

1 314 Problems

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1.1 Phases and Components

1) (2014) For each of the following thermodynamic systems, indicate the number of components, the number of phases, and whether the system is open or closed.

1. An open jar of water at room temperature (assume that the jar defines the boundaries of the system). Assume that the water molecules do not dissociate.
2. A sealed jar of water at room temperature.
3. A sealed jar of water with ice.
4. An open jar of water with NaCl entirely dissolved within.
5. If the jar is left open, in what ways might your description change?
6. How would your answer to (a) change if you take into account equilibrium between water, protons, and hydroxyl ions?

1.2 Intensive and Extensive Properties

2) (2014) Classify the following thermodynamic properties as intensive or extensive:

1. The mass of an iron magnet.
2. The mass density of an iron magnet.
3. The concentration of phosphorous atoms in a piece of doped silicon.
4. The volume of the piece of silicon.
5. The fraction by weight of copper in a penny.
6. The temperature of the penny in your pocket.
7. The volume of gas in a hot air balloon.

1.3 Differential Quantities and State Functions

3) (2014) Consider the function $z = 6x^2y^3 \cos^2 u$.

1. Write down the total differential of z . Identify the coefficients of the three differentials in this expression as partial derivatives.
2. Demonstrate that three Maxwell relations (see section 2.3) hold between the coefficients identified under (a).

- 4) (2014) Why are state functions so useful in calculating the changes in a thermodynamic system?
- 5) (2014) Derive equation 4.41 starting from 4.34 and 4.31. Note that other equations listed in table 4.5 can be derived in a similar fashion.

1.4 Entropy

- 6) (2015) Following Section 3.6, compute the change in entropy in the formation of one mole of SiO_2 from Si and O at room temperature.
- 7) (2015) Consider an isolated system consisting of three compartments A, B, and C. Each compartment has the same volume V , and they are separated by partitions that have about. Initially, the valves are closed and volume A is filled with an ideal gas to a pressure P_0 at 298 K. Volumes B and C are under vacuum.
1. Calculate the change in entropy when the valve between compartment A and B is opened.
 2. Calculate the change in entropy when the valve between compartment B and compartment C is opened.
 3. Without considering the calculations above, how would you know that the overall change in entropy is positive?
 4. What would you need to do to the system to restore the initial condition?

1.5 Thermodynamic Data

- 8) (2015) This problem requires you to find sources to look up the values of important materials parameters that will be used to compute thermodynamic functions.
1. Find values of the coefficient of thermal expansion for a metal, a semiconductor, an insulator, and a polymer. Provide the information below in your answer.

Material Type	Specific Material	α	Source (include page or link info)
Elemental Metal	<i>e.g.</i> Gold		
Semiconductor			
Insulator			
Polymer			

2. What is a common material with a negative α ?
 3. How is the coefficient of compressibility related to the bulk modulus?
 4. Which metal has the highest bulk modulus at room temperature, and what is the value?
 5. The heat capacity is an extensive quantity. Define the related intensive quantity.
 6. What trend do you observe in elemental solids?
 7. What is the smallest value you can find for a solid material? (Explain your search method, and cite your sources.)
- 9) (2014) The density of silicon carbide at 298 K and 1 atm is $\sim 3.2 \text{ g/cm}^3$. Estimate the molar volume at 800 K and a pressure of 1000 atm. See tables 4.1 and 4.2 on page 61 of DeHoff for useful materials parameters.
- 10) (2015) The density of aluminum at 298 K and 1 atm (or "bar") is 2.7 g/cm^3 . Estimate the molar volume at 1000 K and a pressure of 1000 atm. See tables 4.1 and 4.2 on page 61 of DeHoff, and Appendix B, for useful materials parameters. Hint: break the problem into two steps, each corresponding to a path.

- 11)** (2015) Use the car mileage dataset provided to do the following:
1. Create a second order polynomial fit to determine the coefficients for the mileage dataset online. Use the systems of equations we developed during discussion to help you solve for the coefficients. Write your polynomial coefficients down in your submitted assignment.
 2. Using your curve of best fit, determine the optimal speed for driving that maximizes your mileage.
 3. Identify an obvious failure of your model and comment on it below.

