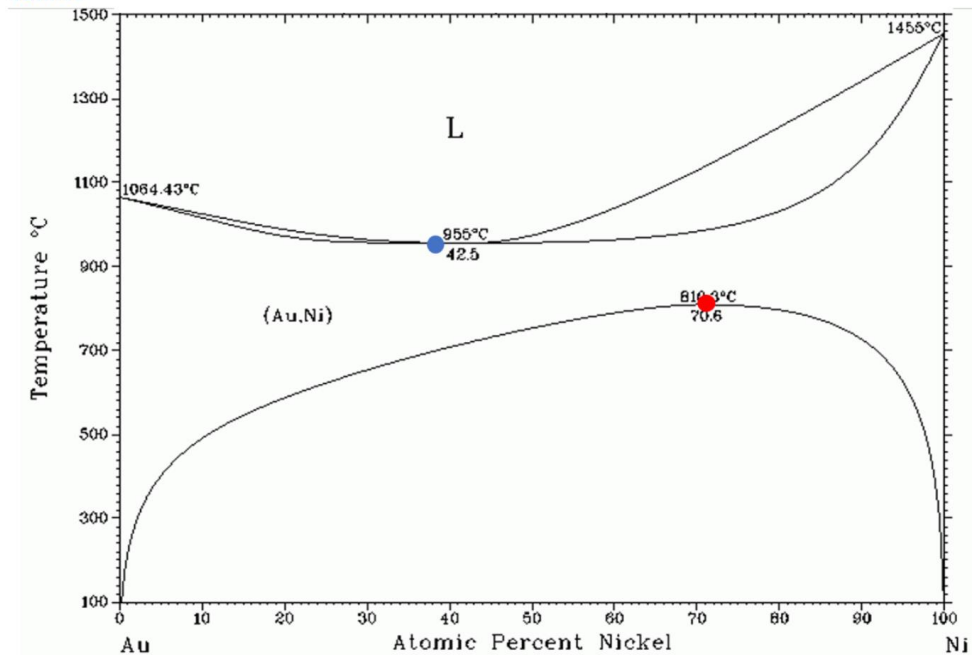
Exercise 2

The phase diagram of gold and nickel at $p = 1$ atm is shown below.



- a. Label the invariant points on the phase diagram, if they exist, and indicate how you came to this conclusion by appropriately applying the Gibbs phase rule.

There is two invariant points on this phase diagram. They are highlighted in blue and red on the diagram below.



The blue invariant point is a congruent point. At this point, there is two phases (liquid and solid), one component (the (Au-Ni) solution) and, as the diagram is at constant pressure, the middle term of the Gibbs phase rule is 1. Thus, we have

$$F = 1 + 1 - 2 = 0$$

The red invariant point is a critical point from the miscibility gap between Au and Ni. At this point, there is three different phases (the solid (Au-Ni) solution and the two solid solutions from the spinodal decomposition in the miscibility gap), two components (Au and Ni) and, as the diagram is at constant pressure, the middle term of the Gibbs phase rule is 1. Thus, we have

$$F = 2 + 1 - 3 = 0$$

- b. Looking at the characteristic shape of the phase diagram, what can you say about the interaction parameter of the solid and the liquid solution of gold and nickel, Ω^{sol} and Ω^{liq} ?

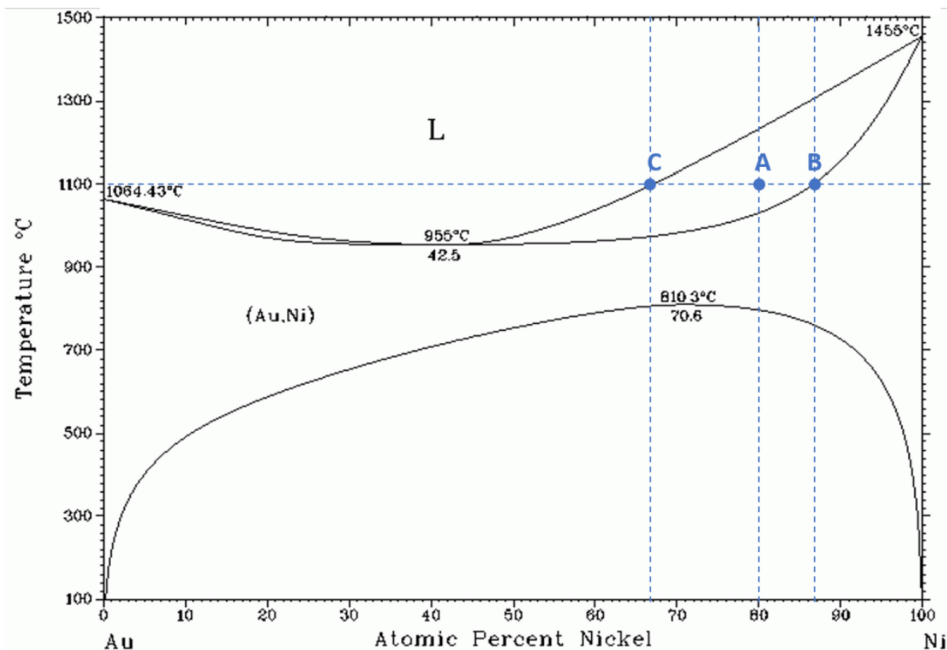
Based on the presence of a miscibility gap, we can tell that the interaction parameter of the solid solution is positive ($\Omega^{\text{sol}} > 0$). Regarding the interaction parameter of the liquid solution, it is either negative or equal to zero, as we see a favored mixing or an ideal solution behavior ($\Omega^{\text{liq}} \leq 0$, $\Omega^{\text{liq}} < 0$ or $\Omega^{\text{liq}} = 0$ also accepted as a correct answer).

