Lab # 13 – Molecular Weight Determination by Freezing Point Depression

INTRODUCTION

If a nonvolatile solid compound (the solute) is dissolved in a liquid (the solvent), the vapor pressure of the liquid solvent is lowered. This decrease in the vapor pressure of the solvent results in several easily observable physical changes, including a boiling point elevation and a freezing point depression.

Many years ago, chemists observed that at low solute concentrations the changes in the boiling point, the freezing point and the vapor pressure of a solution are all proportional to the amount of solute. These three properties are collectively known as colligative properties of solutions. The colligative properties of a solution depend on the number of solute particles present in a given amount of solvent and not on the kind of particles dissolved.

When working with boiling point elevations or freezing point depressions of solutions, it is convenient to express the solute concentration in terms of its molality, m, defined by the relationship in equation 1.

$$\text{molality of A} = \text{m} = \frac{\text{mol A}}{\text{kg solvent}} \qquad (1)$$

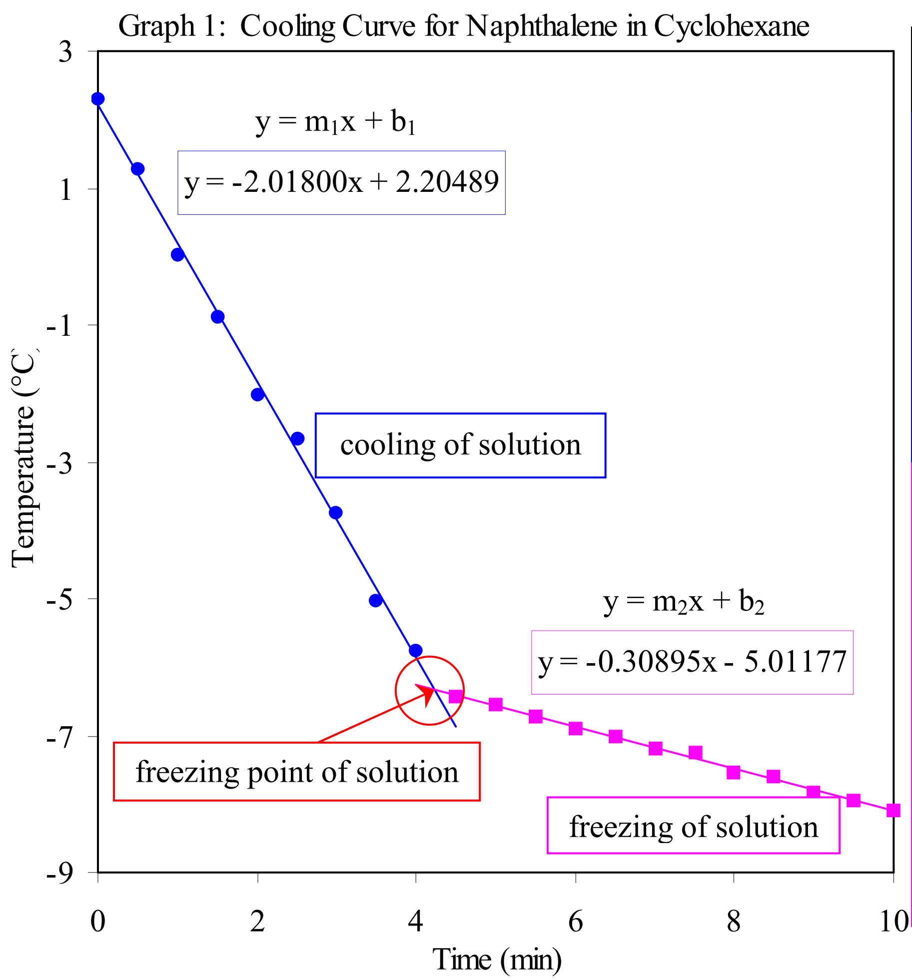
The boiling point elevation (T_b - $T_b°$) or ΔT_b and the freezing point depression ($T_f°$ - T_f) or ΔT_f in °C at low concentrations are then given by equations 2 and 3.

$$\Delta T_b = K_b m \qquad (2) \qquad\qquad \Delta T_f = K_f m \qquad (3)$$

T_b and T_f are respectively the boiling point and freezing point of the solution. $T_b°$ and $T_f°$ are respectively the boiling point and freezing point of the pure solvent. The values K_b and K_f are the boiling point elevation and freezing point depression constants whose value depends on the solvent used. For water, for example, K_b is 0.52°C/m and K_f is 1.86°C/m. For benzene, K_b is 2.53°C/m and K_f is 5.12°C/m.

