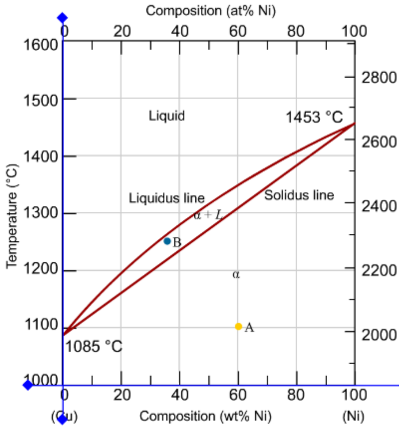
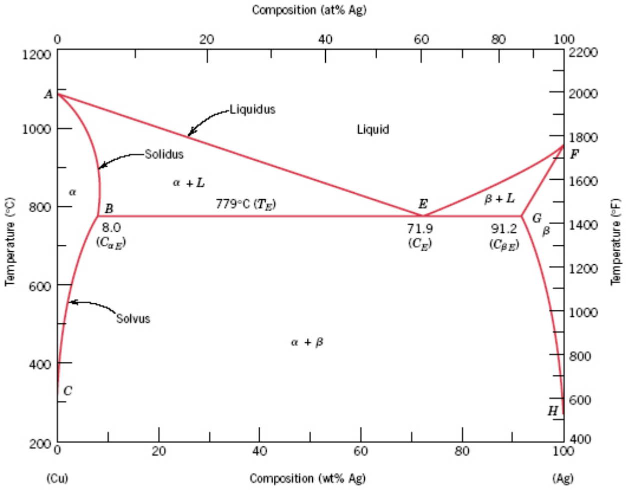
Homework 10_Solution

Exercise 1

Our goal in this exercise is to better understand binary phase diagrams and develop some intuition. Below are the Cu-Ni and Cu-Ag phase diagrams.





a. If the two components A, B of a binary phase diagram have a different crystal structure, is it possible that the binary phase diagram looks like the one on the left close to the ideal mixture model?

No, because we cannot continuously go from one crystal structure to a different one by substitution.

b. The elements Cu, Ni, Ag and Au and Al all have fcc crystal structures, with lattice parameters in Angstrom given in the table.

Ni	Cu	Ag	Au	Al
3.52	3.61	4.09	4.08	4.05

The Ni-Cu and Ag-Au systems have a phase diagram close to the one predicted by the ideal model shown on the left, while Cu-Ag has a eutectic phase diagram shown on the right. Based on just this information: what could influence whether a binary phase diagram is (close to) ideal?

If we assume that the three systems mentioned above can be described by the regular solution model, would their interaction parameter Ω_{solid} be positive, close to zero, or negative? [you can assume that $\Omega_{liquid} = 0$] How can we intuitively understand those values of Ω_{solid} using the lattice parameters? Hint: Recall that Ω_{solid} represents the energetic cost of mixing.

Based only on the provided information, we might hypothesize that nearly ideal phase diagrams only appear when the crystal structure is the same and the lattice constants are close.

In the regular solution model, the interaction parameter will be close to zero for Ni-Cu and Ag-Au and have a relatively large positive value for the Cu-Ag system.

This matches our intuition, since there will be a large energetic cost for a Copper atom trying to fit into a crystal lattice of Ag atoms having a larger lattice constant. On the other hand, if the lattice constants are close, having an interaction parameter close to zero is also intuitive, since the environment of an atom doesn't change much before or after mixing.

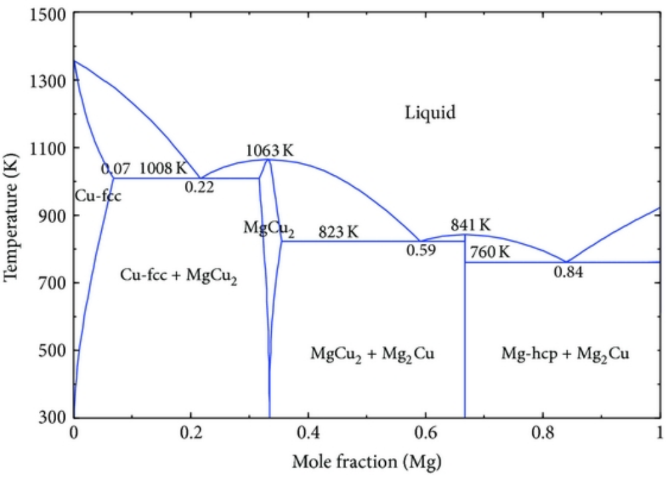
c. Predict for which of the remaining combinations of elements in the table, the phase diagram will look close to ideal.