- c. Let's suppose we have a solution of 80 at.% Ni at 1100°C. What is the proportion of liquid and solid in the solution?

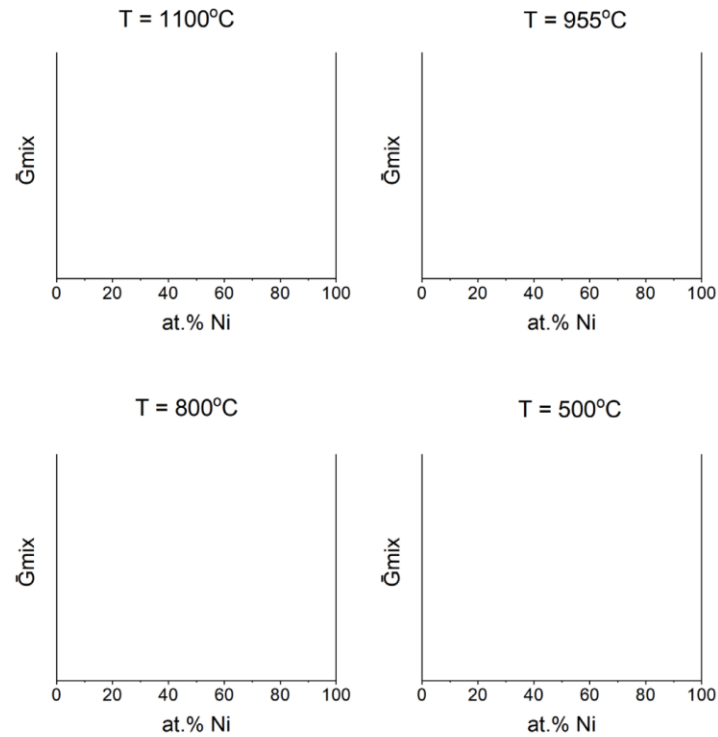
At this specific temperature and composition, we are located between the liquidus and solidus line (point A in the plot below), which means we have part of the solution in the liquid phase and part of it in the solid phase. To determine the proportion of each phase, we can apply the lever rule:

$$P_{\text{sol}} = \frac{AC}{BC} = \frac{80 - 67}{87 - 67} = \frac{13}{20} = 0.65$$

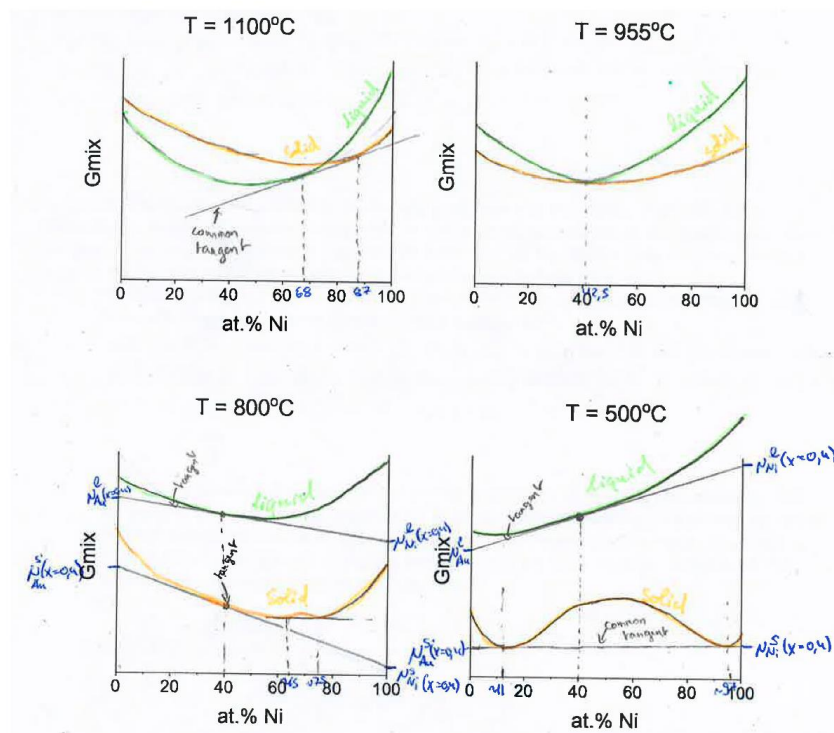
$$P_{\text{liq}} = \frac{AB}{BC} = \frac{87 - 80}{87 - 67} = \frac{7}{20} = 0.35$$