One of the main uses of colligative properties of solutions is in connection with the determination of the molecular weights of unknown substances. If we dissolve a known amount of solute in a given amount of solvent and measure ΔT_f of the solution produced, we can find the molality from equation 3, as long as the appropriate K_f value is also known. From m, moles can be determined. Knowing both grams and moles allows us to calculate a molecular weight.

In this experiment, you will be asked to estimate the molecular weight of an unknown solute using freezing point depression. The solvent used will be paradichlorobenzene (PDB), more commonly used as one form of mothballs. PDB has a convenient melting point and a relatively large value for K_f, 7.10°C/m. The freezing points will be obtained by studying the rate at which liquid PDB and some of its solutions containing the unknown cool in air. Graphs of temperature versus time, called cooling curves, reveal the freezing points very well, since the rate at which a liquid cools is typically quite different from that of a liquid-solid equilibrium mixture. For an example of a cooling curve, see Graph 1.



Time (min)	Temp. (°C)	
0.0	2.31	
0.5	1.28	
1.0	0.03	
1.50	-0.88	
2.0	-2.03	cooling
2.5	-2.65	
3.0	-3.75	
3.5	-5.03	
4.0	-5.76	
4.5	-6.42	
5.0	-6.54	
5.5	-6.71	
6.0	-6.89	
6.5	-7.01	
7.0	-7.18	freezing
7.5	-7.25	
8.0	-7.54	
8.5	-7.61	
9.0	-7.82	
9.5	-7.96	
10.0	-8.09	

The first part of the curve (the blue circles) represents the cooling of the solution. As the solution begins to freeze, the temperature change becomes less dramatic, resulting in a line for the freezing of the solution (the purple squares). The actual freezing point of the solution is the intersection between the two lines, the cooling line and the freezing line. This point can either be determined visually by making a good graph and interpolating the intersection or mathematically by constructing a computer graph. For the latter, if you use Excel, two sets of data (one each for cooling and freezing) must be plotted and two straight lines fitted. (See the Excel directions for help with this.) If you use Graphical Analysis, you may enter one set of data but fit two straight lines. (See the Graphical Analysis directions for help with this.) Simultaneously solving the two equations as shown below will allow you to determine the freezing point of the solution.

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To find the intersection of the two lines, solve the two equations, 4 and 5, simultaneously for y.

$$y = m_1x + b_1 \quad (4)$$

$$y = m_2x + b_2 \quad (5)$$

Solving equation 4 for x gives you $x = \frac{y - b_1}{m_1}$, which can be plugged into equation 5 to give you equation 6.

$$y = m_2\left(\frac{y - b_1}{m_1}\right) + b_2 \quad (6)$$

Equation 6 is rearranged into equation 7, into which you can plug m and b values to solve for y, the freezing point of the solution.

$$y = \frac{m_1b_2 - m_2b_1}{m_1 - m_2} \quad (7)$$

Plugging in the m_1, m_2, b_1 and b_2 values from Graph 1 gives you the following.

$$y = \frac{(-2.01800)(-5.01177) - (-0.30895)(2.20489)}{(-2.01800) - (-0.30895)} = -6.32°C$$

Thus, the freezing point of the solution from above is –6.32°C. If the freezing point of pure cyclohexane is 6.47°C and K_f is 20.0°C/m for the solvent, then ΔT = 6.47°C – (-6.32°C) or 12.79°C. If the original solution was made with 2.462 g of naphthalene dissolved in 29.78 g of cyclohexane, the molecular weight of naphthalene can be calculated using equation 8.

$$\text{molecular weight} = \frac{K_f\left(\frac{g_{solute}}{g_{solvent}}\right)\left(\frac{1000\text{ g}}{1\text{ kg}}\right)}{\Delta T} \quad (8)$$

With the data, the molecular weight of naphthalene is calculated to be 129 g/mol.

