Homework 11 Solutions

Exercise 1

Short questions

a. In the comic song by Flanders and Swann about the laws of thermodynamics, they summarize the first law by the statement: "Heat is work and work is heat." Is this statement correct based on your understanding of the first and second law of thermodynamics? Explain your reasoning with regards to the two laws.

According to the first law, $\Delta U=\Delta Q+\Delta W$, where only U is a state function. Therefore, having $\Delta Q=5$ and $\Delta W=2$ or $\Delta Q=2$ and $\Delta W=5$ could both lead to the same final state. In that sense, we can "convert" heat to work and vice versa, so we could say that the quote is accurate.
On the other hand, Kelvin's formulation of the second law states that it is not possible to have a process whose sole effects are to completely convert heat into work. Therefore, according to the second law, the quote would be inaccurate.

b. The change of Gibbs free energy for 1 mole of water at 2 and 10 degrees Celsius is about 50 J. Can you approximate the change in the Helmholtz free energy of the same system? Would your method work if it were a gas in question?

The Gibbs and the Helmholtz free energy are related by $A = G - pV$.
Since there is no mention of the pressure in the text, we assume that the heating process is taking place at constant pressure (most likely: ambient pressure). For such processes, the change in the Gibbs and Helmholtz free energy between the initial and final state are related by:

$$\Delta A = \Delta G - p\Delta V$$

For most condensed materials like solids and liquids, the change in the volume due to a change in temperature by 8 degrees Celsius is not going to be significant, and we can thus drop the second term (this is especially true for water which first contracts up to 4 degrees Celsius, which compensates some of the expansion afterwards). We can this approximately say that

$$\Delta A \approx \Delta G = 50J$$

For a gas, the change in volume would typically be larger by many orders of magnitude. Thus, neglecting the change in volume would not be acceptable.

Exercise 2

Heat capacity at constant pressure of a solid at low temperature

The heat capacity at constant pressure C_p of a solid material is important for low temperature experiments.

a. Assuming the system is closed, show that the entropy of a solid undergoing an isobaric process from temperature 0 K to T K is:
$S = S_0 + \int_0^T \frac{C_p}{T} dT$ where S_0 is the entropy at 0 K

b. On the basis of **a** above and the knowledge of thermodynamics, what conclusion can you make about the low temperature behavior of C_p of a solid as the temperature approaches absolute zero? Try these possibilities:
   i. C_p remains constant
   ii. C_p varies inversely as T, inversely as T^2, etc.
   iii. C_p varies directly as T, as T^2, etc.

a. For a closed system and isobaric condition

$$dH = TdS + Vdp + \sum_i \mu_i dn_i$$

$$dH = TdS$$

$$\left(\frac{dH}{dT}\right)_p = T\left(\frac{dS}{dT}\right)_p$$

$$C_p = T\left(\frac{dS}{dT}\right)_p$$

$$\frac{C_p}{T} = \left(\frac{dS}{dT}\right)_p$$

$$dS = \frac{C_p}{T} dT$$

$$S = S_0 + \int_0^T \frac{C_p}{T} dT$$

b.

i. C_p is constant

$$S = S_0 + C_p \int_0^T \frac{1}{T} dT = S_0 + C_p lnT + c$$

As $T \to 0$ $\quad lnT \to -\infty \quad S \to -\infty$

ii. C_p varies inversely as T, inversely as T^2, etc

$$C_p \propto \frac{1}{T} \qquad C_p = \frac{a}{T}$$

$$S = S_0 + \int_0^T \frac{C_p}{T} dT = S_0 + \int_0^T \frac{1}{T^2} dT = S_0 - \frac{a}{T} + c$$

$$\text{As } T \to 0 \qquad \frac{a}{T} \to \infty \qquad S \to -\infty$$

iii. C_p varies directly as T, as T^2, etc

$$C_p \propto T \qquad C_p = aT$$

$$S = S_0 + \int_0^T \frac{C_p}{T} dT = S_0 + \int_0^T dT = S_0 + aT + c$$

$$\text{As } T \to 0 \qquad aT \to 0 \qquad S \to S_0$$

According to third law of thermodynamics, the entropy of all substances is S_0 at absolute zero temperature. Therefore, C_p varies directly as T, as T^2, etc

