

1. (10%) How many grams of urea $[(\text{NH}_2)_2\text{CO}]$ must be added to 450 g of water to give a solution with a vapor pressure 2.50 mmHg less than that of pure water at 30°C? (The vapor pressure of water at 30°C is 31.8 mmHg.) (urea = 60.06 g mol⁻¹)

This problem is very similar to Problem 9.24.

$$\Delta P = x_{\text{urea}} P_{\text{water}}^{\circ}$$

$$2.50 \text{ mmHg} = x_{\text{urea}}(31.8 \text{ mmHg})$$

$$x_{\text{urea}} = 0.0786$$

The number of moles of water is:

$$n_{\text{water}} = 450 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 25.0 \text{ mol H}_2\text{O}$$

$$x_{\text{urea}} = \frac{n_{\text{urea}}}{n_{\text{water}} + n_{\text{urea}}}$$

$$0.0786 = \frac{n_{\text{urea}}}{25.0 + n_{\text{urea}}}$$

$$n_{\text{urea}} = 2.13 \text{ mol}$$

$$\text{mass of urea} = 2.13 \text{ mol urea} \times \frac{60.06 \text{ g urea}}{1 \text{ mol urea}} = 128 \text{ g of urea}$$

2. (10%) A mixture of liquids A and B exhibits ideal behavior. At 84°C, the total vapor pressure of a solution containing 1.2 moles of A and 2.3 moles of B is 331 mmHg. Upon the addition of another mole of B to the solution, the vapor pressure increases to 347 mmHg. Calculate the vapor pressures of pure A and pure B at 84°C.

First find the mole fractions of the solution components. We will keep an extra

significant figure and then round at the end.

$$x_A = \frac{1.2 \text{ mol}}{1.2 \text{ mol} + 2.3 \text{ mol}} = 0.343$$

$$x_B = \frac{2.3 \text{ mol}}{1.2 \text{ mol} + 2.3 \text{ mol}} = 0.657$$

We can now use Dalton's law and Raoult's law to derive the following:

$$P_{\text{Total}} = x_A P_A^{\circ} + x_B P_B^{\circ} = 0.343 P_A^{\circ} + 0.657 P_B^{\circ} = 331 \text{ mmHg}$$

We do the same calculations for after an additional mole of B is added.

$$x_A = \frac{1.2 \text{ mol}}{1.2 \text{ mol} + 3.3 \text{ mol}} = 0.267$$

$$x_B = \frac{3.3 \text{ mol}}{1.2 \text{ mol} + 3.3 \text{ mol}} = 0.733$$

$$P_{\text{Total}} = x_A P_A^{\circ} + x_B P_B^{\circ} = 0.267 P_A^{\circ} + 0.733 P_B^{\circ} = 347 \text{ mmHg}$$

Now we have two equations and two unknowns. If we solve for P_A° in our two equations and then set them equal to each other we get the following:

$$965 \text{ mmHg} - 1.915 P_B^{\circ} = 1300 \text{ mmHg} - 2.745 P_B^{\circ}$$

Solving for P_B° we get:

$$P_B^{\circ} = \frac{335 \text{ mmHg}}{0.8303} = 403 \text{ mmHg} = \mathbf{400 \text{ mmHg}}$$

When we plug this value of P_B° into either of the two equations that we started with, we get

$$P_A^{\circ} = \mathbf{190 \text{ mmHg}}$$

3. (10%) Estimate the molar heat of vaporization of a liquid whose vapor pressure doubles when the temperature is raised from 85°C to 95°C.

Using Equation 9.4 of the text:

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln\left(\frac{1}{2}\right) = \left(\frac{\Delta H_{\text{vap}}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}\right) \left(\frac{1}{368 \text{ K}} - \frac{1}{358 \text{ K}}\right) = \Delta H_{\text{vap}} \left(\frac{-7.59 \times 10^{-5}}{8.314 \text{ J mol}^{-1}}\right)$$

$$\Delta H_{\text{vap}} = 7.59 \times 10^4 \text{ J mol}^{-1} = \mathbf{75.9 \text{ kJ mol}^{-1}}$$

- 4. (10%) Explain why reverse osmosis is (theoretically) more desirable as a desalination method than distillation or freezing. What minimum pressure must be applied to seawater at 25°C in order for reverse osmosis to occur? (Treat seawater as a 0.70M NaCl solution.)**

Reverse osmosis uses high pressure to force water from a more concentrated solution to a less concentrated one through a semipermeable membrane. Desalination by reverse osmosis is considerably cheaper than by distillation and avoids the technical difficulties associated with freezing.

