Experiment 7: Solid-Liquid Phase Diagram

Procedure

CHE 347 TA: Alec Beaton

Introduction

In this experiment, we will construct the solid-liquid phase diagram for the binary system naphthalene and biphenyl. Both materials are organic solids at room temperature but have melting points below 90℃. As such, we will prepare different mixtures of these two substances, heat them *beyond* the melting point, and record the temperature of the mixtures as they cool from liquid to solid. By carefully recording the mass of both naphthalene and biphenyl added to the mixtures, as well as the temperatures of the phase transitions (in this case, solidification), we can construct solid-liquid phase diagrams for this mixture that will reveal thermodynamic information on this system, such as shown in Figure 1.

In this experiment, we will be recording data points that lie along the curved (liquidus) lines for this binary mixture. At their intersection is the eutectic point, which occurs at the eutectic temperature T_E (the lowest temperautre at which the liquid phase is present in the system).

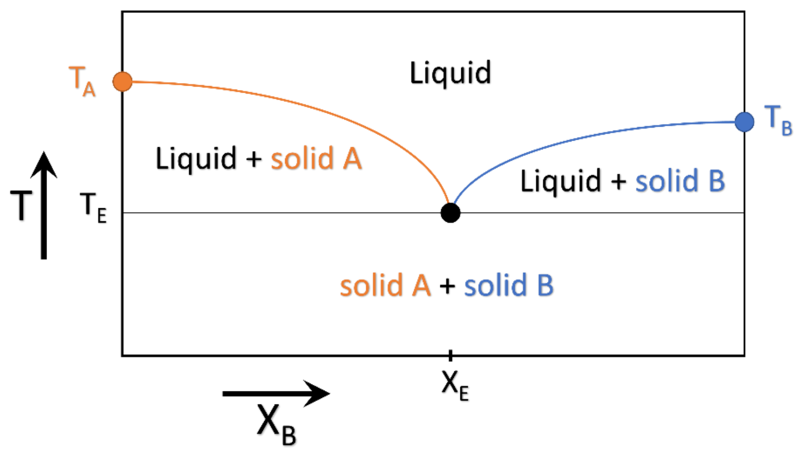

Figure 1. Solid-liquid phase diagram for a two-component mixture.

Fitting the orange liquidus curve to a decreasing line of the form[1]

$$T = T_A - \frac{R(T_A)^2}{\Delta H_{f,A}} x_B \; [1]$$

gives the y-intercept as the melting point of pure component A (T_A), and the heat of fusion for pure component A ($\Delta H_{f,A}$ in kJ/mol) can be derived from the slope. Note that this equation holds true only at low mole fractions of x_B.

Similarly, the blue liquidus curve can be fit as

$$T = T_B - \frac{R(T_B)^2}{\Delta H_{f,B}} x_A \; [2]$$

which can likewise provide the melting point of pure component B (T_B) and the heat of fusion for pure component B ($\Delta H_{f,B}$ in kJ/mol) can be derived from the slope. Note that this equation holds true only at low mole fractions of x_A. Also note that, by definition, for a binary system, $x_A = 1 - x_B$.

For a pre-lab assignment, **please come to the lab section with the mass of biphenyl and naphthalene that you plan to measure out to attain the desired mole fractions** outlined below.

Note: The melting point of naphthalene is 353.4 K (80.3℃) and the melting point of biphenyl is 342.1 K (69.0℃), and these should be the lower and upper limits of the solid-liquid phase diagram (provided that we are plotting mole fraction of biphenyl on the x-axis – at 0 mole fraction biphenyl, the system is 100% naphthalene and thus the melting point we observe should therefore be the melting point of pure naphthalene; likewise, at 1 mole fraction biphenyl, the system is 100% biphenyl and the melting point we observe should be the melting point of pure biphenyl.

Objectives

- Monitor phase transitions *via* cooling curves (temperature *vs.* time)

- Construct simple solid-liquid phase diagram for a binary system

- Analyze liquidus curves to obtain thermodynamic quantities

Equipment:

- Vernier LabQuest 2
- Vernier temperature probe
- Stir and heating plate

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[1] If you are interested in the derivation of this equation, please see Gallus, J. et al. *J. Chem. Educ.* 2001, 78 (7), 961. https://doi.org/10.1021/ed078p961. Refer to the section 'Solid-Liquid Phase Equilibrium' on pages 1 and 2.

