Colligative Properties of Solutions

Introduction:

Consider a hypothetical cooling curve which describes the changes in phase of a pure substance in which heat is lost at a steady rate at constant pressure (see figure 1).

Note that the gas, liquid, and solid have different heat capacities and cool at different rates. This is responsible for the different negative slopes for cooling of each phase in the above curve. Kinetic energy is the energy of motion and is directly proportional to the absolute temperature. At high temperatures, a stable compound will have enough kinetic energy to exist as independent molecules in the gaseous state. As heat is lost, the temperature and average kinetic energy of the gas decline. A point is reached at which intermolecular attractive forces become competitive with the kinetic energy and the molecules begin to associate in the liquid phase.

Here the molecules maintain continuous contact but still retain enough energy to migrate randomly throughout the system. As gas molecules continue to condense to liquid, potential energy is lost as heat and the temperature of the system remains the same until all of the gas has liquefied (this is the boiling temperature of the liquid). Now with only liquid present, the liquid cools and the temperature drops until the average kinetic energy becomes low enough for the intermolecular forces to lock the molecules in place within a solid crystal lattice; the molecules are no longer free to wander. As solidification (freezing) continues, the temperature of the system remains constant as potential energy converts to heat and is released (this the freezing or melting temperature of the liquid). When conversion to solid is complete, the temperature of the system then declines as the solid itself cools. The molecules within the lattice vibrate in place, and as the temperature falls a minimum in vibrational energy is approached (absolute temperature, 0 K, or -273°C).
The Freezing Point of Pure Liquid:

This experiment will focus on the region in which the cooling liquid approaches and achieves the freezing point (The boxed area on cooling curve in figure 1 is seen close up in figure 2).

At the freezing point both liquid and solid are present. If the system becomes thermally insulated from its surroundings, that is, heat can neither enter or leave the system, a state of equilibrium will be established. Here the number of molecules moving from solid to liquid is the same as the number of molecules moving from liquid to solid. This means that the relative quantities of solid and liquid present will remain constant.

The Freezing Point of a Solution:

Now consider the effect of a nonvolatile solute upon a freezing solution. Any added solute would dissolve in the liquid phase and be excluded from the solid crystal lattice. This means that, in effect, the concentration of liquid solvent molecules has been diminished and the rate of liquid solvent molecules moving to solid will decrease. On the other hand, the molecules of solid solvent (which remains pure), continue to move from solid to liquid at the same rate. If the temperature is held at the normal freezing point of the pure solvent, the system is thrown out of equilibrium and liquid phase is formed at the expense of solid phase, to a point where only liquid solution is present. In order to reestablish freezing, the temperature of the system needs to be lowered. This causes heat to be removed from the system and restores an equilibrium in which solid is present. The solution, therefore, has a lower freezing temperature than the pure solvent and the freezing point is said to be depressed.

Now as a solution freezes, solvent molecules are removed from the liquid solution and deposited on the solid. This increases the concentration of solute in the liquid solution and the freezing point further declines. A solution therefore does not have a sharply defined freezing point (FP); usually the freezing point of a solution is taken as the temperature at which solid solvent crystals first begin to appear (See figure 3).
The FP depression is one of a set of physical properties of solutions (vapor pressure lowering, boiling point elevation, and osmotic pressure) known collectively as Colligative properties. These properties are affected by the relative quantity of solute particles to the relative quantity of solvent particles, regardless of the identity of the solute particles. The FP depression is described quantitatively by the following equation: $\Delta T = k_f \cdot m$. 

"$\Delta T$" is the number of Celsius degrees the freezing of the solution is depressed relative to the pure solvent. "$m$" is the molality of the solution, that is, the number of moles of solute per one kg of solvent; this relates the quantity of solute to the quantity of solvent. "$k_f$" is the molal freezing point depression constant and expresses the sensitivity of the solvent to having its FP depressed by an added solute. The units are °C/m, which may be viewed as the number of degrees the FP is depressed per one molal of solute concentration. Each solvent has its own unique value for $k_f$.

