

# Determination of a Liquid/Solid Phase Diagram of a Binary Mixture and Determination of $\Delta_{\text{fus}}H$ using freezing point depression.

## Introduction

In this experiment you will determine the freezing point depression of several different compositions of a binary mixture (components A and B). The difference between the freezing point of the pure solvent (which we will consider to be the component with the higher mole fraction) and that of the binary solution is called the freezing point depression,  $\Delta T$ .<sup>1</sup> The magnitude of  $\Delta T$  depends only on the identity of the solvent and molality,  $m$ , but not the identity, of the solute and is defined as the simple product

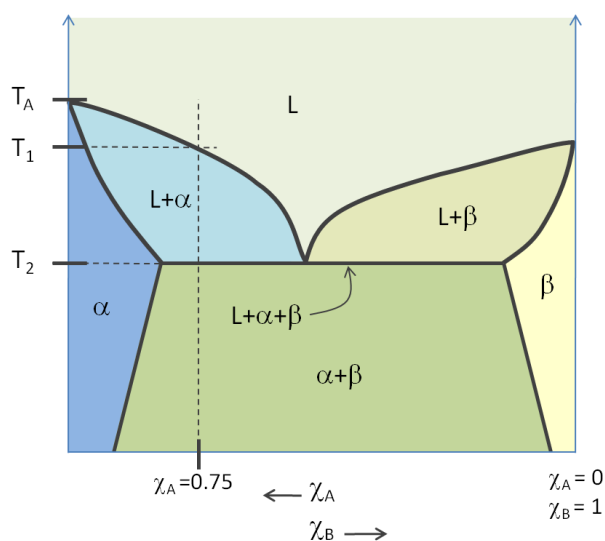
$$\Delta T = K_f m \quad (1),$$

where  $K_f$  is the cryoscopic constant and depends only on solvent properties, including the enthalpy of fusion,  $\Delta_{\text{fus}}H$ , of the solvent. This is shown by equation 2:

$$K_f = \frac{MRT_f^2}{\Delta_{\text{fus}}H} \quad (2),$$

where  $M$  is the molar mass in kg/mol and  $T_f$  is the freezing point (in K) of the pure solvent. By measuring the freezing point of pure solvent and that of a solution of known molality, one can determine  $\Delta_{\text{fus}}H$ .

Measuring the freezing point of several compositions of A and B allows a phase diagram for the binary mixture to be constructed. For a pure substance, a phase diagram is a plot of the equilibrium curves in pressure/volume space, as in



**Figure 1.** Binary phase diagram in  $T$ - $\chi$  space. Solids of components A and B are represented by  $\alpha$  and  $\beta$ , respectively, with liquid represented by L. To the far right and far left, the mole fractions are pure in one component or the other, so that only one phase transition is seen.

the previous  $\text{CO}_2$  Lab. However, for a system of more than one component, the temperature at which the solution changes phase will depend on pressure, temperature, and composition.<sup>2</sup> We represent composition using mole fraction ( $\chi$ ). Since all of our experiments are done at atmospheric pressure, we can plot a simpler “slice” of the full phase surface. Such a slice is shown in Fig. 1. Just as in a single-component system, the curves drawn represent the points in  $T$ - $\chi$  space at which the solution is at equilibrium. Thus, at mole fraction  $\chi_A=1$  on the diagram (pure component A), we see that melting temperature of A is  $T_A$ . At  $\chi_A = 0.75$ , there are multiple phases possible, depending on the temperature. Above  $T_1$ , a homogeneous mixture of liquid will be observed. Between  $T_1$  and  $T_2$ , the system will contain solid A (denoted  $\alpha$ ) and a liquid (L) which contains both A and B. Below the *eutectic line* at  $T_2$ , the mixture is solid. Each team or individual will be assigned either naphthalene or paradichlorobenzene to be the solvent, and will be responsible for obtaining enough data for the side of the phase diagram for which their solvent is in higher concentration. Data will be exchanged for the construction of a more complete phase diagram.

## Experimental Procedures

Place about 5 grams of your solvent component (either naphthalene or paradichlorobenzene) in the tube. It is not critical that it be exactly 5 grams, but it is important that you measure the amount precisely. Heat the test tube in the hot water until all the solid melts, then transfer it to a small sandbath to insulate the assembly. When heating, do not allow the test tube to touch the bottom of them beaker. When stirring, stir briskly, but carefully (you are working with glass, but splashes can result in liquid resolidifying on the colder glass above). Record the temperature of the liquid as a function of time until the freezing point has been accurately determined. You should find that as the liquid is

cooling, the rate of heat loss and temperature drop is fast, but consistent. Once solid begins to form, the heat released by crystal formation offsets the rate of heat loss from the liquid and so the overall rate of temperature drop slows down. What is observed is a relatively sharp turn in the cooling curve (the plot of temperature vs. time) that occurs when the solid begins to first freeze out. The temperature at which the turn occurs is the temperature you should use as your “freezing point” for the heat of fusion calculation for your mixture. The solution must be stirred uniformly and continuously during the cooling process. Improper or inefficient stirring of the solution as it is cooling is usually the largest source of error in this lab. Another possible problem is a solution which freezes very rapidly, which will result in insufficient data points if they are not monitored correctly. After the solution has cooled to the point where stirring is difficult or impossible, remove the test tube. Allow it to cool to room temperature and weigh the assembly again.

