1) The following question concerns mixing of liquids.

   a) Consider mixing two liquids where mixing is exothermic ($\Delta H_{\text{soln}} < 0$). Would you expect a solution to form (yes/maybe/no)? Justify your answer.

   Yes. Mixing increases randomness, which favors solution formation. Since the mixing is exothermic, mixing lowers the energy, which also favors solution formation. Since both factors favor solution formation, I would expect a solution to form.

   b) Consider mixing two liquids where mixing is endothermic ($\Delta H_{\text{soln}} > 0$). Would you expect a solution to form (yes/maybe/no)? Justify your answer.

   Maybe. Mixing increases randomness, which favors solution formation. However, the mixing is endothermic, and so mixing raises the energy, which favors not forming a solution. Since one factor favors solution formation and one factor does not, a solution might form. Whether a solution forms depends on which of the two opposing factors is more important, and so will mainly depend on how large the value is for $\Delta H_{\text{soln}}$. The larger the value for $\Delta H_{\text{soln}}$ (the more endothermic the mixing process) the less likely a solution will form.

2) (13.12) Explain the variation in the solubility in water of the listed alcohols:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g/100 g H$_2$O) at T = 20. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>$\infty$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OH</td>
<td>$\infty$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$OH</td>
<td>$\infty$</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$CH$_2$OH</td>
<td>9.0</td>
</tr>
<tr>
<td>CH$_3$CH$_2$CH$_2$CH$_2$CH$_2$OH</td>
<td>2.7</td>
</tr>
</tbody>
</table>

$\infty$ means the alcohol and water are completely miscible

The longer the C–C chain, the more the molecule "looks like" a hydrocarbon and the less significant the –OH group becomes. Hence, as the C–C chain length increases, the molecule becomes less polar. Since “like dissolves like”, as the molecules become more nonpolar, the solubility in polar water decreases.

The –OH group of the alcohols can form strong hydrogen bonds with water molecules, but this property diminishes in importance as the chain length increases.
3) What does the statement \textit{like dissolves like} mean with respect to solution formation?

The statement \textit{"like dissolves like"} means that polar solutes tend to dissolve well in polar solvents, and that nonpolar solutes tend to dissolve well in nonpolar solvents. Polar solutes usually do not dissolve well in nonpolar solvents, and nonpolar solutes usually do not dissolve well in polar solvents.

4) (13.18) Calculate the molality of each of the following aqueous solutions.
   a) 2.55 M NaCl solution, density = \( \rho = 1.08 \) g/mL.
   b) 45.2 percent by mass KBr.

Recall that \( \text{molality} = \frac{\text{moles solute}}{\text{kg solvent}} \)

Assume 1000. mL of solution, Then the mass of solution is 1080. g, and the moles of NaCl is 2.55 moles.

a) \[
\text{mass of water} = 1080 \text{ g} - \left( 2.55 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol NaCl}} \right) = 0.931 \text{ kg}
\]

\[
\text{molality} = \frac{2.55 \text{ mol NaCl}}{0.931 \text{ kg H}_2\text{O}} = 2.74 \text{ mol/kg}
\]

b) 100 g of the solution contains 45.2 g KBr and 54.8 g H\(_2\)O.

\[
\text{mol of KBr} = 45.2 \text{ g KBr} \times \frac{1 \text{ mol KBr}}{119.0 \text{ g KBr}} = 0.380 \text{ mol KBr}
\]

\[
\text{mass of H}_2\text{O (in kg)} = 54.8 \text{ g H}_2\text{O} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0548 \text{ kg H}_2\text{O}
\]

\[
\text{molality} = \frac{0.380 \text{ mol KBr}}{0.0548 \text{ kg H}_2\text{O}} = 6.93 \text{ mol/kg}
\]

5) (13.24) The density of an aqueous solution containing 15.0 percent ethyl alcohol (CH\(_3\)CH\(_2\)OH) by mass is 0.984 g/mL.

a) Calculate the molality of this solution.

b) Calculate the molarity of the solution.

c) What volume of solution would contain 0.250 moles of ethyl alcohol?
Assume 100.0 g of solution.

a) The mass of ethanol in the solution is $0.150 \times 100.0 \text{ g} = 15.0 \text{ g}$.

The mass of the water is

$100.0 \text{ g} - 15.0 \text{ g} = 85.0 \text{ g} = 0.0850 \text{ kg}$.