<u>Exercise 3</u>

Thermodynamics of electrochemical cells

In general, an electrochemical cell is a simple device in which an electric current (a flow of electrons through a circuit) can be produced by two different types of chemical reaction. In the case of voltaic cells (also known as galvanic cells), the electric current is produced by a spontaneous chemical reaction, whereas in the case of electrolytic cells a non-spontaneous reaction occurs.

The objective of this exercise is to determine which cell is described by the following thermodynamic properties and understand its thermodynamic properties.

We consider the cell to provide a positive electromotive force ε that enables a transfer of a quantity of positive charge dZ to an external circuit. Under this convention, the electrical work is defined by:

$$\delta w_{el} = -\varepsilon dZ$$

Consider the system to be closed.

a. Write the differential form of the enthalpy.

$$dH = TdS + Vdp - \varepsilon dZ$$

b. Write the differential form of the Gibbs free energy.

$$dG = -SdT + Vdp - \varepsilon dZ$$

c. Find a Maxwell's relationship for $\left(\frac{\partial S}{\partial Z}\right)_{p,T}$.

$$\left[\frac{\partial}{\partial Z}\left(\frac{\partial G}{\partial T}\right)_{p,Z}\right]_{p,T} = \left[\frac{\partial}{\partial T}\left(\frac{\partial G}{dZ}\right)_{p,T}\right]_{p,Z}$$

$$-\left(\frac{\partial S}{\partial Z}\right)_{p,T} = -\left(\frac{\partial \varepsilon}{\partial T}\right)_{p,Z}$$

$$\left(\frac{\partial S}{\partial Z}\right)_{p,T} = \left(\frac{\partial \varepsilon}{\partial T}\right)_{p,Z}$$

Now we assume that the process is taking place under isothermal and isobaric conditions.

d. Determine the change in the enthalpy ΔH with respect to the change of charge ΔZ. Note that the electromotive force is only temperature-dependent ($\varepsilon = \varepsilon(T)$).

$$dH = TdS + Vdp - \varepsilon dZ \overset{p \text{ is constant} \rightarrow \text{dp}=0}{\widehat{=}} TdS - \varepsilon dZ$$

$$\left(\frac{\partial H}{\partial Z}\right)_T = T\left(\frac{\partial S}{\partial Z}\right)_T - \varepsilon$$

$$\left(\frac{\partial H}{\partial Z}\right)_T = -\left[\varepsilon - T\left(\frac{\partial \varepsilon}{\partial T}\right)_Z\right]$$

Since $\varepsilon = \varepsilon(T)$

$$\left(\frac{\partial H}{\partial Z}\right)_{T,V} = -\left[\varepsilon - T\frac{d\varepsilon}{dT}\right]$$

Thus, we have

$$\int_{H_0}^{H} dH = -\int_{Z_0}^{Z}\left(\varepsilon - T\frac{d\varepsilon}{dT}\right)dZ$$

$$\Delta H = -\left(\varepsilon - T\frac{d\varepsilon}{dT}\right)\Delta Z$$

Exercise 4

Single component

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.

Question: 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?