To reverse the osmotic migration of water across a semipermeable membrane, an external pressure exceeding the osmotic pressure must be applied. To find the osmotic pressure of 0.70 M NaCl solution, we must use the van't Hoff factor given in Table 9.4 in the text, because NaCl is a strong electrolyte ($i = 1.9$).

The osmotic pressure of sea water is:

$$\Pi = icRT = (1.9)(0.70 \text{ mol L}^{-1})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = \mathbf{33 \text{ bar}}$$

To cause reverse osmosis a pressure in excess of 33 bar must be applied.

- 5. (10%) The osmosis pressure of 0.010M solutions of CaCl₂ and urea at 25°C are 0.613 and 0.247 bar, respectively. Calculate the van't Hoff factor for the CaCl₂ solution.**

The temperature and molarity of the two solutions are the same. If we divide Equation 9.31 of the text for one solution by the same equation for the other, we can find the ratio of the van't Hoff factors in terms of the osmotic pressures ($i = 1$ for urea).

$$\frac{\Pi_{\text{CaCl}_2}}{\Pi_{\text{urea}}} = \frac{icRT}{cRT} = i = \frac{0.613 \text{ bar}}{0.247 \text{ bar}} = \mathbf{2.48}$$

6. (10%) The solubility of N₂ in blood at 37°C and at a partial pressure of 0.80 bar is $5.6 \times 10^{-4} \text{ mol L}^{-1}$. A deep-sea diver breathes compressed air with the partial pressure of N₂ equal to 4.0 bar. Assume that the total volume of blood in the diver's body is 5.0 L. Calculate the amount of N₂ gas released (in liters at 37°C and 1 bar) when the diver returns to the surface of the water where the partial pressure of N₂ is 0.80 bar.

Strategy: The given solubility allows us to calculate Henry's law constant (k), which can then be used to determine the concentration of N₂ at 4.0 bar. We can then compare the solubilities of N₂ in blood under normal pressure (0.80 bar) and under a greater pressure that a deep-sea diver might experience (4.0 bar) to determine the moles of N₂ released when the diver returns to the surface. From the moles of N₂ released, we can calculate the volume of N₂ released.

Solution: First, calculate the Henry's law constant, k , using the concentration of N₂ in blood at 0.80 bar.

$$k = \frac{c}{P}$$

$$k = \frac{5.6 \times 10^{-4} \text{ mol L}^{-1}}{0.80 \text{ bar}} = 7.0 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1}$$

Next, we can calculate the concentration of N₂ in blood at 4.0 bar using k calculated above.

$$c = kP$$

$$c = (7.0 \times 10^{-4} \text{ mol L}^{-1} \text{ bar}^{-1})(4.0 \text{ bar}) = 2.8 \times 10^{-3} \text{ mol L}^{-1}$$

From each of the concentrations of N₂ in blood, we can calculate the number of moles of N₂ dissolved by multiplying by the total blood volume of 5.0 L. Then, we can calculate the number of moles of N₂ released when the diver returns to the surface.

The number of moles of N₂ in 5.0 L of blood at 0.80 bar is:

$$(5.6 \times 10^{-4} \text{ mol L}^{-1})(5.0 \text{ L}) = 2.8 \times 10^{-3} \text{ mol}$$

The number of moles of N₂ in 5.0 L of blood at 4.0 bar is:

$$(2.8 \times 10^{-3} \text{ mol L}^{-1})(5.0 \text{ L}) = 1.4 \times 10^{-2} \text{ mol}$$

The amount of N₂ released in moles when the diver returns to the surface is:

$$(1.4 \times 10^{-2} \text{ mol}) - (2.8 \times 10^{-3} \text{ mol}) = 1.1 \times 10^{-2} \text{ mol}$$

Finally, we can now calculate the volume of N₂ released using the ideal gas equation. The total pressure pushing on the N₂ that is released is atmospheric pressure (1 atm).

The volume of N₂ released is:

$$V_{\text{N}_2} = \frac{nRT}{P}$$

$$V_{\text{N}_2} = \frac{(1.1 \times 10^{-2} \text{ mol})(273 + 37)\text{K}}{(1.0 \text{ bar})} \times \frac{0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}}{1} = 0.28 \text{ L}$$

7. (10%) A solution is prepared by dissolving 35.0 g of hemoglobin (Hb) in enough water to make up 1 L in volume. If the osmotic pressure of the solution is found to be 10.0 mmHg at 25°C, Calculate the molar mass of hemoglobin.

