## Vapor Pressure & Raoult's Law

1. What is Vapor Pressure?

This is the pressure above a solid or liquid due to evaporation.

2. Can a solute affect the vapor pressure of a solvent?

Yes.

3. What do solutes do to the vapor pressure of the solvent?

Lower it. Please note that it is the vapor pressure of the *solvent* is lowered, not necessarily the vapor pressure for the overall solution

4. How does it lower vapor pressure of solvent?





Less of the solvent is able to escape due to its path for evaporation being blocked by the new solute particles. Less particles escaping means lowered vapor pressure.

- 5. What are two categories of solute?
  - a. <u>Non-volatile Solute</u>

This type of solute has no tendency to escape from the solution into the vapor phase – meaning it makes no contribution to the vapor

## Consider:

pressure above the solution.

i. What is Raoult's Law for this type of solute?

$$\frac{P_{\text{solvent}}}{P_{\text{solvent}}} = \frac{P_{\text{solvent}}}{X_{\text{solvent}}} \frac{P_{\text{solvent}}}{P_{\text{solvent}}}$$

b. Volatile Solute

This type of solute does have a tendency for evaporation so it will contribute to the overall vapor pressure above the solution.

i. What is Raoult's Law for this type of solute?

 $\frac{\text{observed VP}}{P_{\text{sol'n}}} = P_{\text{A}} + P_{\text{B}} = \underbrace{X_{\text{solvent}}}_{X \text{solvent}} P^{\text{o}}_{\text{solvent}} + \underbrace{X_{\text{solute}}}_{X \text{solute}} P^{\text{o}}_{\text{solute}} P^{\text{o}}_{\text{solute}}$ 

6. What type of solution obeys Raoult's Law?

Ideal Solutions. This is a type of solution where the solute and solvent have similar attractions. Meaning they are not strongly attracted to or repelled by one another.

a. How does an ideal solution differ from a non-ideal solution?

In an ideal solution there is no interaction between molecules. It would be like adding water to water.

b. How do these interactions affect the predictions of Raoult's Law?

If there are strong interactions, the IMFs are higher than for the pure substances. This means that the molecules, being highly attracted to one another, are less likely to escape (vapor pressure decreases). These kinds of interactions are exothermic and said to have a, "negative deviation", from Raoult's Law predictions. If there are weak interactions, the IMFs are lower than for the pure substances – sometimes even repulsive. This makes it easier for molecules to escape (vapor pressure increases). These kinds of interactions are endothermic and said to have a "positive deviation" from Raoult's Law.

c. Label which of the following graphs obeys Raoult's Law, which has strong exothermic interactions and which has endothermic interactions that cause a deviation from Raoult's Law.



d. Give an example of each type of interaction

- i. Benzene and Toluene = Ideal
- ii.  $CH_3CH_2OH + C_6H_{14}$  = endothermic (polar and nonpolar combination)
- iii.  $C_3H_6O + H_2O = exothermic$ (polar and polar combination)
- 7. When pure methanol is mixed with water, the solution gets warmer to the touch. Would you expect this solution to be ideal? Why or why not?

No. We would expect this solution to have a negative deviation from an ideal sol'n as it was an exothermic reaction. In an exothermic reaction

the solute-solvent interactions are strong.

Ideal solutions have a  $\Delta H_{sol'n} = 0$  (i.e. no net heat flow)

8. Given



Which of the following statements is false concerning solutions of A and B?

a. The solutions exhibit negative deviations from Raoult's Law.

True.

b.  $\Delta H_{mix}$  for the solutions should be exothermic.

True – negative deviation = exothermic.

c. The intermolecular forces are stronger in solution than in either pure A or B.

True – negative deviation indicates stronger interactions between solute and solvent.

d. Pure liquid B is more volatile than pure liquid A.

True. Higher  $P_B^{o}$  vapor pressure compared to  $P_A^{o}$ .

e. The solution with  $\chi_B$  = 0.6 will have a lower boiling point than either pure A or pure B.

False. Lower vapor pressure means higher boiling point.

Which of the following will have the lowest total vapor pressure at 25°C? Which has the highest vapor pressure at 25°C? At 25°C, the vapor pressure of pure water is 23.8 torr.

a. Pure water.