The amount of ethanol in moles is:

$$15.0 \text{ g ethanol} \times \frac{1 \text{ mol ethanol}}{46.07 \text{ g ethanol}} = 0.3256 \text{ mol ethanol}$$

Note that we retain an extra digit until the end of the calculation, to avoid rounding error.

$$\text{molality} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{0.3256 \text{ mol ethanol}}{0.0850 \text{ kg H}_2\text{O}} = 3.83 \text{ mol/kg}$$

b) The volume of the solution is:

$$100.0 \text{ g} \times \frac{1 \text{ mL}}{0.984 \text{ g}} = 102 \text{ mL} = 0.102 \text{ L}$$

The amount of ethanol in moles is 0.3256 mole [part (a)].

$$\text{molarity} = \frac{\text{mol solute}}{\text{L soln}} = \frac{0.3256 \text{ mol ethanol}}{0.102 \text{ L soln}} = 3.19 \text{ mol/L}$$

c) solution volume $= 0.250 \text{ mol} \times \frac{1 \text{ L}}{3.19 \text{ mol}} = 0.0784 \text{ L}$ or 78.4 mL

6) An aqueous KNO$_3$ solution is made using 72.5 g of KNO$_3$ dissolved to a total solution volume of 2.00 L. Calculate the molarity, molality, and mass percent KNO$_3$ in the solution. Assume a density of 1.050 g/mL for the solution.

$$\text{M(KNO}_3\text{)} = 101.1 \text{ g/mol} \quad \text{M(H}_2\text{O) = 18.02 g/mol}$$

$$\text{g(KNO}_3\text{)} = 72.5 \text{ g} \quad \text{mol(KNO}_3\text{)} = \frac{72.5 \text{ g}}{1 \text{ mol}} = 0.7171 \text{ mol}$$

$$\text{g solution} = 2000 \text{ mL} \times \frac{1.05 \text{ g}}{1 \text{ mL}} = 2100. \text{ g}$$

Since $\text{g solution} = \text{g water} + \text{g KNO}_3$,

$\text{g water} = \text{g solution} - \text{g KNO}_3 = 2100. \text{ g} - 72.5 \text{ g} = 2027.5 \text{ g}$
So...

molarity (M) = \(0.7171\, \text{mol KNO}_3 = 0.359\, \text{mol/L}\)
\[\text{2.00 L soln}\]

molality (m) = \(0.7171\, \text{mol KNO}_3 = 0.354\, \text{mol/kg}\)
\[\text{2.0275 kg water}\]

mass percent KNO\(_3\) = \(72.5\, \text{g KNO}_3 \cdot 100\% = 3.45\%\) KNO\(_3\) by mass
\[\text{2100. g soln}\]

7) The Henry's law constant for methyl bromide (CH\(_3\)Br) in water is 0.159 mol/L·atm at \(T = 25.\, ^\circ\text{C}\). How many grams of methyl bromide will dissolve in 1.000 L of water at this temperature when the pressure of methyl bromide above the water is \(p = 320.\, \text{torr}\)?

Let MBr = methyl bromide

From Henry's law
\[[\text{MBr}] = k\, p_{\text{MBr}}\]

\(p_{\text{MBr}} = 320.\, \text{torr} \quad \frac{1\, \text{atm}}{760\, \text{torr}} = 0.421\, \text{atm}\)

\[[\text{MBr}] = (0.159\, \text{mol/L·atm}) (0.421\, \text{atm}) = 0.0669\, \text{mol/L}\]

So 1.000 L of water contains 0.0669 moles of methyl bromide. Since \(\text{MW} = 94.9\, \text{g/mol}\)

grams MBr = \((0.0669\, \text{mol}) (94.9\, \text{g/mol}) = 6.36\, \text{g}\)

8) A solution contains a mixture of pentane and hexane at room temperature. The solution has a vapor pressure of 258. torr. Pure pentane and hexane have vapor pressures of 425 torr and 151 torr, respectively, at room temperature. What is the mole fraction composition of the mixture? Assume ideal behavior.

Let P = pentane and H = hexane, and assume Raoult's law applies.

\(p_{\text{total}} = p_{\text{P}} + p_{\text{H}} = X_{\text{P}}\, p_{\text{P}}^\circ + X_{\text{H}}\, p_{\text{H}}^\circ\)

We have one equation and two unknowns. But \(X_{\text{P}} + X_{\text{H}} = 1\), so \(X_{\text{P}} = 1 - X_{\text{H}}\), so

\(p_{\text{total}} = (1 - X_{\text{H}})\, p_{\text{P}}^\circ + X_{\text{H}}\, p_{\text{H}}^\circ = p_{\text{P}}^\circ - X_{\text{H}}\, p_{\text{P}}^\circ + X_{\text{H}}\, p_{\text{H}}^\circ\)

\[= p_{\text{P}}^\circ + X_{\text{H}}\, (p_{\text{H}}^\circ - p_{\text{P}}^\circ)\]
Or, finally, \( X_H = \frac{(p_{\text{total}} - p^o)}{(p_{H^2O} - p^o)} = \frac{(258 - 425) \text{ torr}}{(151 - 425) \text{ torr}} = 0.609 \)

And so \( X_P = 1 - 0.609 = 0.391 \)

9) How many grams of glucose \((C_6H_{12}O_6)\) must be added to 552. g of water to give a solution with a vapor pressure 2.0 torr less than that of pure water at 20.0 °C? The vapor pressure of pure water at this temperature is \( p^o_{H2O} = 17.5 \) torr.