- 12)** (2015) Answer the following questions using the heat capacity dataset and the following model:

$$C_p = a + bT + c/T^2 + dT^2$$

1. Use the system of equations derived in class to determine the coefficients a, b, c, d.
2. Give a possible Gibbs free energy function for bulk silicon using your heat capacity fit. The Gibbs free energy is related to the heat capacity through the following equation:

$$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_P$$

- 13)** (2015) Compare the change in entropy for the specific examples below of isothermal compression and isobaric heating of gases and solids.

1. One mole of nitrogen (N_2) at 1000 K is compressed isothermally from 1 to 105 bar.
2. One mole of silicon at 300 K is compressed isothermally from 1 to 105 bar.
3. One mole of oxygen (O_2) at 300 K is heated isobarically from 300 to 1200 K.
4. One mole of tungsten at 300 K is heated isobarically from 300 to 1200 K.

- 14)** (2015) For each of the following processes carried out on one mole of a monatomic ideal gas, calculate the work done by the gas, the heat absorbed by the gas, and the changes in internal energy, enthalpy, and entropy (of the gas). The processes are carried out in the specified order.

1. Free expansion into the vacuum to twice the volume, starting from 300 K and 4 bar. Then,
2. Heating to 600 K reversibly with the volume held constant. Then,
3. Reversible expansion at constant temperature to twice the volume of the previous state. Then,
4. Reversible cooling to 300 K at constant pressure.

- 15)** (2015) Consider one mole of a monatomic ideal gas that undergoes a reversible expansion one of two ways.

1. Under isobaric conditions, the gas absorbs 5000 J of heat in the entropy of the gas increases by 12.0 J/K. What are the initial and final temperatures of the gas?
2. Under isothermal conditions, 1600 J of work is performed, resulting in an entropy increase of 5.76 J/K and a doubling of the volume. At what temperature was this expansion performed?

- 16) (2015) In class we learned that the change in entropy of a material with temperature is given by:

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_p(T)}{T} dT \quad (1.1)$$

In a prior homework, we fit the heat capacity to a polynomial, which we could then integrate. Now, we will numerically integrate the data points using the Trapezoid Rule discussed in class:

$$\int_{T_1}^{T_2} f(x) \approx (T_2 - T_1) \left[\frac{f(T_1) + f(T_2)}{2} \right] \quad (1.2)$$

where the function $f(T)$ in our case is the right hand side of Equation 1.1, is simply the right hand side of Equation 1.1. Do this by creating a "FOR" loop in MATLAB that sums up all the trapezoids in the temperature range. Email your MATLAB script to the TA by the due date.

1. What is the difference in entropy at 300 K and 1300 K?
2. Previously, we determined that the heat capacity is given by:

(a)

$$C_p = 22.83 + 3.826 \times 10^{-3} T - \frac{3.533 \times 10^5}{T^2} + 2.131 \times 10^{-8} T^2 \quad (1.3)$$

- (b) Use Equation 1.1 to analytically solve for the change in entropy using Equation 1.3. Which method do you think is more accurate? Explain your reasoning.

1.6 Temperature Equilibration

- 17) (2015) 100 g of ice at 250 K is added to 100 g of water at 300 K, and the mixture is allowed to come to equilibrium in an isolated container at constant pressure. You may assume that C_p is constant for this problem (though it is not the same for water and ice) and that the melting point is 273 K.

1. What is the final temperature?
2. How much liquid is present?
3. How would your answer change if the initial liquid was 40% ethanol?

- 18) (2015) A square block of Al, initially at a uniform temperature of 300 K, is brought into contact with another block of aluminum, initially at a uniform temperature of 600K. Both blocks are of equal mass, and they are isolated at constant pressure while they come to equilibrium. The questions below assume equilibrium has been reached.

1. What do you know about the final temperatures of the Al blocks?
2. Will the final temperature(s) be 450 K? Justify your answer.
3. Find the final temperature.

1.7 Statistical Thermodynamics

- 19) (2015) DeHoff 6.3: Consider a system of two particles (A and B) that may each occupy any of the four energy levels ($\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4$).

