Solutions Colligative Properties DCI

Name \_\_\_\_\_ Section \_\_\_\_\_

1. Define the term *colligative property* and list those physical properties of a solution that can be classified as colligative properties.

Colligative properties are properties which depend on the number of molecules or ions of solute present, and not on what the particles are (as long as they are not volatile). Properties of solutions which are colligative properties,

- 1) Vapor Pressure lowering
- 2) Boiling Point elevation
- 3) Freezing Point depression
- 4) Osmotic Pressure
- 15. Illustrate and explain how the presence of a nonvolatile solute affects the vapor pressure of a liquid. See Appendix III for recommended demonstration, video, or computer resources.



Before addition of the solute

The vapor above a pure liquid is shown on the right. The equilibrium vapor pressure is a result of the presence of molecules in the vapor phase above the molecules in the liquid phase. The figure below shows the affect on the vapor pressure of the solution upon addition of a nonvolatile solute.



After addition of the solute

The addition of a nonvolatile solute decreases the vapor pressure due to the liquid in the vapor phase. This occurs because there is a decreased entropic drive for the vapor to form above the solution compared to the vapor forming above the pure liquid.



## **Figure I**

For vapor to form above the pure liquid the chemical equation is  $H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta S^{\circ}_{solvent}$ For vapor to form above the solution the chemical equation is  $H_2O_{(solution)} \rightarrow H_2O_{(g)} \qquad \Delta S^{\circ}_{solution}$ 

As shown in figure I because the  $S^{\circ}_{solution} > S^{\circ}_{solvent}$  then  $\Delta S^{\circ}_{solution} < \Delta S^{\circ}_{solvent}$  and there is a lower tendency for water (solvent) particles to escape into the vapor phase.

3a. How does the vapor pressure exerted by the solvent change as the concentration of solute increases?

## Looking at the data in Table I below it clear that as the mol fraction of solvent decreases the pressure exerted by the vapor above the solution also decreases.

Vapor Pressure (mm Hg)
23.600
21.240
18.880
16.520
14.160
11.800
9.440
7.080
4.720
2.360
0

Table I

## The addition of a nonvolatile solute decreases the vapor pressure of the solvent.

b. Write Raoult's law and define each term.

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

Where;

 $\mathbf{P}_{\text{solution}}$  is the vapor pressure of the solvent above the solution at the particular temperature

 $\chi_{solvent}$  is the mole fraction of the solvent in the solution

**P°**<sub>solvent</sub> is the vapor pressure of the pure solvent at the particular temperature.

Mole Fraction (solvent)	Vapor Pressure (mm Hg)	Mol fraction * Vapor Pressure
1.0	23.600	1.0*23.6 = 23.6
.9	21.240	0.9*23.6 = 21.24
.8	18.880	0.8*23.6 = 18.88
.7	16.520	0.7*23.6 = 16.52
.6	14.160	0.6*23.6 = 14.16
.5	11.800	0.5*23.6 = 11.80
.4	9.440	0.4*23.6 = 9.44
.3	7.080	0.3*23.6 = 7.080
.2	4.720	0.2*23.6 = 4.72
.1	2.360	0.1*23.6 = 2.36
0	0	0.0*23.6 = 0

c. Calculate the expected vapor pressure at 25 °C for a solution prepared by dissolving 97.4 g of common table sugar (sucrose, MM =  $342 \frac{g}{mol}$ ) in 453 mL of water. We will use Raoult's law in the form  $P_{soln} = \chi_{H_2O}P^{\circ}H_2O$ We need to determine the mol fraction of water  $97.4 g \left(\frac{1 \text{ mol}}{342 \text{ g}}\right) = 0.285 \text{ mol sucrose}$   $453 \text{ mL}\left(\frac{1.00 \text{ g}}{1 \text{ mL}}\right)\left(\frac{1 \text{ mol}}{18 \text{ g}}\right) = 25.2 \text{ mol } H_2O$   $\chi_{H_2O} = \frac{25.2 \text{ mol}}{(25.2 \text{ mol} + 0.285 \text{ mol})}$   $\chi_{H_2O} = .989$ The vapor pressure of water at 25 °C is 23.76 mm Hg (Appendix C in Brown & LeMay).  $P_{soln} = .989 (23.76 \text{ mm}) = 23.5 \text{ mm of Hg}$ 

d. A solution was prepared by adding 20.0 g of urea to 125 g of water at 25 °C, a temperature at which pure water has a vapor pressure of 23.76 mm of Hg. The observed vapor pressure of the solution was found to be 22.67 mm of Hg. Calculate the molecular weight of urea.