E.g., Calculate the FP of a solution containing 600. g of CHCl₃ and 42.0 g of eucalyptol, C₁₀H₁₈O, a fragrant substance found in the leaves of eucalyptus trees. The FP of pure CHCl₃ is -63.5 °C and its $k_f$ is 4.68 °C/m.

$$\text{moles } C_{10}H_{18}O = \frac{42.0 \text{g}}{154.252 \text{g}} = 0.272\text{mol}$$

$$\text{solution molality} = \frac{0.272\text{mol}}{0.600\text{kg}} = 0.453 \text{ mol/kg or 0.453 m}$$

$$\Delta T = k_f m = \frac{4.68 \text{ C}}{\text{m}} \times 0.453 \text{ m} = 2.12 \text{ °C}$$

$$\text{FP solution} = -63.5 \text{ °C} - 2.12 \text{ °C} = -65.6 \text{ °C}$$

If a solute is a molecular nonelectrolyte, the solute's molality is a straightforward expression of the concentration of molecules in solution, that is, the solution's molality. If, however, the solute is a strong electrolyte, the effective molality is a whole number multiple (called the van't Hoff i factor) of the solute molality.

Consider a CaCl₂ solution. CaCl₂ is ionic, and each mole of CaCl₂ that dissolves delivers three moles of ions to the solution, which is indicated by the factor "i":

$$\text{CaCl}_2 \text{ (s) ssd } \text{Ca}^{2+} \text{ (aq) + 2 Cl}^- \text{ (aq)} \quad i = 3$$

The effective molality of the above solution is "im" or 3m and the FP depression equation becomes:

$$\Delta T = k_f \cdot i \cdot m \text{ or } \Delta T = k_f \cdot 3 \cdot m$$

All of the examples in the experimental section to follow will be assumed to remain molecular in solution and carry an "i" factor of one.
Colligative Properties of Solutions

EXPERIMENTAL DISCUSSION Experimental Goals:

The experiment to be performed is divided into three sections:

(a) In part A, the FP of the pure solvent, cyclohexane, is determined.

(b) Section B determines the value of the molal freezing point depression constant, $k_f$, of cyclohexane by measuring the freezing point depression (relative to the FP of pure cyclohexane determined in part A) of a solution with a known molality of solute.

(c) In part C the molality of cyclohexane solution with an unknown solute is found. This makes possible the calculation of the molar mass of the unknown.

However, prior to beginning the experiment the temperature probe and CBL must be set up properly.

Setting up the temperature probe and CBL.

See CBL Instructions on my website.

- Set ymin = -5
- Set ymax = 25
- Set yscale = 1  **Do not begin data collection until directed to do so.**

A. FP Determination of Pure Solvent, cyclohexane: In this section, a known mass of cyclohexane will be cooled and its temperature will be measured as it changes with time. This data will be plotted yielding a graph similar to figure 2. Ideally the plot would show the steady cooling of the liquid, leading to a constant temperature plateau (the FP or MP) where both the liquid and solid phases are present (refer again to the boxed area in the cooling curve in figure 1). The transition from the cooling liquid to the freezing plateau is often marked by irregularities and temperatures that are temporarily below the actual freezing temperature. This delay is largely due to the statistical difficulty in achieving the first microscopic seed crystal from the highly random liquid molecules. Once this tiny cluster forms, individual molecules may easily add to the crystal, subsequent crystallization is rapid, and the normal freezing temperature is established.

Laboratory Procedure for Part A:

1) Weigh a clean dry test tube by placing it in a 125 mL Erlenmeyer flask. Measure out about 15 mL of dry cyclohexane into large test tube. Weigh the test tube and cyclohexane. Record the data in part B.

2) The temperature probe should be placed in the test tube so that the end is at the midpoint of the cyclohexane and centered away from the walls of the test tube.

3) Clamp the test tube to a ring stand in an upright manner.

4) Check the connections between the probe, the CBL system, and the calculator. Make sure the CBL and calculator are turned on.
5) Make an ice bath by placing ice in a beaker and covering it with salt. Add water to cover the ice.

6) Trigger the CBL and collect 2 or 3 data points at room temperature. Then put the test tube into the ice bath. Stir continuously until the cyclohexane becomes slushy or until you can no longer move the stirring rod. When collecting temperature and time data, the TI-83 calculator will automatically shut off after about 5 minutes. This is not a problem unless the CBL unit finishes collecting data while the calculator is still off (“DONE” appears on the CBL screen); if this happens, you will lose your data and have to start over. You can avoid this by watching the calculator screen and promptly turning it back on when you notice it is blank. So if the TI-83 screen goes blank, quickly press ON to turn the calculator back on.

8) When the CBL unit finishes collecting data raise the test tube assembly out of the ice bath.

9) After the cyclohexane has melted, remove the temperature probe from the test tube and set aside to dry. Cover the large test tube containing the cyclohexane and save for later use.

10) Record the temperature of the ice bath. The temperature of the bath should be below the lowest temperature recorded in your freezing point data.