P<sub>sol'n</sub> = 23.8 torr

b. A solution of glucose in water with  $\chi_{glucose} = 0.01$ 

If the mole fraction of glucose is 0.01. The mole fraction of  $H_2O = 0.99$  (remember that the mole fraction has to add up to one)

 $P_{sol'n} = (0.99)(23.8 \text{ torr}) = 23.6 \text{ torr}$ 

c. A solution of sodium chloride in water with  $\chi_{NaCl} = 0.01$ 

This one is a little bit trickier. The mole fraction of water would be 0.99, as it was in the case above – thus calculating you would determine the same vapor pressure using Raoult's Law. The key difference here is that the NaCl breaks up into 2 ions and glucose is a non-electrolyte. This means that there are more particles blocking the path for evaporation with the NaCl, thus it would have lower overall vapor pressure.

d. A solution of methanol in water with  $\chi_{methanol} = 0.2$ (at 25°C, the vapor pressure of pure methanol is 143 torr)

In this case, we are given a vapor pressure for methanol, this means that it is a volatile solute. So we would have to use

$$P_{solin} = P_A + P_B = X_{solvent} P_{solvent}^0 + X_{solute} P_{solute}^0$$

Plugging in, we get:

 $P_{sol'n} = (0.8)(23.8 \text{ torr}) + (0.2)(143 \text{ torr}) = 47.64 \text{ torr}$ 

Because methanol adds to the total vapor pressure – this solution would have the highest total.

The final order would be:

Glycerin (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>) is a nonvolatile liquid. What is the vapor pressure of a solution made by adding 164 g of glycerin to 338 mL of H<sub>2</sub>O at 39.8°C? The vapor pressure of pure water at 39.8°C is 54.74 torr and its density is 0.992 g/cm<sup>3</sup>.

This is a Raoult's Law problem – we can identify this as it is looking at the affects of a solute on the vapor pressure of the solute.

We are told that it is a nonvolatile solute, this means that we will use:

 $P_{solin} = \chi_{solvent} P^{o}_{solvent}$ 

First we will determine the mole fraction of water in the solution.

Mole Fraction ( $\chi_a$ ) =  $\frac{\text{moles }_a}{\text{moles }_{\text{total}}}$ 

$$\frac{338 \text{ mL H}_2\text{O}}{\text{mL}} \quad \frac{0.992 \text{ g}}{\text{mL}} \quad \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}} = 18.6 \text{ mol H}_2\text{O}$$

$$\frac{164 \text{ g C}_3\text{H}_8\text{O}_3}{92.11 \text{ g}} = 1.78 \text{ mol C}_3\text{H}_8\text{O}_3$$

$$\chi = \frac{18.6}{18.6 + 1.78} = 0.913$$

Plugging this value into the formula we get:

 $P_{sol'n} = (0.913) (54.74 \text{ torr}) = 50.0 \text{ torr}$ 

11. At a certain temperature the vapor pressure of pure benzene  $(C_6H_6)$  is 0.930 atm. A solution was prepared by dissolving 10.0 g of a nondissociating, nonvolatile solute in 78.11 g of benzene at that temperature. The vapor pressure of the solution was found to be 0.900 atm. Assuming that the solution behaves ideally, determine the molar mass of the solute.

Once again, based on the information present we know we are dealing with a Raoult's Law problem.

 $P_{b}^{0} = 0.930$  atm  $P_{sol'n} = 0.900$  atm

As this is a nonvolatile solute we will be dealing with

 $P_{sol'n} = \chi_{solvent} P^{o}_{solvent}$ 

From the information provided we are able to provide  $\chi_{solvent.}$ .

$$X_{\text{solvent}} = \frac{P_{\text{sol'n}}}{P_{\text{solvent}}^0} = \frac{(0.900 \text{ atm})}{(0.930 \text{ atm})} = 0.968$$

Remember that the mole fraction is equal to:

Mole Fraction (
$$\chi_a$$
) =  $\frac{\text{moles}_{\text{solvent}}}{\text{moles}_{\text{sol'n}}}$ 

We can determine the moles of solvent present in the solution using the initial mass given:

$$\frac{78.11 \text{ g}}{78.12 \text{ g}} = 1 \text{ mol } C_6 H_6$$

Plugging what we know into the mole fraction equation:

$$0.968 = \frac{1}{1 + x}$$
  
x = 0.033 mol

Given that we know that there were 10.0g of solute added to the solution we can solve for the molar mass of the solute.

Molar Mass = 
$$\frac{g}{mol} = \frac{10.0 \text{ g}}{0.033 \text{ mol}} = 302.5 \frac{g}{mol}$$