Colligative Properties Set II

1. (85B) The formula and the molecular weight of an unknown hydrocarbon compound are to be determined by elemental analysis and the freezing-point depression method.

(a) The hydrocarbon is found to contain 93.46 percent carbon and 6.54 percent hydrogen. Calculate the empirical formula of the unknown hydrocarbon.

(b) A solution is prepared by dissolving 2.53 grams of p-dichlorobenzene (molecular weight 147.0) in 25.86 grams of naphthalene (molecular weight 128.2). Calculate the molality of the p-dichlorobenzene solution.

(c) The freezing point of pure naphthalene is determined to be 80.2°C. The solution prepared in (b) is found to have an initial freezing point of 75.7°C. Calculate the molal freezing-point depression constant of naphthalene.

(d) A solution of 2.42 grams of the unknown hydrocarbon dissolved in 26.7 grams of naphthalene is found to freeze initially at 76.2°C. Calculate the apparent molecular weight of the unknown hydrocarbon on the basis of the freezing-point depression experiment above.

(e) What is the molecular formula of the unknown hydrocarbon?

2. (93A) Elemental analysis of an unknown pure substance indicated that the percent composition by mass is as follows.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percent by Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>49.02%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.743%</td>
</tr>
<tr>
<td>Chlorine</td>
<td>48.23%</td>
</tr>
</tbody>
</table>

A solution that is prepared by dissolving 3.150 grams of the substance in 25.00 grams of benzene, C₆H₆, has a freezing point of 1.12°C. (The normal freezing point of benzene is 5.50°C and the molal freezing-point depression constant, Kₓ, for benzene is 5.12°C/molal.)

(a) Determine the empirical formula of the unknown substance.

(b) Using the data gathered from the freezing-point depression method, calculate the molar mass of the unknown substance.

(c) Calculate the mole fraction of benzene in the solution described above.

(d) The vapor pressure of pure benzene at 35°C is 150. millimeters of Hg. Calculate the vapor pressure of benzene over the solution described above at 35°C.

3. (95D)

![Phase Diagram](image)

The phase diagram for a pure substance is shown above. Use this diagram and your knowledge about changes of phase to answer the following questions.

(a) What does point V represent? What characteristics are specific to the system only at point V?

(b) What does each point on the curve between V and W represent?

(c) Describe the changes that the system undergoes as the temperature slowly increases from X to Y to Z at 1.0 atmosphere.

(d) In a solid-liquid mixture of this substance, will the solid float or sink? Explain.
4. The normal boiling and freezing points of argon are 87.3 K and 84.0 K, respectively. The triple point is at 82.7 K and 0.68 atmosphere.

(a) Use the data above to draw a phase diagram for argon. Label the axes and label the regions in which the solid, liquid and gas phases are stable. On the phase diagram, show the position of the normal boiling point.

(b) Describe any changes that can be observed in a sample of solid argon when the temperature is increased from 40 K to 160 K at a constant pressure of 0.50 atmosphere.

(c) Describe any changes that can be observed in a sample of liquid argon when the pressure is reduced from 10 atmospheres to 1 atmosphere at a constant temperature of 100 K, which is well below the critical temperature.

(d) Does the liquid phase of argon have a density greater than, equal to, or less than the density of the solid phase? Explain your answer, using information given in the introduction to this question.

5. The molar mass of an unknown solid, which is nonvolatile and a nonelectrolyte, is to be determined by the freezing-point depression method. The pure solvent used in the experiment freezes at 10°C and has a known molal freezing-point depression constant, \( K_f \). Assume that the following materials are also available.

- test tubes
- thermometer
- stirrer
- pipet
- stopwatch
- balance
- beaker
- hot-water bath
- graph paper
- ice

(a) Using the two sets of axes provided below, sketch cooling curves for (i) the pure solvent and for (ii) the solution as each is cooled from 20°C to 0.0°C

(b) Information from these graphs may be used to determine the molar mass of the unknown solid.

(i) Describe the measurements that must be made to determine the molar mass of the unknown solid by this method.

(ii) Show the setup(s) for the calculation(s) that must be performed to determine the molar mass of the unknown solid from the experimental data.

(iii) Explain how the difference(s) between the two graphs in part (a) can be used to obtain information needed to calculate the molar mass of the unknown solid.

(c) Suppose that during the experiment a significant but unknown amount of solvent evaporates from the test tube. What effect would this have on (he calculated value of the molar mass of the solid (i.e., too large, too small, or no effect)? Justify your answer.