Data Workup for Part A:

1. Press ENTER to display a graph of temperature vs. time. Use ▶ to examine the data points along the curve. As you move the cursor right or left, the time (X) and temperature (Y) values of each data point are displayed below the graph. Based on your data, what was the freezing temperature of pure cyclohexane (to the nearest 0.1 °C)? Show this to your instructor.

2) Copy the data in L2 from the calculator memory into the data table below.

3) For the lab write-up you will need to prepare a cooling curve by plotting temperature along the y-axis versus time in seconds along the x-axis using a spreadsheet. Turn off the line in the spreadsheet so the graph shows only the data point themselves. In order to maximize precision, expand the scale along each axis as much as possible so the data plots allow the reading of the temperature on the graph to ±0.1 °C. Along both the cooling-liquid portion of the data and along the freezing portion, draw for each the best straight line possible (use a straight edge) that gives a weighted average of all the data points (see figure 2). Note that no one data point is required to fall on this line; in fact, it is possible that none of these points may fall on this line. The intersection of these two lines in the region of supercooling yields the best estimate of the freezing temperature of the liquid. Record this temperature on the data sheet below (with greatest possible precision) as the observed freezing point of pure cyclohexane.
Data Table for Part A:

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Observed FP of pure cyclohexane:__________

Ice Bath Temperature:__________
B. Determination of $k_f$ of cyclohexane: In this procedure, the molal freezing point depression constant, $k_f$, of cyclohexane will be determined experimentally. The freezing temperature will be found for a solution using a known mass of cyclohexane as the solvent and a measured mass of naphthalene as the solute. The freezing point depression, $\Delta T$, of the solution is found by calculating the difference between the freezing temperature of the solution and the freezing temperature of the pure solvent found in part A. After the molality of the solution, $m$, is computed from the known masses of solute and solvent, the $k_f$ may be calculated: $k_f = \Delta T / m$

Laboratory Procedure for Part B:

1) Place the test tube and cyclohexane from part A into a 250 mL Erlenmeyer flask. Carefully, add about 0.6 g of naphthalene to the test tube, and record the mass of the naphthalene, cyclohexane and glassware to the nearest 0.001 g.

2) Repeat steps 2 - 10 in part A.

3) After the cyclohexane has melted, remove the stopper, stirrer, and temperature probe assembly. Discard the cyclohexane/naphthalene mixture into the proper waste container. Rinse the stopper assembly with fresh cyclohexane being sure to collect the rinse and to discard it into the waste container. Dry for use in Part C.

Data Workup for Part B:

1. Press \text{ENTER} to display a graph of temperature vs. time. Use \text{ } \rightarrow to examine the data points along the curve. As you move the cursor right or left, the time (X) and temperature (Y) values of each data point are displayed below the graph. Based on your data, what was the freezing temperature of cyclohexane/naphthalene mixture (to the nearest 0.1°C)? Show this to your instructor.

2) Copy the data in L2 from the calculator memory into the data table below.

3) As in Part A, prepare a cooling curve by plotting temperature along the y-axis versus time in seconds along the x-axis using a spreadsheet. Turn off the line in the spreadsheet so the graph shows only the data points themselves. Use a straight edge to draw a line through the data along both the cooling-liquid portion of the data and along the freezing portion. Remember that as the solution freezes, the liquid becomes ever more concentrated in solute, and the freezing temperature steadily decreases. The intersection of these two lines in the region of supercooling yields the best estimate of the freezing temperature of the mixture. Record this temperature on the data sheet (with greatest possible precision) as the observed freezing point of the solution.

Data Table for Part B:

\begin{align*}
\text{Mass of test-tube and flask:} & \quad \underline{\text{---------}} \\
\text{Mass of test-tube, flask, and cyclohexane:} & \quad \underline{\text{---------}} \\
\text{Calculated mass of cyclohexane:} & \quad \underline{\text{---------}} \\
\text{Mass of test-tube, flask, naphthalene and cyclohexane:} & \quad \underline{\text{---------}}
\end{align*}
Calculated mass of naphthalene:___________

Temperature/time data:

- 15 s________ 105 s________ 195 s________ 285 s________
- 30 s________ 120 s________ 210 s________ 300 s________
- 45 s________ 135 s________ 225 s________ 315 s________
- 60 s________ 150 s________ 240 s________ 330 s________
- 75 s________ 165 s________ 255 s________ 345 s________
- 90 s________ 180 s________ 270 s________ 360 s________

Observed FP of cyclohexane/naphthalene solution: ____________

Ice Bath Temperature:__________
C. Determination of the Molar Mass of the Unknown: In this section, a measured mass of an unknown solute will be added to a fresh sample of cyclohexane solvent, whose mass is also known. The freezing point depression, \( \Delta T \), of this solution will be determined. Since \( k_f \) has been found in part B, the molality of the solution containing the unknown, \( m \), may be calculated:

\[
m = \frac{\Delta T}{k_f}
\]

The molality, which is in units of moles solute per kg of solvent, may now be used to find the number of moles of unknown solute present, and, since the mass of the unknown was determined in the beginning, the molar mass may now be calculated. Watch your units. They insure a proper sequence of calculations.