We predict that Ag-Al and Au-Al show a close to ideal diagram since these have similar lattice parameters.

d. Experimentally, the Al-Ag and Al-Au phase diagrams are very complicated and far from the ideal mixture model. On top of having the same crystal structure and lattice constant, the components also need to have very close chemical behavior: similar electronegativities, bonding etc., to be miscible at all temperatures. How could this explain the difference in the Ag-Au and Ag-Al diagrams?

Aluminum has a larger electronegativity. Also, because Aluminum is in a different column in the periodic table, we could expect it to have different bonding characteristics, as can for instance also be guessed from the fact that Aluminum is the only element with p orbitals in the outermost shell. Thus, it is no surprise that Aluminum and Silver don't simply mix at all concentrations.

e. To better understand a further common characteristic of phase diagrams that also contributes to the behavior of the Al-Ag and Al-Au systems, consider the (much simpler) Mg-Cu system shown below. Explain what mechanism makes this diagram different from the previously discussed ones and how you can decompose it into simpler parts. Comment on the melting and solubility properties of the compounds in this system.

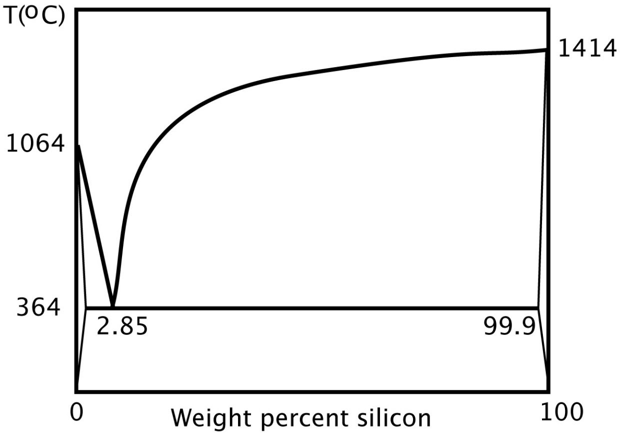


The phase diagram looks more complicated because of the intermediate compounds, namely $MgCu_2$ and Mg_2Cu. We can decompose the phase diagram into three parts: For Mg concentrations between 0 and $1/3 \approx 0.33$, we can consider the phase diagram to be a binary phase diagram between pure Cu and $MgCu_2$, which in this case is eutectic. Similarly, for the intervals [1/3,2/3] and [2/3, 1], we obtain eutectic diagrams of the $MgCu_2$-Mg_2Cu, and Mg_2Cu-Mg systems, respectively.

For the melting properties of the intermediate compounds, we can see that both are melting congruently. Regarding solubility, Mg_2Cu looks stochiometric due to the sharp line, while the region for $MgCu_2$ is broader, meaning that some amount of excess Cu or Mg beyond to the perfect stoichiometry can be dissolved (similar observations also apply between pure Cu and pure Mg, so the higher Cu concentration might be helping the solubility in $MgCu_2$).

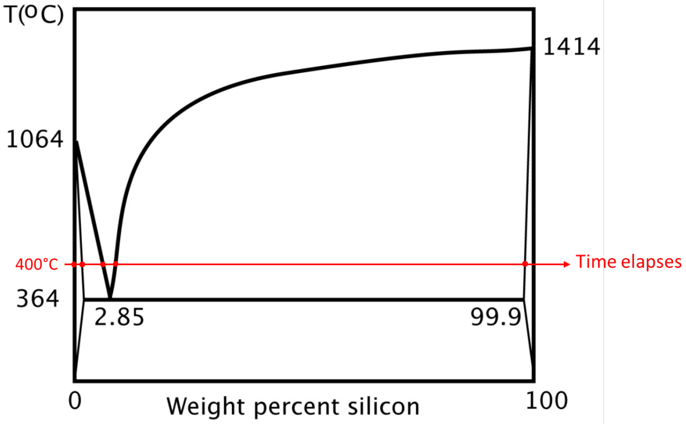
Exercise 2

Nanowires are explored as the functional component for next generation electronic devices. One possible way of growing silicon nanowires is to place gold nanoparticles of a given diameter (for example, 5 nm) on an inert surface and supply them with a supersaturated silicon vapor. A property of the supersaturated gas is that it continuously ‘pushes’ silicon onto the gold nanoparticles. In other words the gold particles start as pure gold but as time progresses they become gold-silicon particles with an ever-increasing atomic fraction of silicon. In this problem we try to understand why this process leads to silicon nanowires. The phase diagram of gold and silicon is shown in the figure below. Notice that the x-axis is not linear as the extremes (i.e. the parts close to 0 and 1) are enlarged for the sake of visualization. Assume that the gold nanoparticles never change shape and size during the nanowire growth.