1. How many distinct microstates are there for this system?
2. List each of the microstates and indicate which microstates have the same energy.
3. How many macrostates are there?
4. List the most probable macrostates.

20) (2015) DeHoff 6.5 Variant: Consider the system consisting of 9 identical but distinguishable particles, each of which can be in any of three states. The respective energy levels of the states are $\epsilon_0 = 0, \epsilon_1 = \epsilon, \epsilon_2 = 2\epsilon$. The system has a temperature T .

1. Write the partition function for a single particle.
2. Calculate the average number of particles in each state.
3. Determine the number of configurations that have the following occupation numbers for the three states: $n_0 = 4, n_1 = 3, n_2 = 2$.
4. Calculate the entropy of the macrostate described by the occupation numbers above.
5. Calculate the internal energy.
6. Choose a different set of occupation numbers to give the same internal energy (e.g. (3,5,1)) and repeat your calculation of the entropy. Which macrostate is more likely?

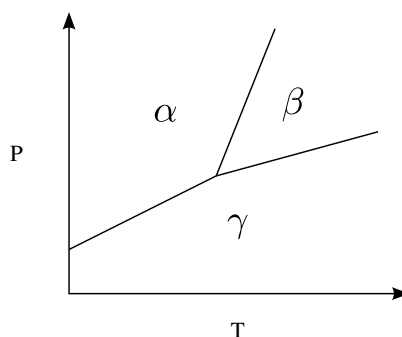
21) (2015) DeHoff 6.7 variant: A System containing 500 particles and 15 energy levels is in the following macrostate: {14, 18, 27, 38, 51, 78, 67, 54, 32, 27, 23, 20, 19, 17, 15}. Estimate the change in entropy when the system undergoes a process leading to the following changes in occupation numbers: {0, 0, -1, -1, -2, 0, 1, 0, 3, 2, -1, 1, -1, 0, -1}.

1.8 Single Component Thermodynamics

22) (2015) DeHoff 6.10: Compute the change in entropy when one mole of a monatomic ideal gas is compressed from an initial condition at 273K and 1 bar to 500K at 3.5 bar.

1. Calculate using the phenomenological thermodynamics of Chapter 4.
2. Calculate using the results of statistical thermodynamics. Hint: first calculate the initial and final volumes.

23) (2015) DeHoff 7.5: Sketch $G(T)$ for an element that the pressure corresponding to the triple point. Repeat the sketch for a pressure slightly above and slightly below the triple point.



24) (2015) DeHoff 7.6 See Lecture 17, last page.

25) (2015) DeHoff 7.7 variant: At what pressure will ice melt at -2°C ?

26) (2015) DeHoff 7.8: At 1 atm pressure and below 1155 K, the ϵ form of titanium is stable; above 1155 K, the β form is the stable phase (ϵ becomes metastable). Given the following data:

- $\Delta S^{\epsilon \rightarrow \beta} = 3.43 \text{ J/mol} \cdot \text{K}$ (This is the difference in molar entropy 3 between the phases).
- The change in molar entropy upon melting is $9.02 \text{ J/mol} \cdot \text{K}$.
- $T_m^\beta = 1940 \text{ K}$.

1. Sketch G^ε , G^β and G^ℓ in the temperature range of interest.
2. What is T_m^ε ?
3. There is a database of the Gibbs free energy of 78 pure elements as a function of temperature. The database can be found here: <http://www.crct.polymtl.ca/sgte/unary50.tdb>
 - (a) Find the ε phase of titanium (labeled as GHSERTI), the β phase (labeled as GBCCTI), and the liquid phase (labeled as GLIQTII) and repeat a and b using the empirical formulas. Compare your answers and comment on the accuracy of your assumptions.

NOTE: The formula is written so that a program called Thermocalc can read them. Each free energy curve is a piecewise formula. The “;” separates the parts of the function over different temperature ranges. In addition, a “**” is the same as an exponent or “^”.