- d. Using the diagrams below, draw qualitatively the partial molar Gibbs free energy of mixing of all solutions at the temperatures indicated:

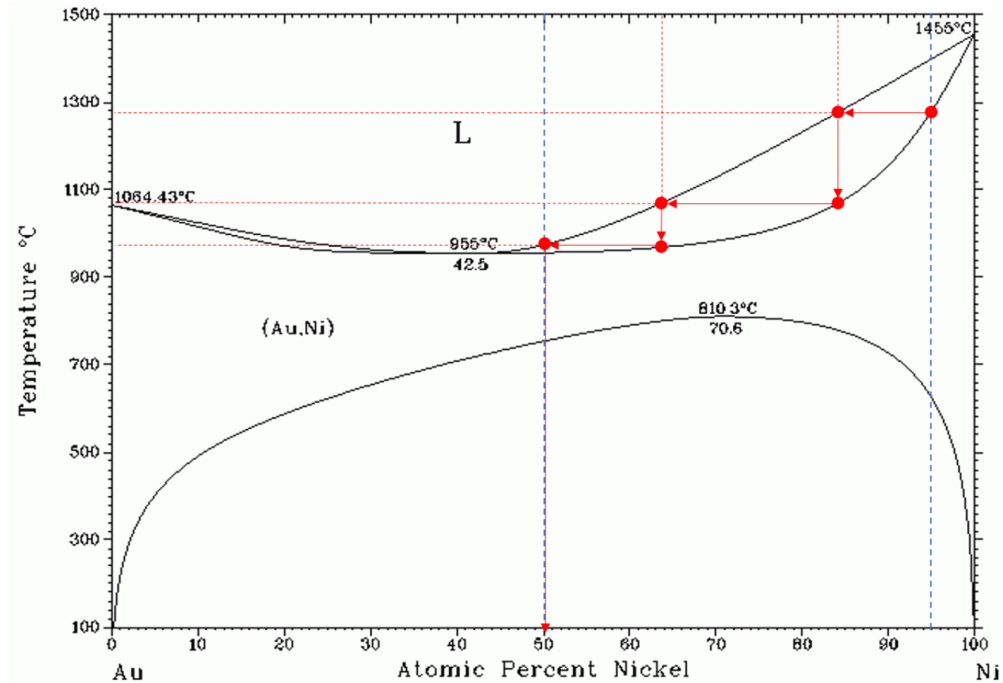


- e. On two of these diagrams, you can see coexistence of solid phases. Indicate on both diagram the value of the chemical potential of each component on each phase for a composition of 40 at.% Ni.



- f. Gold-nickel alloys are used in jewelry to obtain the so called “white gold”. Let’s assume this alloy has a composition of 50 at.% of Ni. Starting from a solution with 95 at.% Ni, propose a mechanism to reach the composition of a “white gold” alloy.

The mechanism would follow the path presented in the figure below:



Thus, it would involve purifying the liquid composition within the phase separation region of the Au-Ni solution. By starting at $x_B = 95$ at% Ni, we heat up the solid solution to $\sim 1280^\circ\text{C}$. At this temperature and at equilibrium, the liquid phase has a composition of ~ 84 at% Ni. Thus, we collect the liquid and cool it down to $\sim 1060^\circ\text{C}$. Similarly, the liquid phase has a composition of ~ 64 at% Ni at this temperature when the equilibrium is reached. Again, we collect the liquid phase and cool it down to $\sim 970^\circ\text{C}$. At this temperature, the liquid phase at equilibrium has the aimed value of ~ 50 at% Ni. We can thus cool down the liquid solution to get a solid solution with the desired composition.