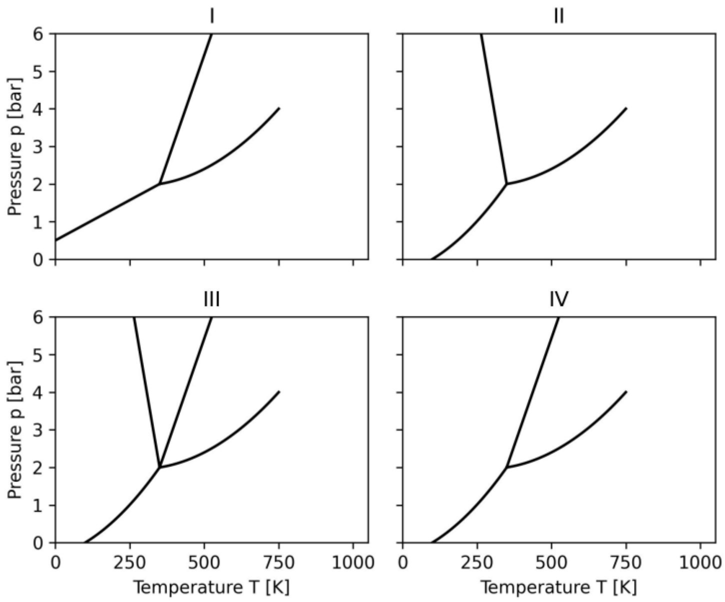
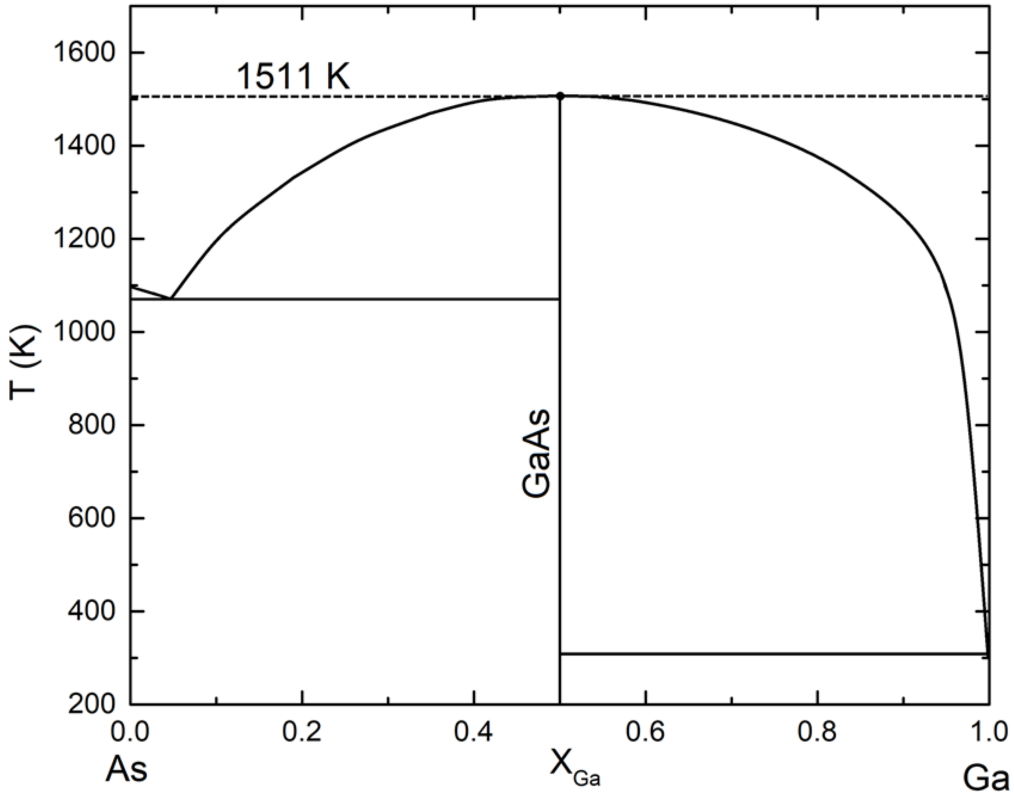