1.9 Multicomponent Thermodynamics

27) (2015) DeHoff 8.1: Titanium metal is capable of dissolving up to 30 atomic percent oxygen. Consider a solid solution in the system Ti–O containing an atom fraction, $X_0 = 0.12$. The molar volume of this alloy is 10.68 cc/mol. Calculate the following:

1. The weight percent of O in the solution.
2. The molar concentration (mol/cc) of O in the solution.
3. The mass concentration (gm/cc) of O in the solution.
4. Use these calculations to deduce general expressions for weight percent, molar, and mass concentrations of a component in a binary solution in terms of the atom fraction, X_2 , the molar volume, V , and the molecular weights, MW_1 and MW_2 , of the elements involved.

28) (2015) DeHoff 8.4: Use the partial molal volumes computed in Problem 8.3 (worked out in class) to demonstrate that the Gibbs – Duhem equation holds for these properties in this system.

29) (2015) DeHoff 8.6: For an ideal solution it is known that, for component 2, $\Delta G_2 = RT \ln X_2$. Use the Gibbs – Duhem integration to derive corresponding relation for component 1.

30) (2015) One mole of solid Cr_2O_3 at 2500 K is dissolved in a large volume of a liquid Raoultian solution (also at 2500 K) of Al_2O_3 and Cr_2O_3 with $X_{\text{Cr}_2\text{O}_3} = 0.2$. Calculate the resulting changes in the total enthalpy and entropy given the following:

$$T_{m,\text{Cr}_2\text{O}_3} = 2538 \text{ K}; \Delta H_{m,\text{Al}_2\text{O}_3} = 107,500 \text{ J/mol at } T_{m,\text{Al}_2\text{O}_3} = 2324 \text{ K}; \Delta S_{m,\text{Al}_2\text{O}_3} = \Delta S_{m,\text{Cr}_2\text{O}_3}$$

1.10 Computational Exercises

31) (2015) For this problem, you will be using MATLAB’s symbolic solver (fzero) and function handles to find the zero of an equation. On last week’s quiz we found that 89.1 grams of ice were necessary to cool a 1 kg block of Pb down to 300 K from 600 K. We will be plotting the change in temperature for both the Pb and ice. You will need the following parameters:

$$\begin{aligned} C_p^{\text{Pb}} &= 0.1169 + 4.2 \times 10^{-5} T \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \\ C_p^{\text{H}_2\text{O}} &= 4.2 \frac{\text{kJ}}{\text{kg}\cdot\text{K}} \\ \Delta H_{fus}^{\text{H}_2\text{O}} &= 344 \frac{\text{kJ}}{\text{kg}} \\ \frac{dH}{dt} &= a\Delta T \end{aligned}$$

Here a is a coefficient that controls the heat transfer in conduction, which we will assume to be $3.33 \times 10^{-3} \text{ kJ/K}\cdot\text{s}$, and ΔT is the temperature difference between the two materials.

32) Use the equations derived in class to plot the change in temperature for H₂O and Pb. Assume dt=1 s and calculate the first 200 time steps. How do you know when the system is at equilibrium?

1. Create a plot that shows the amount of water in the system as a function of time. At what time is all the ice gone?
2. Create a plot that shows the total heat transfer occurring between the Pb and H₂O. How can you tell when equilibrium is reached from this plot?

33) (2015) We will be putting together a program to help calculate phase diagrams of all sorts piece by piece. The first step is to create a MATLAB script that solves a system of two equations. The system is below:

$$G_s - X_s \frac{dG_s}{dX_s} = G_\ell - X_\ell \frac{dG_\ell}{dX_\ell} \quad (1.4)$$

$$\frac{dG_s}{dX_s} = \frac{dG_\ell}{dX_\ell} \quad (1.5)$$

where G_s and G_ℓ are given by the following expressions:

$$G_s(X_s) = \Omega_s X_s (1 - X_s) + RT [X_s \ln X_s + (1 - X_s) \ln (1 - X_s) + 200X_s - 400(1 - X_s)].$$

$$G_\ell(X_\ell) = \Omega_\ell X_\ell (1 - X_\ell) + RT [X_\ell \ln X_\ell + (1 - X_\ell) \ln (1 - X_\ell)].$$