$$\chi_{H_2O} = \frac{P_{soln}}{P_{\infty}_{H_2O}}$$

$$\chi_{H_2O} = \frac{22.67 \text{ mm}}{23.76 \text{ mm}}$$

$$\chi_{H_2O} = .9541$$

$$\chi_{H_2O} = \frac{\text{mol } H_2O}{(\text{mole } H_2O + \text{mol } \text{urea})}$$
mole  $H_2O = 125 \text{ g}\left(\frac{1 \text{ mol}}{18.0 \text{ g}}\right) = 6.94 \text{ mol}$ 

$$\chi_{H_2O} = \frac{6.94 \text{ mol } H_2O}{(6.94 \text{ mole } H_2O + \text{mol } \text{urea})} = 0.954$$
let x = moles of urea
$$0.954(6.94 \text{ mole } H_2O + x) = 6.94 \text{ mol } H_2O$$

$$6.62 \text{ mole } H_2O + 0.954x = 6.94 \text{ mol } H_2O$$

$$0.954x = 6.94 \text{ mol } H_2O - 6.62 \text{ mole } H_2O$$

$$0.954x = 0.32 \text{ mol}$$

$$x = \frac{0.32 \text{ mol}}{0.954} = 0.34 \text{ mol}$$

$$\frac{20.0 \text{ g}}{.34 \text{ mol}} = 59 \frac{\text{g}}{\text{mol}}$$

e. Show the derivation of a mathematical relationship for the vapor pressure lowering  $(P^{\circ}_{solvent} - P_{solution})$  of a liquid following the addition of a nonvolatile solute.  $P_{solution} = \chi_{solvent} P^{\circ}_{solvent}$ let  $\chi_{solvent} = 1 - \chi_{solute}$ Substituting for  $\chi_{solvent}$  $P_{solution} = (1 - \chi_{solute}) P^{\circ}_{solvent}$  $P_{solution} = P^{\circ}_{solvent} - \chi_{solute} P^{\circ}_{solvent}$  $\chi_{solute} P^{\circ}_{solvent} = P^{\circ}_{solvent} - P_{solution} = vapor pressure lowering$ 

4. Explain how the addition of a nonvolatile solute affects the freezing point and boiling point of water.

## **Boiling Point:**

The boiling point is defined in the chemical equation for the pure solvent, water

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$

So when the solvent is water, we already know the boiling point, it is 100 °C. At the boiling point of

the pure solvent  $\Delta G = 0$  in  $\Delta G = \Delta H - T\Delta S$ , so  $T_{bp} = \frac{\Delta H^{\circ}}{\Delta S^{\circ} \text{ solvent}}$  where  $\Delta S^{\circ}$  is for the first

chemical equation.

The boiling point is defined in the chemical equation for the solution, (note that it is only water that vaporizes from the solution. The solute is defined as nonvolatile.)

$$H_2O_{(solution)} \rightarrow H_2O_{(g)}$$

The question is when a nonvolatile solute is added does the boiling point increase, decrease or remain the same? To answer this question we consider the following;

For the solution the boiling point is defined the same way, except the  $\Delta S^{\circ}$  is the  $\Delta S^{\circ}$  for the second equation above

 $T_{bp} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}_{solution}}$ 

Since  $\Delta S^{\circ}_{solution} < \Delta S^{\circ}_{solvent}$  (see Figure I) and we are assuming that  $\Delta H^{\circ}$  is the same in both relationships, the  $T_{bp}$  of the solution will be greater compared to the  $T_{bp}$  of the pure solvent. So the addition of a nonvolatile solute will increase the boiling point of the solution.

**Freezing Point:** 

The freezing point is defined in the chemical equation for the pure solvent, water

$$H_2O_{(l)} \rightarrow H_2O_{(s)}$$

So when the solvent is water, we already know the freezing point, it is 0 °C. At the freezing point of

the pure solvent  $\Delta G = 0$  in  $\Delta G = \Delta H - T\Delta S$ , so  $T_{fp} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}_{solvent}}$  where  $\Delta S^{\circ}$  is for the first

chemical equation.