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PROCEDURE

1. Work in pairs using a computer interfaced with a temperature probe set-up to record all the temperatures and times. Record the name of your partner(s) in the space provided.

2. If the computer is not on, turn it on. Open the *LoggerPro* file on the desktop. When the program is up, open the file *General Chemistry I Freezing Point Depression*. In the bottom left corner of the screen, you should now see a temperature. If you do not, stop and get your instructor. Be careful not to spill anything on or near the computer or the interface box.

3. Heat about 300 mL of water to about 75°C in a 400 mL beaker. Keep this water warm until the end of the experiment.

4. Obtain a test tube of the appropriate size from the cart in the front of the room. Weigh 10 g of PDB into this test tube. The suggested method for doing this follows.

   a. Put the test tube into a small beaker and place both on the balance pan.
   b. TARE the balance.
   c. Using your spatula, gently place PDB into the test tube until you have near 10 g.
   d. Record the mass of the PDB.

5. Clamp the test tube to a ring stand and put the test tube into the hot water bath. Make sure no water gets into the PDB. Heat the PDB with occasional gentle jiggling of the test tube until it has all melted. Without undoing the clamp from the test tube, remove the test tube from the hot water bath and dry off the outside. Work quickly from this point as the PDB will begin to resolidify fast.

6. Gently insert the temperature probe into the melted PDB. **CAUTION:** To keep from damaging the temperature probe wire, hang it over another utility clamp pointing away from the hot plate, as shown in Figure 1.

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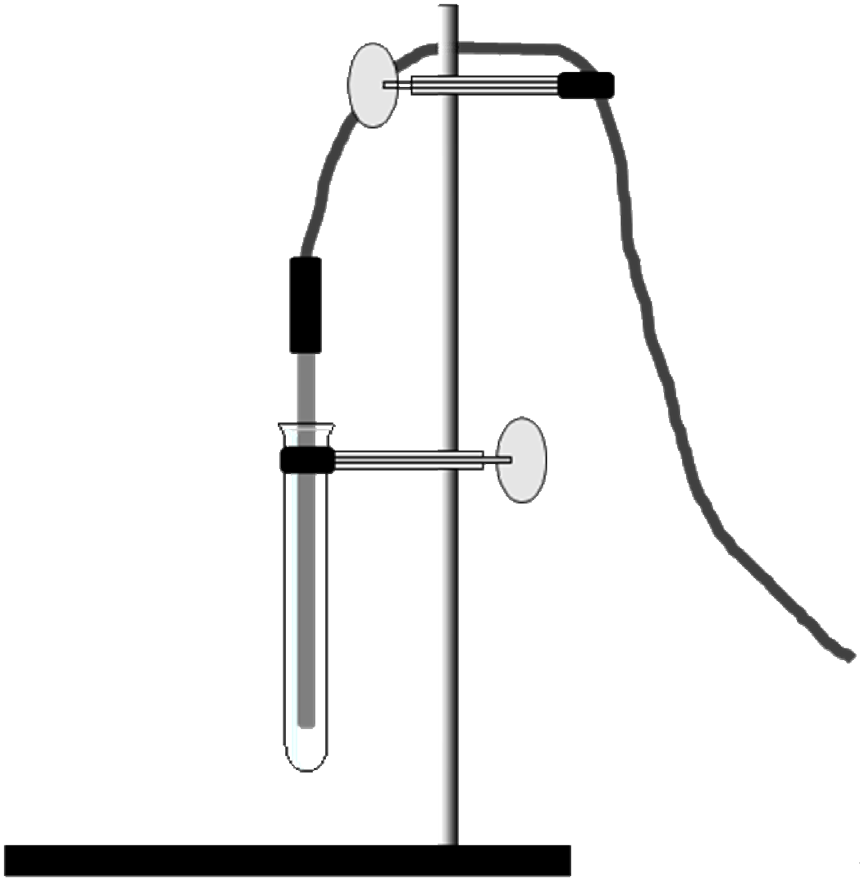
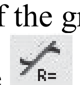


Figure 1

7. Begin the experiment by clicking the **COLLECT** button on the tool bar.

8. With a very slight up and down motion of the temperature probe, *continuously* stir the PDB in the test tube. Be careful not to poke the probe through the bottom of the test tube. Hold the top of the probe and not its wire. If the probe becomes stuck in the solid PDB, stop stirring.