When the freezing point of the pure component has been determined, add approximately 0.5 gram of your solute (i.e., the other component, again measured precisely). Heat and melt the mixture until a homogenous liquid solution is reached. Repeat the cooling procedure with the solution and determine the freezing point of this mixture.

When the freezing point of the first mixture has been determined, add another 0.5 gram of your solute. Weigh the assembly again between each freezing point measurement. Melt the mixture until a homogenous solution is reached. Repeat the cooling procedure with the solution and determine the freezing point of this mixture.

Finally, repeat the procedure for a fourth composition (pure solvent, plus three different mixtures). To clean your test tube, melt the mixture and quickly dump into the labelled waste container. Rinse thoroughly with a small amount of acetone to remove any residue, then leave the tube in the hood to evaporate off what remains.

### Pre-Lab

Complete the following before you begin the lab:

1. Look up the freezing points and enthalpies of fusion for naphthalene and paradichlorobenzene. From this information, calculate the cryoscopic constant,  $K_f$  for each. The enthalpies of fusion will serve as your literature values for comparison to your laboratory data, but  $K_f$  values allow you to predict how much change in melting temperature you can expect to observe for each addition. Don't forget to write down your source for this data, since you will need it for the report.
2. Summarize the experimental procedure in your notebook, noting ways you could make use of the rather long periods during which your sample is heating in the water bath.

### Data Analysis and Lab Reports

*Introduction:* Standard – no need for a full discussion of binary phase diagrams, but remember all equations you will use later need to be included. A one-sentence description of the apparatus should be included as part of your experimental explanation; a diagram will be helpful.

*Data:* As with the  $\text{CO}_2$  lab, raw data will be better presented as plots rather than tables. Plot cooling curves (a plot of temperature as a function of time) for each determination of freezing point. You will find that the curve does not always show a sharp change, but that you will need to determine the freezing point by fitting two different lines to your curve: one for the initial, steep slope, and a second for the flatter slope. The intersection of these two lines will give a good approximation for the freezing temperature of your solutions. The intersection can be determined based on the equations for the best fit lines. Set them equal to one another, and solve for  $x$ , which will give you the time of your phase transition point. Determine the temperature at that time using either of the best fit lines (now solving for  $y$ , knowing  $x$ ). In some cases, you may even see the slope increase again, indicating that you have crossed out of the equilibrium region. This is unlikely for most solutions, but can often be observed for the pure solvent. If this is observed, do not include those points in your flat region. The plots do not need to be large, just enough to show the lines you fit to get your freezing point. The primary source of error is likely to come from your fitting: play around with where you choose to “break up” your data, and see how that affects your freezing temperature. Because of the plots, this section may be a little longer than in previous labs. Don't forget to include a discussion of your errors in temperature and time in the narrative portion of your data.

*Discussion:* There are two major thrusts here, the colligative properties and the binary phase diagram. Be sure you address them in an organized, logical way, and include discussions of all of the following:

1. Determine mole fraction, molality, and the  $\Delta T$  (relative to the pure solvent) for each mixture. For each component, calculate  $K_f$  and determine the value of  $\Delta_{\text{fus}}H$  based on that. Note that you will get values for  $\Delta_{\text{fus}}H$  and  $K_f$  for each mixture. Put all this data into a table. Compare to the known  $\Delta_{\text{fus}}H$  values for each component. Calculate a percent error and determine if it is within your error bars based on the uncertainty in determining your melting temperature.
2. Construct your side of the phase diagram curve by plotting freezing point versus mole fraction (be specific! mole fraction of what?). Obtain and plot the data for the other half of the curve from another group (remember to credit this group) who performed this lab the same day you did. For this plot, you should include estimated error bars on your data points.
3. Estimate the eutectic temperature and composition based on your phase diagram. As you can see in Figure 1, the phase boundaries are not straight lines, so you might need to account for that in some way. Be sure to explain what you do.

*Conclusions:* Extend, evaluate, and connect to the big picture. Did all of your mixtures freeze completely when cooled to room temperature? Why or why not? Relate this to the phase diagram shown in Figure 1. Would it be possible to freeze the mixtures completely, based on this diagram? As always, account for any discrepancies or irregularities.

*Safety/References:* You will need to get key safety information (hazards) from the MSDS for naphthalene and paradichlorobenzene. You do not need to include the MSDS, just a web reference to get the information. Don't forget to reference background material (textbook is ok, but if you find better sources, feel free!) and to cite the reference for your literature values.

#### References:

1. Engel, T; Reid, P. *Thermodynamics*, 4<sup>th</sup> Ed.; Pearson Education: Glenview, IL, 2019; pp. 216-219.
2. Shoemaker, D. P., Garland, C. W., and Nibler, J. W. *Experiments in Physical Chemistry*, 6ed.; WCB McGraw-Hill: New York, 1996; pp. 215-221.