The freezing point is defined in the chemical equation for the solution, (note that it is only water that freezes from the solution. The solute is defined as nonvolatile.)

$$H_2O_{(solution)} \rightarrow H_2O_{(s)}$$

The question is when a nonvolatile solute is added does the freezing point increase, decrease or remain the same? To answer this question we consider the following;



For the solution the freezing point is defined the same way, except the  $\Delta S^{\circ}$  is the  $\Delta S^{\circ}$  for the second equation above

 $T_{bp} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}_{solution}}$ 

Since  $\Delta S^{\circ}_{solution} > \Delta S^{\circ}_{solvent}$  and we are assuming that  $\Delta H^{\circ}$  is the same in both relationships, the  $T_{fp}$  of the solution will be smaller compared to the  $T_{fp}$  of the pure solvent. So the addition of a nonvolatile solute will decrease the freezing point of the solution.

The addition of a nonvolatile solute increases the boiling point of the solution and decreases the freezing point of the solution.

5. Write the general mathematical relation which describes the dependence of the freezing point or boiling point on the concentration of solution.

 $\Delta \mathbf{T}_{\mathbf{f}} = \mathbf{k}_{\mathbf{f}} \mathbf{m}$  or  $\Delta \mathbf{T}_{\mathbf{b}} = \mathbf{k}_{\mathbf{b}} \mathbf{m}$ 

where:

 $\Delta T_f$  or  $\Delta T_b$  is the change in freezing point or the change in boiling point. k<sub>f</sub> or k<sub>b</sub> are the freezing point and boiling point constants

m is the molality of the particles in the solution  $\left(\frac{\text{mol solute}}{\text{kg solvent}}\right)$ 

b. Calculate the freezing point and boiling point of a solution prepared by mixing 6.00 g of  $C_6H_{12}O_6$  with 35.0 g of  $H_2O$ .

6.00 g C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> 
$$\left(\frac{1 \text{ mol}}{180 \text{ g}}\right) = 0.0333 \text{ mol } C_6H_{12}O_6$$

molality =  $\frac{\text{mol } C_6 H_{12} O_6}{\text{kg } \text{H}_2 \text{O}} = \frac{0.0333 \text{ mol } C_6 H_{12} O_6}{0.035 \text{ kg } \text{H}_2 \text{O}} = 0.952 \text{ molal}$ 

$$\Delta T_{\rm fp} = k_{\rm fm} = 1.86 \frac{{}^{\circ}{\rm C}}{\rm m} (0.952 \text{ m})$$

$$\begin{split} &\Delta T_{fp} = 1.77 \ ^{\circ}C \\ &\Delta T_{fp} = freezing \ point \ of \ water \ - \ freezing \ point \ of \ the \ solution \\ &1.77 \ ^{\circ}C = 0 \ ^{\circ}C \ - \ T_{f} \\ &T_{fp \ of \ the \ solution} = -1.77 \ ^{\circ}C \end{split}$$

$$\Delta T_{bp} = k_{b}m = 0.51 \frac{\text{°C}}{m} (0.952 \text{ m})$$

 $\begin{array}{l} \Delta T_{bp} = 0.486 \ ^{\circ}C \\ \Delta T_{bp} = boiling \ point \ of \ the \ solution - boiling \ point \ of \ water \\ 0.486 \ ^{\circ}C = T_{bp} - 100 \ ^{\circ}C \\ T_{bp} = 100.486 \ ^{\circ}C \end{array}$ 

c. A solution containing a nonelectrolyte dissolved in water has a boiling point of 100.305 °C. Calculate the freezing point of the same solution.

 $\Delta T_{bp} = k_b m$   $\Delta T_{bp} = 0.305 °C$   $m = \frac{\Delta T_{bp}}{k_b} = \frac{0.305 °C}{0.51 \frac{°C}{m}} = 0.598 \text{ molal}$   $\Delta T_{fp} = k_f m = 1.86 \frac{°C}{m} (0.587 m)$   $\Delta T_{fp} = 1.11 °C$  $T_{fp} = -1.11 °C$ 

d. What is the molecular mass of nicotine if 5.04 grams of this compound changes the freezing point of 90.0 g of water by 0.647 °C?

$$\Delta T_{fp} = k_f m$$

$$m = \frac{\Delta T_{fp}}{k_f} = \frac{0.647 \degree C}{1.86 \degree C} = 0.348 \text{ molal}$$

$$0.090 \text{ kg H}_2 O\left(\frac{0.348 \text{ mol nicotine}}{1 \text{ kg H}_2 O}\right) = 0.0313 \text{ mol nicotine}$$

$$molar \text{ mass} = \frac{5.04 \text{ g nicotine}}{0.0313 \text{ mol nicotine}} = 161 \frac{g}{\text{ mol}}$$

e. Calculate the freezing point and the boiling point of a saturated solution of  $Li_2CO_3$ . The solubility of lithium carbonate is 0.72 g per 100 g of water at 100 °C.