Here G_s is the Gibbs energy of the solid phase, G_ℓ the Gibbs free energy of the liquid phase, R the gas constant (8.314 J/K), T the absolute temperature, X_s and X_ℓ are the compositions of the solid and liquid phase respectively, and Ω_s , Ω_ℓ are parameters to be defined later. We can rewrite Eqs. 1.4 and 1.5 as follows:

$$G_s - X_s \frac{dG_s}{dX_s} - G_\ell + X_\ell \frac{dG_\ell}{dX_\ell} = 0 \quad (1.6)$$

$$\frac{dG_s}{dX_s} - \frac{dG_\ell}{dX_\ell} = 0 \quad (1.7)$$

Create a MATLAB function that takes X_s , X_ℓ , T , Ω_s and Ω_ℓ as inputs and then create a script that uses the MATLAB command `fsolve` to calculate X_s and X_ℓ for $T=700\text{K}$, $\Omega_\ell = 1500 \text{ cal/mol}$ and $\Omega_s = 3000 \text{ cal/mol}$.

34) (2015) Now that we are able to solve for the composition of the solid and liquid at one point, we will improve our script to calculate it over a range of temperatures. Start with an initial guess for both the solid and liquid near zero and a temperature of 900 K. Determine the composition of the liquid and solid down to 1 K for each temperature using a for loop. Make sure to update your guess with the correct answer for the previous temperature to help your program converge. Repeat again starting from 600 down to 1 K, this time starting with an initial guess near 1, and plot your results. Use the following parameters to make the Gibbs energy more physical:

$$T_m^\alpha = 900 \text{ K}$$

$$T_m^\beta = 600 \text{ K}$$

$$\Delta H_f^\alpha = 2000 \frac{\text{cal}}{\text{mol}}$$

$$\Delta H_f^\beta = 1300 \frac{\text{cal}}{\text{mol}}$$

The liquid and solid free energies are given by the following expressions. (Note that the Gibbs energy for the solid phase has changed slightly and should be adjusted in your code. In these units $R = 1.987 \text{ cal/mol} \cdot \text{K}$)

$$G_s(X_s) = \Omega_s X_s (1 - X_s) + RT + \left[X_s \ln X_s + (1 - X_s) \ln (1 - X_s) + X_s \Delta G_\beta^{\ell \rightarrow s} + (1 - X_s) \Delta G_\alpha^{\ell \rightarrow s} \right].$$

$$G_\ell(X_\ell) = \Omega_\ell X_\ell (1 - X_\ell) + RT [X_\ell \ln X_\ell + (1 - X_\ell) \ln (1 - X_\ell)].$$

As a reminder, the free energy change for the melting transition can be written in terms of the enthalpic and entropic contributions to the free energy:

$$\Delta G^{s \rightarrow \ell} = \Delta H^{s \rightarrow \ell} - T \Delta S^{s \rightarrow \ell}$$

35) (2015) Our phase diagram calculation is almost complete! We only have to find the equilibrium between the two solid phases left. To do that, we simply take the derivative of the Gibbs free energy of the solid phase and set it equal to zero. The equation becomes:

$$RT \ln \left(\frac{X_s}{1 - X_s} \right) - \Omega_s (2X_s - 1)$$

Again, assume that $\Omega_s = 3000$ cal/mol. This is easily done by creating a for loop that solves for the temperature at each composition between .01 and .99. Plot your results on the same figure from the previous homework and voila, your first phase diagram!

Now with your working code, replot the diagrams for the following interaction coefficients. You will have to change the range of temperatures for one of the sets below. You can figure out which one it is, if you think of the physical significance of the parameters.

1. $\Omega_s = 3000$ cal/mol : $\Omega_\ell = 0$
2. $\Omega_s = 0$: $\Omega_\ell = 3000$ cal/mol
3. $\Omega_s = 0$; $\Omega_\ell = 0$
4. $\Omega_s = 3000$ cal/mol : $\Omega_\ell = 3000$ cal/mol

For each phase diagram, plot your results and describe how the changing interaction parameters changed the shape of the plot.