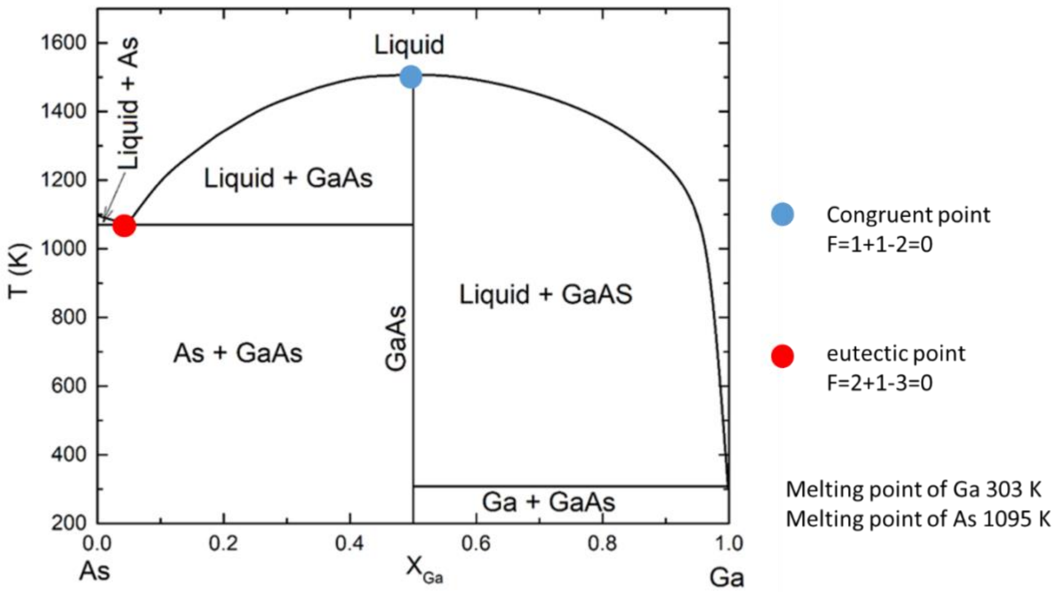
Diagram I: This diagram looks similar to IV with one difference: at low temperatures $T \rightarrow 0$K, the material stays in the gas phase. While this might be possible in principle, it is highly unlikely.
Diagram II: This is the phase diagram of materials like water, for which the liquid phase is 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.

Exercise 4

The binary Ga-As phase diagram at p=1 atm can be approximated with the one below



a. Please label all possible phases in the diagram and note the temperatures of fusion of the two components.



b. The mixture of x_{Ga} =0.4 is cooled down from 1600 K to 1400 K. What is the relative proportion of each phase in the system? Apply the lever rule.

At 1400 K. there are two phases Liquid xGa=0.3 and GaAs xGa=0.5
Ratio of the liquid=(0.5-0.4)/(0.5-0.3)=0.5
Ratio of the GaAs=1-0.5=0.5

c. You continue cooling down the system slowly. What are the equilibrium phases and their compositions at a temperature just above the eutectic line and what are they just below the eutectic line?

Above eutectic liquid and GaAs
Below eutectic As and GaAs

d. Consider you have a powder of Ga and a powder of As. You are asked to make GaAs at as low temperature as possible. Devise a possible approach to do this so that the final GaAs phase contains as little impurities as you can.

The easiest way is to have powders in the exact composition of the GaAs stoichiometry and bring it above the congruent temperature of the stoichiometric compound before cooling it. However, we typically want to produce it with the minimum amount of energy, meaning at the lowest temperature as possible. Therefore, this can be done by working at the Ga rich end of the phase diagram. Create a mixture of starting elements with x = 0.95 Ga. Increase the temperature to obtain completely liquid phase. Slowly cool it down to the region of Liquid + GaAs and gather the solid phase.

Exercise 5

Consider the diagram below (Figure 1a) for the change in molar Gibbs free energy of mixing of a two-component (A and B) regular solution at a certain temperature T1 and pressure P.

a. At which range of compositions the material will precipitate by the nucleation and growth mechanism?