$$\frac{0.72 \text{ g Li}_2\text{CO}_3}{100 \text{ g H}_2\text{O}} \left(\frac{1 \text{ mol Li}_2\text{CO}_3}{73.9 \text{ g}}\right) \left(\frac{1000 \text{ g}}{1 \text{ kg}}\right) = 0.0974 \text{ molal Li}_2\text{CO}_3$$

$$\text{Li}_2\text{CO}_3(s) \longrightarrow \text{H}_2\text{O} \rightarrow 2\text{Li}^+(aq) + \text{CO}_3^{2-}(aq)$$

$$0.0974 \text{ molal Li}_2\text{CO}_3 \left(\frac{3 \text{ mol particles}}{1 \text{ mol Li}_2\text{CO}_3}\right) = 0.292 \text{ molal particles}$$

$$\Delta T_{\text{fp}} = \text{k}_{\text{f}}\text{m} = 1.86 \frac{^{\circ}\text{C}}{\text{m}} (0.292 \text{ m}) = 0.544 \ ^{\circ}\text{C}$$

$$T_{\text{fp}} = -0.544 \ ^{\circ}\text{C}$$

$$\Delta T_{\text{bp}} = \text{k}_{\text{f}}\text{m} = 0.51 \frac{^{\circ}\text{C}}{\text{m}} (0.292 \text{ m}) = 0.149 \ ^{\circ}\text{C}$$

$$T_{\text{bp}} = 100.149 \ ^{\circ}\text{C}$$

f. 2.57 g of an ionic compound with the formula KX are dissolved in 120 g of water. The freezing point of the solution was lowered by 1.37  $^{\circ}$ C. Determine the formula weight of X.

$$\Delta T_{f} = mK_{f}$$

$$1.37 \ ^{\circ}C = m\left(1.86\frac{^{\circ}C}{m}\right) \qquad \qquad m = \frac{1.37 \ ^{\circ}C}{1.86\frac{^{\circ}C}{m}} = 0.737 \text{ molal}$$

KX is an ionic compound and is soluble in water. Therefore it will dissociate, w added to water, according to the equation

 $KX(aq) \rightarrow K^+(aq) + X^-(aq)$ 

The equation suggests that 2 moles of particles are produced for every mol of KX.

In the equation

 $\Delta T_f = mK_f$ 

the molality is the molality of particles. To obtain the molality in terms of KX the following conversion is required.

$$0.737 \text{ molal particles} \left(\frac{1 \text{ mol KX}}{2 \text{ mol particles}}\right) = 0.368 \text{ molal KX}$$
$$\frac{0.368 \text{ mol KX}}{1 \text{ kg H}_2\text{O}} \times 0.120 \text{ kg} = 0.0442 \text{ moles KM}$$
$$\frac{2.57 \text{ g KX}}{0.0442 \text{ mol KX}} = 58.2 \frac{\text{g}}{\text{mol}}$$
$$58.2 \text{ g/mol}$$
$$-\frac{39.1 \text{ g/mol} (1 \text{ mol K})}{19 \text{ g/mol}} \text{ is the molar mass of X (F-)}$$

6a. Define the terms semipermeable membrane, osmosis and osmotic pressure.

A semipermeable membrane is a membrane which will allow certain molecules to pass from one side of the membrane to the other, but not all molecules.

Osmosis is the net movement of solvent molecules from a solution of high concentration to a solution of low concentration.

Osmotic pressure is the pressure which must be exerted on the surface of the more concentrated solution to prevent osmosis.

b. Using a kinetic molecular model illustrate the movement of solvent molecules across a semipermeable membrane which separates pure water from a solution of sugar and water. Using this illustration explain what happens in reverse osmosis. See Appendix III for recommended demonstration, video, or computer resources.



The semipermeable membrane which separates the solution from the pure solvent (on the left side) only allows the solvent particles to move from one side of the membrane to the other. In the drawing the net follow of solvent particles is from the solution of low concentration of solute (in this case the pure solvent) to the solution of high concentration of solute.

In reverse osmosis a pressure greater than the osmotic pressure of the more concentrated solution is placed on the solution of higher concentration. The result is to force solvent particles in the more concentrated solution to pass through the membrane into the pure solvent.

7. Give three examples of colloids.

Some examples listed in the textbook include; fog (a solid dispersed in a gas), whipped cream (a gas dispersed in a liquid) and marshmallows (a gas dispersed in a solid).