

Homework 11

Exercise 1

Short questions

- 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.
- 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?

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.

- 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
- 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:
 - C_p remains constant
 - C_p varies inversely as T, inversely as T^2 , etc.
 - C_p varies directly as T, as T^2 , etc.

Exercise 3

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.

- Write the differential form of the enthalpy.
- Write the differential form of the Gibbs free energy.
- Find a Maxwell's relationship for $\left(\frac{\partial S}{\partial Z}\right)_{p,T}$.

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

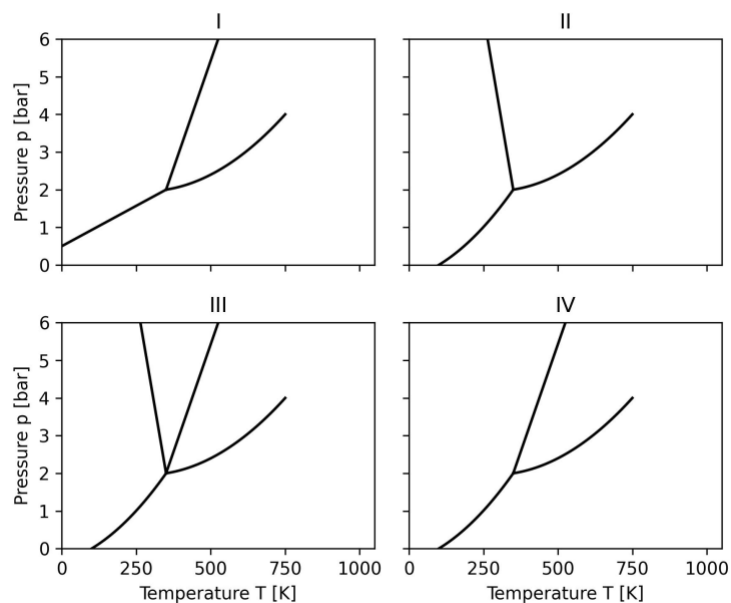
- Determine the change in the enthalpy ΔH with respect to the change of charge ΔZ . Note that the electromotive force is only temperature-dependent ($\varepsilon = \varepsilon(T)$).

Exercise 4

Single component

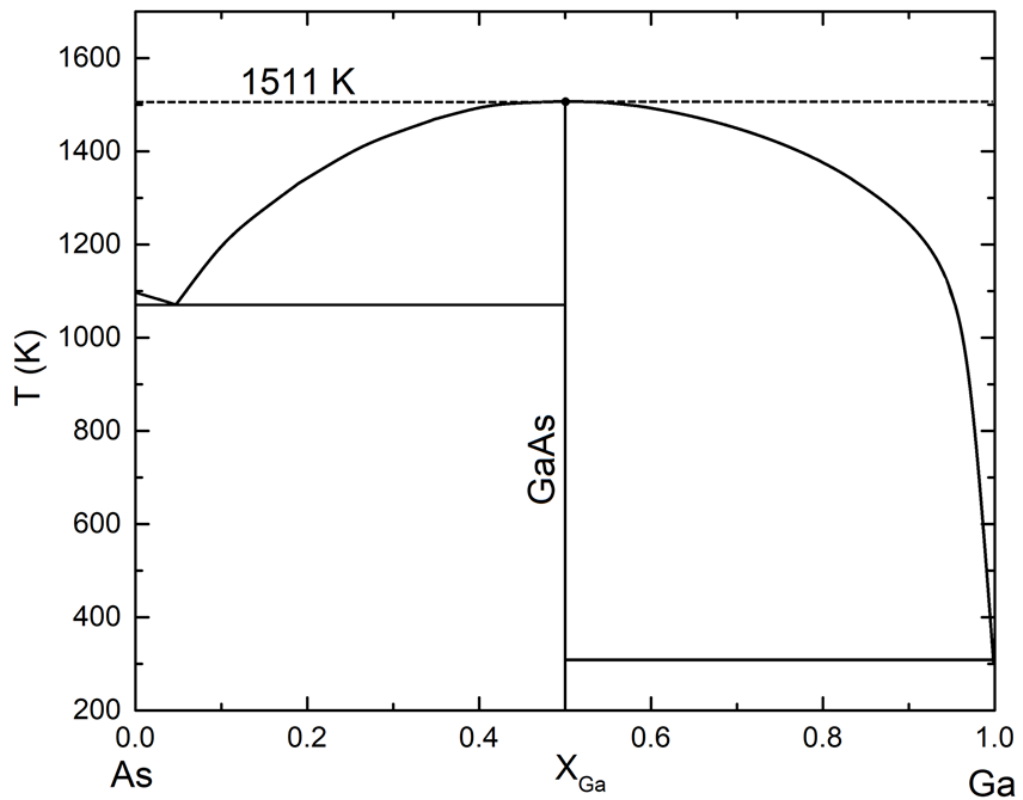
Four hypothetical phase diagrams of different pure substances are shown below. Note that at least one gas, one liquid, and one solid phases are present in the diagrams below.

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?



Exercise 4

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



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

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 T_1 and pressure P .

- At which range of compositions the material will precipitate by the nucleation and growth mechanism?
- At composition X_2 and composition X_3 what condition is met?
- Draw the phase diagram of such a two-component system as a function of temperature and label all curves.
- At T_2 that is $T_1 < T_2 < T_c$ (where T_c is the critical temperature of this system) and still at pressure P , draw the $\Delta \bar{G}$ vs. X_B on Figure 1b.