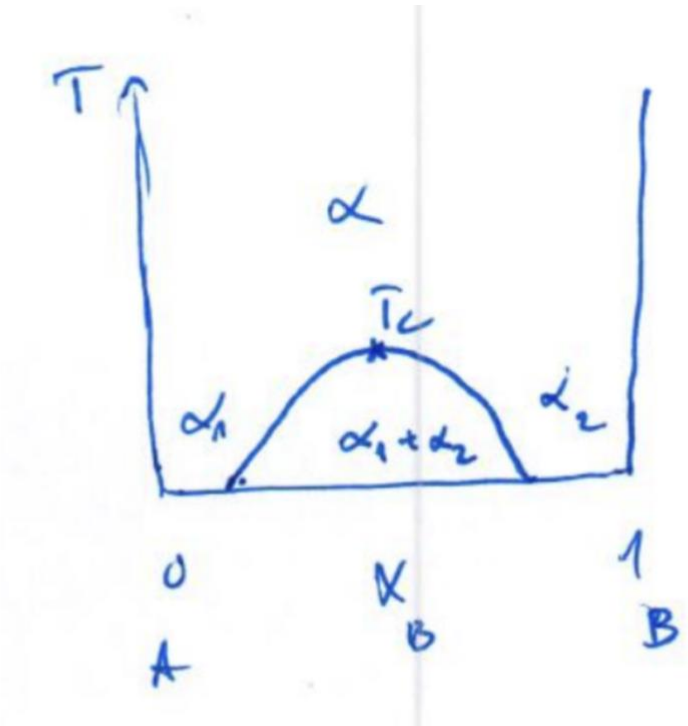
If the solution has a composition in between X1 and X2 or X3 and X4, respectively.

b. At composition X2 and composition X3 what condition is met?

X2 and X3 are compositions that mark the boundaries between nucleation & growth mechanism from the spinodal decomposition mechanism regime, defined by the condition:

$$\left(\frac{\partial^2 \Delta \bar{G}}{\partial XB^2}\right)_{X2} = 0 \qquad \left(\frac{\partial^2 \Delta \bar{G}}{\partial XB^2}\right)_{X3} = 0$$

c. Draw the phase diagram of such a two-component system as a function of temperature and label all curves.



d. At T2 that is T1<T2<Tc (where Tc is the critical temperature of this system) and still at pressure P, draw the ***ΔG***) vs. XB on Figure 1b.

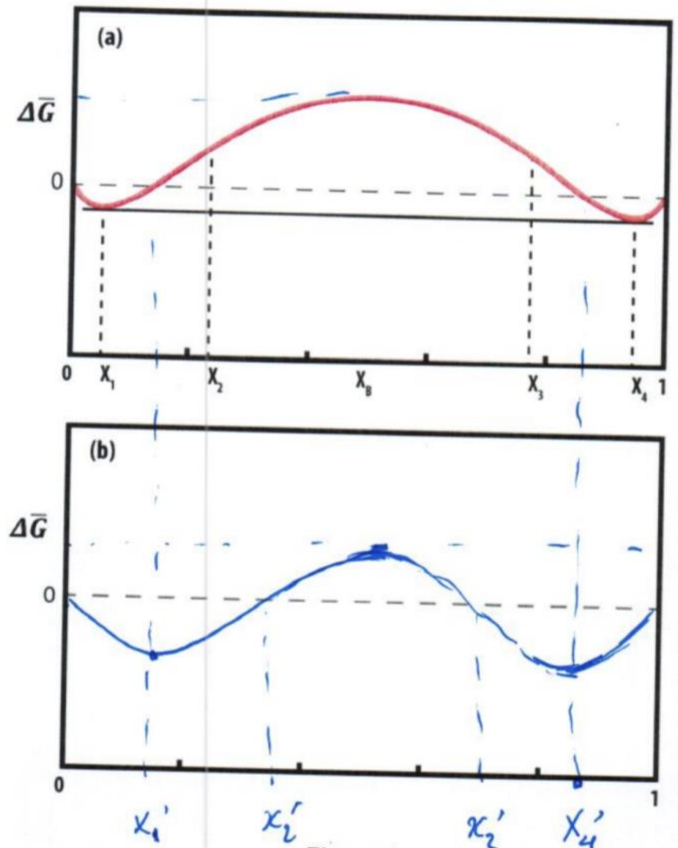


Figure 1