(d) Show the setup for the calculation of the percentage error in a student’s result if the student obtains a value of 126 g mol\(^{-1}\) for the molar mass of the solid when the actual value is 120. g mol\(^{-1}\).
Answers:

1. (a) Assume 100 g sample of the hydrocarbon

\[
\begin{align*}
93.46 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} &= 7.782 \text{ mol C} \\
6.54 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} &= 6.49 \text{ mol H} \\
\frac{7.782 \text{ mol C}}{6.49 \text{ mol H}} &= 1.20 : \text{ C}_{1.20}\text{H}_{1.00} = \text{C}_6\text{H}_5
\end{align*}
\]

(b) \[ m = \frac{\text{mol solute}}{1.0 \text{ kg solvent}} = \frac{2.53 \text{ g} \times \frac{1 \text{ mol}}{147.0 \text{ g}}}{0.02586 \text{ kg}} = 0.666 \text{ molal} \]

(c) \( \Delta T_f = (80.2 - 75.7) \degree C = 4.5 \degree C \)

\[ k_f = \frac{\Delta T_f}{m} = \frac{4.5 \degree C}{0.666 \text{ molal}} = 6.8 \degree C/\text{molal} \]

(d) \[ \Delta T_f = (80.2 - 76.2) \degree C = 4.0 \degree C \]

\[ \frac{1}{4.0 \degree C} \times \frac{6.8 \degree C}{\text{kg solvent}} \times \frac{2.43 \text{ g solute}}{0.0267 \text{ kg solvent}} = 154 \text{ g/mol} \]

(e) \( \text{C}_6\text{H}_5 = 77 \)

# empirical units/mol = 154/77 = 2

molecular formula = \( (\text{C}_6\text{H}_5)_2 = \text{C}_{12}\text{H}_{10} \)

2. (a) moles / 100 g

\[
\begin{align*}
\text{C} & = 4.081 \\
\text{H} & = 2.722 \\
\text{Cl} & = 1.360 \\
\end{align*}
\]

mol ratio \( 3 \quad 2 \quad 1 \)

empirical formula: \( \text{C}_3\text{H}_2\text{Cl} \)

(b) \( \Delta T_f = (K_f)(m) \)

\[ 4.38 = (5.12 \degree \text{C/\text{molal}}) \times \frac{3.150 \text{ g/mol mass}}{0.02500 \text{ kg}} = 147 \text{ g/mol} \]

(c) mol fraction = mol benzene / total mol = \[ \frac{25.00}{3.150 + 25.00} = 0.938 \]

(d) vapor pressure = mol fraction \( \times P_o = (0.938)(150 \text{ mm}) = 141 \text{ mm Hg} \)

3. (a) Triple point. All three states of the substance coexist (equilibrium); the solid and the liquid have identical vapor pressures.

(b) Curve \( VW \) represents the equilibrium between the liquid and its vapor. Along this line the liquid will be boiling. The points represent the vapor pressure of the liquid as a function of temperature.

(c) At point \( X \) the substance is a solid, as its temperature increases (at constant pressure), at point \( Y \) the solid is in equilibrium with its vapor and will sublime. From point \( Y \) to \( Z \) it exist only as a vapor.

(d) Sink. A positive slope of the solid-liquid line indicates that the solid is denser than its liquid and, therefore, will sink.
4. (a) 
(b) The argon sublimes. 
(c) The argon vaporizes. 
(d) The liquid phase is less dense than the solid phase. Since the freezing point of argon is higher than the triple point temperature, the solid-liquid equilibrium line slopes to the right with increasing pressure. Thus, if a sample of liquid argon is compressed (pressure increased) at constant temperature, the liquid becomes a solid. Because increasing pressure favors the denser phase, solid argon must be the denser phase.

5. (a) 

<table>
<thead>
<tr>
<th>pure solvent</th>
<th>solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

(b) (i) mass of pure solvent; freezing point of pure solvent; mass of unknown solid solute added to pure solvent; freezing point of resulting solution 
(ii) determine the change in freezing point, $\Delta T$

$$\Delta T = K_f \cdot m$$

where $m = \frac{\text{mol solute}}{1 \text{ kg of solvent}}$ and moles solute = $\frac{\text{mass solute}}{\text{molar mass}}$ molar mass = $\frac{\text{mass of solute} \cdot K_f}{\text{kg solvent} \cdot \Delta T}$

(iii) the change in temperature is the difference in the flat portions of the graph.
(c) Too small. If solvent evaporates then its mass decreases and the recorded denominator in the equation in (b)(i) is larger than the expt. value and the resulting answer decreases.

(d) \[ \text{% error} = \frac{(126\text{g}\cdot\text{mol}^{-1} - 120\text{g}\cdot\text{mol}^{-1})}{120\text{g}\cdot\text{mol}^{-1}} \times 100\% \]