For vapor pressure lowering \( \Delta p = X_B p^o \)

So \( X_{\text{glu}} = \frac{\Delta p}{p^o} = \frac{2.0 \text{ torr}}{17.5 \text{ torr}} = 0.114 \)

And so \( X_{H2O} = 1.000 - 0.114 = 0.886 \)

The number of moles of \( H_2O \) (MW = 18.02 g/mol) is

\[ n(H_2O) = \frac{552. \text{ g}}{18.02 \text{ g/mol}} = 30.63 \text{ mol H}_2\text{O} \]

Since \( \frac{n(\text{glucose})}{n(H_2O)} = \frac{X_{\text{glu}}}{X_{H2O}} \)

\[ n(\text{glucose}) = n(H_2O) \cdot \frac{X_{\text{glu}}}{X_{H2O}} = (3.063 \text{ mol}) \cdot \frac{0.114}{0.886} = 0.394 \text{ mol glucose} \]

Since MW(glucose) = 180.2 g/mol

\[ g(\text{glucose}) = 0.394 \text{ mol} \cdot \frac{180.2 \text{ g}}{1 \text{ mol}} = 71.0 \text{ g glucose} \]

10) What is the osmotic pressure, in atmospheres, of a 1.57 M aqueous solution of urea \((\text{NH}_2)_2\text{CO}\) at \( T = 27. \) °C.

\[ \pi = MRT = (1.57 \text{ mol/L})(0.08206 \text{ L atm/mol K})(27. + 273.) \text{ K} = 38.7 \text{ atm} \]
11) (13.78) Arrange the following aqueous solutions in order of decreasing freezing point, and explain your reasoning: 0.50 m HCl, 0.50 m glucose, 0.50 m CH₃COOH.

The freezing point will be depressed most by the solution that contains the most solute particles. Classify each solute as a strong electrolyte, a weak electrolyte, or a nonelectrolyte. All three solutions have the same concentration, so comparing the solutions is straightforward. HCl is a strong electrolyte, so under ideal conditions it will completely dissociate into two particles per molecule. The concentration of particles will be 1.00 m. Acetic acid is a weak electrolyte, so it will only dissociate to a small extent. The concentration of particles will be greater than 0.50 m, but less than 1.00 m. Glucose is a nonelectrolyte, so glucose molecules remain as glucose molecules in solution. The concentration of particles will be 0.50 m. For these solutions, the order in which the freezing points become lower is:

\[
0.50 \text{ m glucose} > 0.50 \text{ m acetic acid} > 0.50 \text{ m HCl}
\]

The HCl solution will have the lowest freezing point (greatest freezing point depression).

12) (13.86) A quantity of 7.480 g of an organic compound is dissolved in water to make 300.0 mL of solution. The solution has an osmotic pressure of 1.43 atm at T = 27 °C. The analysis of this compound shows that it contains 41.8 percent C, 4.7 percent H, 37.3 percent O, and 16.3 percent N. Find the molecular formula for the compound.

Find the concentration of the solution, then work out the molar mass. The concentration is:

\[
\text{Molarity} = \frac{\pi}{RT} = \frac{1.43 \text{ atm}}{(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(300 \text{ K})} = 0.0581 \text{ mol/L}
\]

The solution volume is 0.3000 L so the number of moles of solute is:

\[
\frac{0.0581 \text{ mol}}{1 \text{ L}} \times 0.3000 \text{ L} = 0.0174 \text{ mol}
\]

The molar mass is then:

\[
\frac{7.480 \text{ g}}{0.0174 \text{ mol}} = 430 \text{ g/mol}
\]

The empirical formula can be found most easily by assuming a 100.0 g sample of the substance.
moles C = 41.8 g \frac{1 \text{ mol}}{12.01 \text{ g}} = 3.48 \text{ mol C} / 1.16 = 3.00

moles H = 4.7 g \frac{1 \text{ mol}}{1.008 \text{ g}} = 4.7 \text{ mol H} / 1.16 = 4.05

moles O = 37.3 g \frac{1 \text{ mol}}{16.00 \text{ g}} = 2.33 \text{ mol O} / 1.16 = 2.01

moles N = 16.3 g \frac{1 \text{ mol}}{14.01 \text{ g}} = 1.16 \text{ mol N} / 1.16 = 1.00

This gives the empirical formula, C$_3$H$_4$O$_2$N, which has a mass of 86.0 g per formula unit. The molar mass is five times this amount ($430 \div 86.0 = 5.0$), so the molecular formula is (C$_3$H$_4$O$_2$N)$_5$ or C$_{15}$H$_{20}$O$_{10}$N$_5$. 