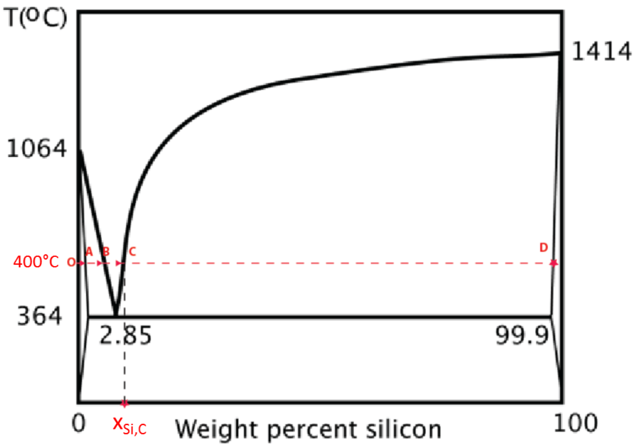


Starting from an initial state of pure gold, the nanowire growth is performed at 400°C.

a. Illustrate with a line on the diagram the evolution of the materials as time progresses.



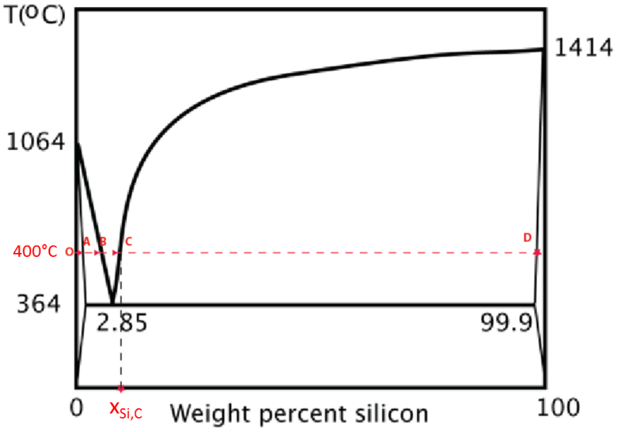
b. Please explain when solid silicon will start forming and why.



Gold nanoparticles in solid state at the beginning of the reaction at point O. When silicon is supplied from the vapor phase, a gold-rich solid mixture is formed and the composition (xSi,C) of this solid phase increases with time. At point A, when more Si is supplied, a liquid mixture is formed according to the phase diagram. The liquid phase composition can be found from point B. Until all of the solid phase is transformed into the liquid phase, the composition of the liquid found at B is unchanged. After point B, more Si that arrives will increase the liquid phase composition until point C. Here at point C, solid silicon wires (with Au as impurity, note that that composition on the right is exaggerated) will be excreted out at point D.

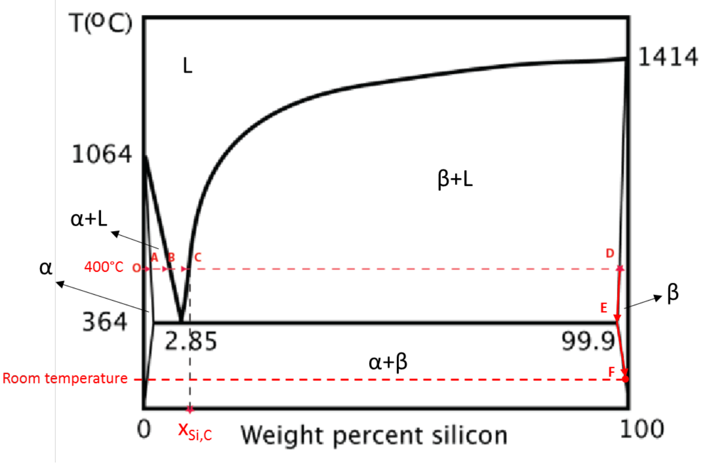
c. Indicate on the phase diagram the composition and physical state (vapour, liquid, or solid) of the gold nanoparticles when silicon nanowires start to form.

When silicon wires start forming, the gold nanoparticles are in the liquid state. This liquid has the composition of $x_{Si,C}$.



d. When the silicon source is removed, the surface is allowed to cool down to room temperature. Describe the nanowire composition if the surface is cooled down slowly in an ideal equilibrium process.

The composition of the nanowires will follow the coexistence line D → E → F in an equilibrium cooling process.



e. In reality, when silicon is solid, very little mobility of gold is achieved. Therefore, as the wires are cooled down, they do not change their composition (i.e. they stay in a kinetically trapped composition that matches the composition at 400°C). Given that for electronic applications, gold is an unwanted impurity, what is a better temperature for growing silicon nanowires, 400°C or 1000°C? Please explain your answer.

In this case, the higher temperature 1000°C is better. At high temperature the β phase has lower Au concentration according to the phase diagram, meaning that the solubility of Au in Si lower. Therefore, the Si nanowires produced at 1000°C would have less Au impurity.

f. What is the lowest temperature at which this process still works?

Above the eutectic line.