- Water bath

Materials

- Naphthalene
- Biphenyl

Procedure:

You will prepare 6 different mixtures of biphenyl and naphthalene, of 0, 0.2, 0.4, 0.6, 0.8, 1 mole fraction of biphenyl in 6 different test tubes (Note: 0 mole fraction biphenyl is 100% naphthalene, and 1 mole fraction biphenyl is 100% biphenyl). Each mixture must measure to 3 g total. You must record the exact masses of biphenyl and naphthalene used to prepare each sample. **Please come to the lab section with the mass of biphenyl and naphthalene that you plan to measure out to attain the desired mole fractions for each sample.**

For each sample, you will submerge the mixture of solids into a hot water bath, allow it to melt into a clear liquid, and then raise the test tube from the water bath to allow it to cool to room temperature. While it is cooling, a Vernier temperature probe will have been inserted into the test tube to record the temperature. Each sample will take approximately 15 minutes to reach room temperature. You will record the plateau or break point in the cooling curve as the phase transition from liquid to solid for that liquid.

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Post-Lab

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Introductory Information

1. Provide some background information on the chemicals used in this experiment, biphenyl and naphthalene: what class of compounds are these? Do either have common uses?

2. What equations will you need to turn the values recorded in your lab notebook into the main values (*i.e.*, meaningful physical quantities) that you wish to report?

Experimental Details

1. Name the chemicals used in this experiment.

2. Report any additional observations during the course of the experiment.

Results

1. In a formatted table **with units**, for **each of the 6 samples** provide: mass of biphenyl, mass of naphthalene, mole fraction of biphenyl, mole fraction of naphthalene, and the 'break' points (freezing points) recorded from each cooling curve.

2. Show work for the mole fraction calculations for each of the 6 samples.

    - If you like, you can generate an excel table. To do this, you need to paste a table showing the numbers (with units in the column headers) as well as a table showing the formulas you used.

    - For the second table, you can press `Ctrl-~` or `Ctrl-`` `to show all your formulas before copying + pasting into your final document (just be sure to resize the columns so everything is legible).

3. Provide the solid-liquid phase diagram for this system with labeled axes, using **mole fraction of biphenyl** as the x-axis.

4. Provide the liquidus curve for biphenyl in one plot and the liquidus naphthalene in another plot, fit to the equations in the lab procedure.

5. In a formatted table **with units**, provide the freezing point of naphthalene, the freezing point of biphenyl, the heat of fusion for naphthalene, and the heat of fusion for

biphenyl, derived from your liquidus curves, and calculate percent errors for each value from the following literature[1] values:

- Biphenyl (melting point: 342.1 K, enthalpy of fusion: 18.57 kJ/mol)
- Naphthalene (melting point : 353.4 K, enthalpy of fusion: 19.01 kJ/mol)

Discussion

1. Discuss possible sources of error in this experiment to account for discrepancy from the literature values
2. According to the phase diagram in question 3, what is the maximum temperature at which you would expect ***only*** solids of either substance to be present (i.e., no liquid phase)?
3. According to the phase diagram in question 3, at which temperature range would you expect solid naphthalene to be present but *no* solid biphenyl to be present?
4. According to the phase diagram in question 3, and utilizing the lever rule (this is a link), at a mole fraction of 0.1 biphenyl and 50°C, what mole fraction of your sample do you expect will be present as solid naphthalene, and what mole fraction will be present as liquid? What will the composition of the liquid be?

   For full credit, please **mark your phase diagram in question 3** with appropriate tie line and points.

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[1] Gallus, J.; Lin, Q.; Zumbühl, A.; Friess, S. D.; Hartmann, R.; Meister, E. C. Binary Solid-Liquid Phase Diagrams of Selected Organic Compounds. A Complete Listing of 15 Binary Phase Diagrams. *J. Chem. Educ.* **2001**, *78* (7), 961. https://doi.org/10.1021/ed078p961.

Experiment 7: Solid-Liquid Phase Diagram – Rubric

Student:

Introductory Information (6 pts)

1. (/3 pts)
2. (/3 pts)

Total: (/ 6 pts)

Experimental Details (6 pts)

1. (/3 pts)
2. (/3 pts)

Total: (/ 6 pts)

Results (68 pts)

1. (/30 pts)
2. (/6 pts)
3. (/10 pts)
4. (/10 pts)
5. (/12 pts)

Total: (/ 68 pts)

Discussion (20 pts)

1. (/5 pts)
2. (/5 pts)
3. (/5 pts)
4. (/5 pts)

Total: (/ 20 pts)

Report Total: (/ 100 pts)

General Comments: