

ALL work must be shown to receive full credit. **Due at the beginning of lecture on Friday, September 21, 2001.**

PS4.1. Calculate the vapor pressure for each of the following solutions at 25 °C;

a) 37.3 g sucrose, $C_{12}H_{22}O_{11}$, dissolved in 200 g of water.

$$P_{\text{solvent}} = \chi_{\text{solvent}} P^{\circ}_{\text{solvent}}$$

$$37.3 \text{ g } C_{12}H_{22}O_{11} \left(\frac{1 \text{ mol}}{342.0 \text{ g}} \right) = 0.109 \text{ mol}$$

$$200 \text{ g of water} \left(\frac{1 \text{ mol}}{18.0 \text{ g}} \right) = 11.1 \text{ mol}$$

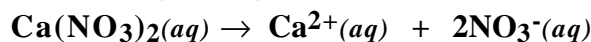
$$\chi_{H_2O} = \frac{11.1 \text{ mol}}{(11.1 \text{ mol} + 0.109 \text{ mol})} = 0.990$$

$$P_{\text{soln}} = 0.990 (23.76 \text{ mm}) = 23.5 \text{ mm of Hg}$$

b) 11.2 g of $Ca(NO_3)_2$ dissolved in 100 g of water.

$$11.2 \text{ g } Ca(NO_3)_2 \left(\frac{1 \text{ mol}}{164 \text{ g}} \right) = 0.0683 \text{ mol}$$

$$100 \text{ g of water} \left(\frac{1 \text{ mol}}{18 \text{ g}} \right) = 5.56 \text{ mol}$$



$$0.0683 \text{ mol } Ca(NO_3)_2 \left(\frac{3 \text{ mol particles}}{1 \text{ mol } Ca(NO_3)_2} \right) = 0.205 \text{ mol}$$

$$\chi_{H_2O} = \frac{5.56 \text{ mol}}{(5.56 \text{ mol} + 0.205 \text{ mol})}$$

$$\chi_{H_2O} = 0.965$$

$$P_{\text{soln}} = 0.965 (23.76 \text{ mm}) = 22.9 \text{ mm of Hg}$$

c) The vapor pressure of pentane and hexane at 25 °C are 511 mmHg and 150 mmHg respectively. Assuming ideal behavior determine the total vapor pressure above a solution prepared by mixing 25.0 mL of pentane (density = $0.63 \frac{\text{g}}{\text{mL}}$) with 45.0 mL hexane (density = $0.66 \frac{\text{g}}{\text{mL}}$).

$$25.0 \text{ mL pentane} \left(\frac{0.63 \text{ g}}{1 \text{ mL}} \right) = 15.8 \text{ g}$$

$$45.0 \text{ mL hexane} \left(\frac{0.66 \text{ g}}{1 \text{ mL}} \right) = 29.7 \text{ g}$$

$$15.8 \text{ g pentane} \left(\frac{1 \text{ mole}}{72.0 \text{ gm}} \right) = 0.219 \text{ mol}$$

$$29.7 \text{ g hexane} \left(\frac{1 \text{ mole}}{86.0 \text{ gm}} \right) = 0.345 \text{ mol}$$

PS4.1. (Continued)

$$\chi_{\text{hexane}} = \frac{0.345 \text{ mol}}{(0.345 \text{ mol} + 0.219 \text{ mol})}$$

$$\chi_{\text{hexane}} = 0.612 \qquad \chi_{\text{heptane}} = 0.388$$

$$P_{\text{soln}} = \chi_{\text{pentane}} P^{\circ}_{\text{pentane}} + \chi_{\text{hexane}} P^{\circ}_{\text{hexane}}$$

$$P_{\text{soln}} = 0.388 \cdot 511 \text{ mmHg} + 0.612 \cdot 150 \text{ mmHg} = 290 \text{ mmHg}$$

PS4.2. To what temperature ($^{\circ}\text{C}$) would a solution containing 28.5 g of urea, $(\text{NH}_2)_2\text{CO}$, in 400. g of water have to be heated to have a vapor pressure of 122 mmHg?

$$P_{\text{soln}} = \chi_{\text{solvent}} P^{\circ}_{\text{H}_2\text{O}}$$

$$28.5 \text{ g } (\text{NH}_2)_2\text{CO} \left(\frac{1 \text{ mol}}{60.0 \text{ g}} \right) = 0.475 \text{ mol}$$

$$400 \text{ gm H}_2\text{O} \left(\frac{1 \text{ mol}}{18.0 \text{ gm}} \right) = 22.2 \text{ mol H}_2\text{O}$$

$$\chi_{\text{solvent}} = \frac{22.2 \text{ mol}}{22.2 \text{ mol} + 0.475 \text{ mol}} = 0.979$$

$$122 \text{ mmHg} = 0.979 P^{\circ}_{\text{H}_2\text{O}}$$

$$124.6 \text{ mmHg} = P_{\text{H}_2\text{O}} \text{ the temperature which water has a vapor pressure of 123.8 mmHg is } 56 \text{ }^{\circ}\text{C}.$$

PS4.3. Determine the freezing point and the boiling point of the solution in PS4.2.

$$\text{molality} = \frac{0.475 \text{ mol } (\text{NH}_2)_2\text{CO}}{0.400 \text{ kg H}_2\text{O}} = 1.19 \text{ molal}$$

$$\Delta T_{\text{fp}} = mK_f = 1.19 \text{ molal} \left(1.86 \frac{^{\circ}\text{C}}{\text{m}} \right)$$

$$\Delta T_{\text{fp}} = 2.21 \text{ }^{\circ}\text{C}$$

$$T_{\text{fp}} = -2.21 \text{ }^{\circ}\text{C}$$

$$\Delta T_{\text{bp}} = mK_b = 1.19 \text{ molal} \left(0.512 \frac{^{\circ}\text{C}}{\text{molal}} \right)$$

$$\Delta T_{\text{bp}} = 0.608 \text{ }^{\circ}\text{C}$$

$$T_{\text{bp}} = 100.608 \text{ }^{\circ}\text{C}$$

PS4.4. What is the boiling point of an 8.7% (by mass) solution of benzoic acid ($\text{C}_6\text{H}_5\text{CO}_2\text{H}$) in benzene? Note: k_b for benzene is $2.53 \text{ }^{\circ}\text{C} \cdot \text{molal}^{-1}$. Assume 100 g of solution;

$$8.70 \text{ g C}_6\text{H}_5\text{CO}_2\text{H} \left(\frac{1 \text{ mol}}{122 \text{ g}} \right) = 0.0713 \text{ mol C}_6\text{H}_5\text{CO}_2\text{H}$$

$$\text{molality} = \frac{0.0713 \text{ mol C}_6\text{H}_5\text{CO}_2\text{H}}{0.0913 \text{ kg C}_6\text{H}_6} = 0.781 \text{ molal}$$

$$\Delta T_{\text{bp}} = mK_b = 0.781 \text{ molal} \left(2.53 \frac{^{\circ}\text{C}}{\text{molal}} \right)$$

$$\Delta T_{\text{bp}} = 1.98 \text{ }^{\circ}\text{C}$$

$$T_{\text{bp}} = 80.1 + 1.98 \text{ }^{\circ}\text{C} = 82.1 \text{ }^{\circ}\text{C}$$

PS4.5. Given the following data;

Compound	(Experimental) ΔT_f of 1 mol of cmpd in 1 kg of H_2O	(Ideal) ΔT_f of 1 mol of cmpd in 1 kg of H_2O	Strong Weak or Nonelectrolyte
$C_6H_{12}O_6$	1.85 °C	1.86 °C	Nonelectrolyte
$(NH_2)_2CO$	1.87 °C	1.86 °C	Nonelectrolyte
NH_3	1.96 °C		Weak electrolyte
CH_3CO_2H	1.97 °C		Weak electrolyte
NaI	3.44 °C	3.72 °C	Strong electrolyte
KBr	3.50 °C	3.72 °C	Strong electrolyte
H_2SO_4	3.73 °C	5.58 °C	Strong electrolyte
K_2SO_4	5.40 °C	5.58 °C	Strong electrolyte

- a) If each of the solutions is prepared by adding 1 mole of compound to 1 kg of water why does each have a different ΔT_f ?

The ΔT_f are different because substances behave differently when added to water. Most covalent substances ($C_6H_{12}O_6$ and $(NH_2)_2CO$) do not dissociate into ions when dissolved in water. Ionic substances (NaI, KBr, H_2SO_4 , K_2SO_4) dissociate into their constituent ions when dissolved in water. The freezing point depends on the number of particles in solution. Generally ionic compounds produce larger ΔT_f , compared to covalent compounds because of the higher number of particles in solution.

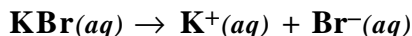
- b) Determine the ideal ΔT_f for the above compounds.
c)

$C_6H_{12}O_6$ and $(NH_2)_2CO$ do not dissociate when added to water. Therefore, the ideal ΔT_f is

$$\begin{aligned}\Delta T_f &= 1.00 \text{ molal} \left(1.86 \frac{^\circ\text{C}}{\text{molal}} \right) \\ &= 1.86^\circ\text{C}\end{aligned}$$

That ΔT_f for NH_3 and CH_3CO_2H is larger than 1.86°C suggests both of these compounds dissociate to a small extent when added to water. They are weak electrolytes. As weak electrolytes it is difficult to know what an 'ideal' freezing point might be.

NaI and KBr are ionic compounds and dissociate when added to water according to the following equations



For each of these substances 1 mole of the compound produces 2 moles of particles.

$$\begin{aligned}\Delta T_f &= 2.00 \text{ mol} \left(\frac{1.86^\circ\text{C}}{\text{molal}} \right) \\ &= 3.72^\circ\text{C}\end{aligned}$$

That both NaI and KBr have a smaller ΔT_f suggests that at the concentration of 1.00 molal some ionpairing is occurring to reduce the total number of particles in solution.

K_2SO_4 is an ionic compound and H_2SO_4 is a polar covalent compound. Both dissociate into ions when added to water according to the following equations



For each of these substances 1 mol dissolved in water produces 3 moles of particles.

$$\begin{aligned}\Delta T_f &= 3.00 \text{ molal} \left(1.86 \frac{^\circ\text{C}}{\text{m}} \right) \\ &= 5.58^\circ\text{C}\end{aligned}$$

- d) Why does the ideal ΔT_f differ from the experimental ΔT_f ?
e)

That each is less than the ideal suggests fewer particles are found experimentally in solution compared to the ideal number of particles. In the case of K_2SO_4 , ion pairing at this high of a concentration (1 molal) lowers the ΔT_f slightly. In the case of H_2SO_4 , the reaction written does not go to completion and fewer particles are produced. (We'll discuss H_2SO_4 in more detail later in the course.)

- d) Classify each compound as a strong, weak or nonelectrolyte.

Classifying strong, weak and nonelectrolyte is done by looking at the experimental i values for each of the compounds. For sucrose and urea $i_{\text{exp}} = 1$ so they must be nonelectrolytes. For ammonia and acetic acid $i_{\text{exp}} = 1.05$ so they have a few ions in solution so they are weak electrolytes. For the remaining compounds i_{exp} is greater than 1 or 2 by quite a bit, so these must all be strong electrolytes.

- PS4.6. Determine the ideal freezing point of a solution prepared by mixing 0.782 g of $MgSO_4$ in 650 g of water. The observed freezing point is -0.0284°C . Explain this difference.

$$\begin{aligned}0.782 \text{ g } MgSO_4 \left(\frac{1 \text{ mol}}{120 \text{ g}} \right) &= 0.00652 \text{ mol } MgSO_4 \\ \text{molality} &= \frac{0.00652 \text{ mol } MgSO_4}{0.650 \text{ kg } H_2O} = 0.0100 \text{ molal} \\ \Delta T_{fp} &= imK_f \\ &= (2)0.0100 \text{ molal} \left(1.86 \frac{^\circ\text{C}}{\text{molal}} \right) \\ \Delta T_{fp} &= 0.0372^\circ\text{C} \\ T_{fp} &= 0 - 0.0372^\circ\text{C} = -0.0372^\circ\text{C}\end{aligned}$$

The observed freezing point is higher suggesting that experimentally i is smaller than the ideal value of 2. This is likely when some ionpairing exists in the solution. So some of the ions are closely associated with each other.

PS4.7. A 2.26 g sample of glycerol dissolved in 20.0 g of water elevated the boiling point by 0.629 °C.

a) What is the molar mass of glycerol?

$$\Delta T_{bp} = imK_b \quad (i=1) \quad 0.629 \text{ } ^\circ\text{C} = m \left(0.512 \frac{^\circ\text{C}}{m} \right)$$

$$m = \frac{0.629 \text{ } ^\circ\text{C}}{0.512 \frac{^\circ\text{C}}{m}} = 1.25 \text{ molal}$$

$$\frac{1.25 \text{ mol glycerol}}{1 \text{ kg H}_2\text{O}} \times 0.020 \text{ kg} = 0.025 \text{ moles glycerol}$$

$$\frac{2.26 \text{ g glycerol}}{0.025 \text{ mol glycerol}} = 90.4 \frac{\text{g}}{\text{mol}}$$

b) Given the composition of glycerol is 39.1% C, 8.7% H, and 52.2% O, by mass, what is its molecular formula?

$$39.1 \text{ g C} \left(\frac{1 \text{ mol C}}{12.0 \text{ g C}} \right) = 3.26 \text{ mol C}$$

$$8.7 \text{ g H} \left(\frac{1 \text{ mol H}}{1.01 \text{ g H}} \right) = 8.62 \text{ mol H}$$

$$52.2 \text{ g O} \left(\frac{1 \text{ mol O}}{16.00 \text{ g}} \right) = 3.26 \text{ mol O}$$

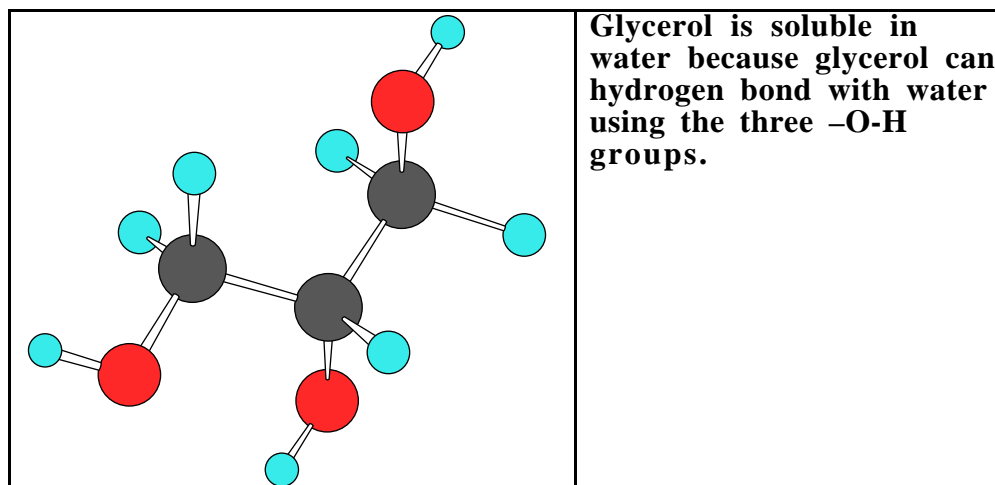
$$\left(\frac{3.26 \text{ mol C}}{3.26 \text{ mol O}} \right) : \left(\frac{8.62 \text{ mol H}}{3.26 \text{ mol O}} \right) : \left(\frac{3.26 \text{ mol O}}{3.26 \text{ mol O}} \right)$$

$$1.0 \text{ C} : 2.64 \text{ H} : 1 \text{ O}$$

$$3 \cdot (1.0 \text{ C} : 2.64 \text{ H} : 1 \text{ O}) = 3.0 \text{ C} : 7.92 \text{ H} : 3 \text{ O}$$



c) Glycerol is very soluble in water. Suggest a possible Lewis structure for the glycerol molecule.



PS4.8. When 2.60 g of sulfur is dissolved in 200. g of diethyl ether the boiling point of ether is elevated by 0.105 °C. Note: k_b for ether is 2.10 °C·molal⁻¹.

a) What is the molar mass of sulfur dissolved in ether?

$$\Delta T_{bp} = imK_b \quad (i=1) \quad 0.105 \text{ } ^\circ\text{C} = m \left(2.10 \frac{^\circ\text{C}}{\text{m}} \right)$$

$$m = \frac{0.105 \text{ } ^\circ\text{C}}{2.10 \frac{^\circ\text{C}}{\text{m}}} = 0.0500 \text{ molal}$$

$$\frac{0.0500 \text{ mol sulfur}}{1 \text{ kg CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3} \times 0.200 \text{ kg} = 0.0100 \text{ moles sulfur}$$

$$\frac{2.60 \text{ g sulfur}}{0.0100 \text{ mol sulfur}} = 260 \frac{\text{g}}{\text{mol}} \text{ sulfur}$$

$$260 \frac{\text{g}}{\text{mol}} \text{ sulfur} \left(\frac{1 \text{ mol S atoms}}{32 \text{ g}} \right) = 8.15 \text{ or } 8 \text{ atoms per molecule.}$$

b) What is the molecular structure of sulfur in ether?

S₈ it is an eight-membered ring. (See page 582 for the ring structure)

PS4.9. The freezing point depression of a 0.091 *m* solution of CsCl is 0.214 °C. The freezing point depression of a 0.091 *m* solution of CaCl₂ is 0.440 °C. In which solution does “ion-pairing” appear to be greater. Explain.

For CsCl:

$$\Delta T_{fp} = imK_f \quad 0.214 \text{ } ^\circ\text{C} = i(0.091 \text{ m}) \left(1.86 \frac{^\circ\text{C}}{\text{m}} \right)$$

$$i = \frac{0.214 \text{ } ^\circ\text{C}}{0.091 \text{ m} \cdot 1.86 \frac{^\circ\text{C}}{\text{m}}} = 1.27$$

	$\text{CsCl}(aq) \rightarrow \text{Cs}^+(aq) + \text{Cl}^-(aq)$		
initial	1	0	0
change	let x be the amount	of the ionizes	
	-x	+x	+x
final	1 - x	x	x

$$\text{Total \# particles} = 1.27 = 1 - x + x + x$$

$$x = 0.27$$

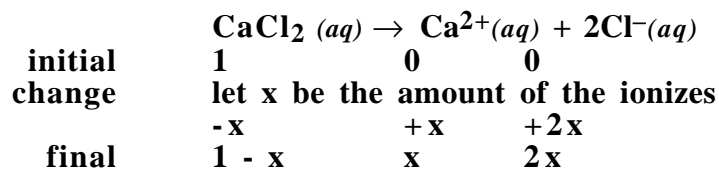
Only 27% of the particles completely ionize.

PS4.9. (Continued)

For CaCl_2 :

$$\Delta T_{\text{bp}} = imK_b \qquad 0.440 \text{ }^\circ\text{C} = 10.091 \text{ m} \left(1.86 \frac{^\circ\text{C}}{\text{m}} \right)$$

$$i = \frac{0.440 \text{ }^\circ\text{C}}{0.091 \text{ m} \cdot 1.86 \frac{^\circ\text{C}}{\text{m}}} = 2.60$$



$$\text{Total \# particles} = 2.60 = 1 - x + x + 2x$$

$$x = 0.80$$

80% of the particles ionize.