Laboratory Procedure for Part C:

1) Obtain your unknown. Record this number on the data sheet.

2) Place the dry, large test tube into a 125 mL Erlenmeyer flask with the tube up-right. Weigh and record the combined mass of this setup to the nearest 0.001 g.

3) Carefully weigh out 0.7 g of your unknown into the test tube and re-weigh the entire apparatus to the nearest 0.001 g.

4) Measure out about 15 mL of fresh cyclohexane with a graduated cylinder and pour it carefully into the test tube with your unknown being sure to rinse down the inside wall of the tube with the cyclohexane.

5) Carefully adjust the probe so that the end is at the midpoint of the cyclohexane and centered away from the walls of the test tube.

6) Repeat steps 2 - 10 in part A.

7) When the CBL unit finishes collecting data raise the test tube assembly out of the ice bath.

8) After the cyclohexane has melted, remove the stopper, stirrer, and temperature probe assembly. Discard the cyclohexane/unknown mixture into the proper waste container. Rinse the stopper assembly with fresh cyclohexane being sure to collect the rinse and to discard it into the waste container. Return the equipment.

Data Workup for Part C:

1. Press \( \text{ENTER} \) to display a graph of temperature vs. time. Use \( \text{Arrow} \) to examine the data points along the curve. As you move the cursor right or left, the time (X) and temperature (Y) values of each data point are displayed below the graph. Based on your data, what was the freezing temperature of cyclohexane/unknown mixture (to the nearest 0.1°C)?

   Show this to your instructor.

2) Copy the data in L2 from the calculator memory onto your lab.

3) As in Part A, prepare a cooling curve by plotting temperature along the y-axis versus time in seconds along the x-axis using a spreadsheet. Turn off the line in the spreadsheet so the graph shows only the data point themselves. Use a straight edge to draw a line through the data along both the cooling-liquid portion of the data and along the freezing portion. Remember that as the solution freezes, the liquid becomes ever more concentrated in solute, and the freezing temperature steadily decreases. The intersection of these two lines in the region of supercooling yields the best estimate of the freezing temperature of the mixture. Record this temperature on the data sheet (with greatest possible precision) as the observed freezing point of the cyclohexane/unknown solution.
Data Table for Part C:

Mass of test-tube and flask: __________

Mass of test-tube, flask, and unknown: __________

Calculated mass of unknown: __________

Mass of test-tube, flask, unknown and cyclohexane: __________

Calculated mass of cyclohexane: __________

Temperature/time data:

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Observed FP of cyclohexane/unknown solution: __________

Ice Bath Temperature: __________

CALCULATIONS/QUESTIONS:

Enter your Time/Temp data in an Excel spreadsheet. Generate 3 graphs. One for the MP of the pure solvent, one for the MP of the Cyclohexane/Naphthalene solution and one for the Cyclohexane/Unknown solution. Attach these three graphs to your lab report.

1. a) From the freezing points of pure cyclohexane and the cyclohexane/naphthalene solution, calculate the freezing point depression, $\Delta T$, of the cyclohexane/naphthalene solution.

b) For the cyclohexane/naphthalene solution in part B, calculate the number of moles of naphthalene added (naphthalene, C$_{10}$H$_{8}$). Then calculate the molality of the solution.
c) From the molality of the cyclohexane/naphthalene solution just calculated, and the freezing point
depression, $\Delta T$, of the cyclohexane/naphthalene solution, calculate the value of the molal freezing
point depression constant, $k_f$, for cyclohexane.

2. a) From the freezing points of pure cyclohexane and the cyclohexane/unknown solution, calculate the
freezing point depression, $\Delta T$, of the cyclohexane/unknown solution.

b) From the $k_f$ of cyclohexane calculated above and the freezing point depression, $\Delta T$, of the
cyclohexane/unknown solution in 2a, calculate the molality, $m$, of the cyclohexane/unknown solution.

c) For part C, having measured the mass of the unknown acid solute and the mass of the cyclohexane
solvent, and having just found the molality of the cyclohexane/unknown solution, calculate the
apparent molar mass of the unknown.