9. After 10 minutes or when you reach a five-minute plateau, whichever comes **last**, click **STOP** on the toolbar.

10. Fit two straight lines to the graph. (The program is very similar to Graphical Analysis.) Using the mouse, highlight the part of the graph that represents the cooling of the liquid. Under Analyze, chose Linear Fit or click the  button on the toolbar. Then highlight the data that represents the freezing of the solid. Under Analyze, chose Linear Fit or click the  button. If

you are having trouble deciding what part of the graph to select, see the instructor. You may have to move the boxes with the slope and intercept information so they do not overlap.

11. Prepare to print the graph. Change the layout to landscape. Put your names in the name box and Pure PDB in the comments box. Print one copy of the graph for each group member and one for the instructor. Write the grams of PDB on the graph for the instructor.

12. Without pulling the temperature probe out of the PDB, place the test tube back in the hot water bath and heat until the contents melt. Using a weighing boat or weighing paper, weigh out 0.7 g of an unknown solid. Add all of it to the PDB in the test tube. There may be some flakes of unmelted solid near the top of the test tube; there is nothing you can do about this.

13. Once all the PDB has melted and the unknown has dissolved, remove the test tube from the water bath, dry it off and click COLLECT on the toolbar. You will be asked if you want to save the old data, as long as you have printed it, click NO.

14. Repeat steps 8 through 11 for this first solution. On the graph for the instructor, write the unknown number and the grams of unknown. Be sure to print your graph before you proceed further.

15. Add 0.7 g more of the unknown to your solution as you did in step 12. (You will now have a total of near 1.4 g of solute in the solution.).

16. Repeat steps 13 through 14 for this second solution. On the graph for the instructor, write the grams of unknown that you added in step 15.

17. Remelt and discard the PDB and unknown solution in the appropriate place in the hood. Do NOT pour it down the drain. Clean your test tube with acetone; this waste must be discarded in the Organic Waste container.

NAME ________________________________

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DATA

Name(s) of Partner(s) ____

Unknown Number ____________________________

Mass of paradichlorobenzene (PDB) ____________________________

Mass of sample I (unknown) ____________________________

Mass of sample II (unknown) ____________________________

Instructor's Initials __________

CALCULATIONS

Attach your 3 graphs to the back of the lab report. Use equation 7 to determine the freezing points and equation 8 to determine the molecular weight. K_f for PDB is 7.10°C/m Show all calculations on separate sheets. Temperatures from the computer are good to 0.1°C.

	Trial 1	**Trial 2**
Mass of unknown sample	________________ (Mass of sample I)	________________ (Mass of sample I + Mass of sample II)
Freezing point of PDB from graph	________________	
Freezing point of solution from graph	________________	________________
ΔT	________________	________________
Molecular Weight	________________	________________
Average Molecular Weight	________________	

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PRESTUDY

1. A student determines the freezing point of a solution of 0.157 g of an unknown sample in 10.24 g of benzene. The student obtains the following time and temperature data.

Time (min)	Temperature (°C)
0.0	10.53
0.5	10.04
1.0	9.50
1.5	8.76
2.0	8.18
2.5	7.54
3.0	7.04
3.5	6.57
4.0	6.05
4.5	5.34
5.0	5.02
5.5	5.00
6.0	4.96
6.5	4.94
7.0	4.91
7.5	4.88
8.0	4.85
8.5	4.82

a. (5) Using the data from the left, plot Temperature vs. Time on a graph. You may either use good graph paper and interpolate for the freezing point or make the graph on the computer using Excel or Graphical Analysis and use equation 7 to calculate the freezing point. Determine the freezing point of the solution to the nearest 0.01°C. Include your graph and any calculations with the prestudy. Cooling runs from 0 to 4.5 minutes. Freezing runs from 5 to 8.5 minutes.

Freezing point of solution _______________ °C

b. (5) Assuming that K_f for benzene is 5.12°C/m and its freezing point ($T_f°$) is 5.48°C, calculate the molecular weight of the unknown solute using equation 8. The grams of solute and solvent are given above.

Molecular weight __________________ g/mol