(R = 0.0821 L atm mol⁻¹ K⁻¹)

Strategy The steps needed to calculate the molar mass of Hb are similar to those outlined in example 9.10, except we use osmotic pressure instead of freezing-point depression. First, we must calculate the molarity of the solution from the osmotic pressure of the solution. Then, from the molarity, we can determine the number of moles in 35.0 g of Hb and hence its molar mass. Because the pressure is given in mmHg, it is more convenient to use R in terms of L atm instead of L bar because the conversion factor from mmHg to atm is simpler.

Solution The sequence of conversions is as follows:

osmotic pressure → molarity → number of moles → molar mass

First, calculate the molarity using Equation 9.26:

$$\Pi = cRT$$
$$c = \frac{\Pi}{RT} = \frac{10.0 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 5.38 \times 10^{-4} \text{ M}$$

The volume of the solution is 1L, so it must contain 5.38×10^{-4} mol of Hb. We use this quantity to calculate the molar mass:

$$\text{molar mass of Hb} = \frac{\text{grams of Hb}}{\text{moles of Hb}} = \frac{35.0 \text{ g}}{5.38 \times 10^{-4} \text{ mol}} = 6.51 \times 10^4 \text{ g mol}^{-1}$$

- 8. (10%) How many liters of the antifreeze ethylene glycol $[\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})]$ would you add to a car radiator containing 6.50 L of water if the coldest winter temperature in your area is -20°C ? Calculate the boiling point of this water/ethylene glycol mixture. (The density of ethylene glycol is 1.11 g mL^{-1} .) ($K_f = 1.86^\circ\text{C m}^{-1}$, $K_b = 0.52^\circ\text{C m}^{-1}$, molar mass of ethylene glycol = 62.07 g mol^{-1})**

We want a freezing point depression of 20°C .

$$m = \frac{\Delta T_f}{K_f} = \frac{20^\circ\text{C}}{1.86^\circ\text{C m}^{-1}} = 10.8 \text{ m}$$

The mass of ethylene glycol (EG) in 6.5 L or 6.5 kg of water is:

$$\text{mass EG} = 6.50 \text{ kg H}_2\text{O} \times \frac{10.8 \text{ mol EG}}{1 \text{ kg H}_2\text{O}} \times \frac{62.07 \text{ g EG}}{1 \text{ mol EG}} = 4.36 \times 10^3 \text{ g EG}$$

The volume of EG needed is:

$$V = (4.36 \times 10^3 \text{ g EG}) \times \frac{1 \text{ mL EG}}{1.11 \text{ g EG}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = \mathbf{3.93 \text{ L}}$$

Finally, we calculate the boiling point:

$$\Delta T_b = mK_b = (10.8 \text{ m})(0.52^\circ\text{C m}^{-1}) = 5.6^\circ\text{C}$$

The **boiling point** of the solution will be $100.0^\circ\text{C} + 5.6^\circ\text{C} = \mathbf{105.6^\circ\text{C}}$.

- 9. (10%) Solution A and B have osmotic pressures of 2.4 and 4.6 bar, respectively, at a certain temperature. What is the osmotic pressure of a solution prepared by mixing equal volumes of A and B at the same temperature?**

At constant temperature, the osmotic pressure of a solution is proportional to

the molarity. When equal volumes of the two solutions are mixed, the molarity will just be the mean of the molarities of the two solutions (assuming additive volumes). Since the osmotic pressure is proportional to the molarity, the osmotic pressure of the solution will be the mean of the osmotic pressure of the two solutions.

$$\Pi = \frac{2.4 \text{ bar} + 4.6 \text{ bar}}{2} = \mathbf{3.5 \text{ bar}}$$

10. (15%) Liquid A (molar mass = 100 g mol⁻¹) and B (molar mass = 110 g mol⁻¹) from an ideal solution. At 55°C, A has a vapor pressure of 95 mmHg and B has a vapor pressure of 42 mmHg. A solution is prepared by mixing equal masses of A and B. (a) Calculate the mole fraction of each component in the solution. (b) Calculate the partial pressures of A and B over the solution at 55°C. (c) Suppose that some of the vapor described in part (b) is condensed to a liquid. Calculate the mole fraction of each component in this liquid and the vapor pressure of each component above this liquid at 55°C.

(a) The solution is prepared by mixing equal masses of A and B. Let's assume that we have 100 grams of each component. We can convert to moles of each substance and then solve for the mole fraction of each component.

Since the molar mass of A is 100 g mol⁻¹, we have 1.00 mole of A. The moles of B are:

$$100 \text{ g B} \times \frac{1 \text{ mol B}}{110 \text{ g B}} = 0.909 \text{ mol B}$$

The mole fraction of A is:

$$x_A = \frac{n_A}{n_A + n_B} = \frac{1}{1 + 0.909} = \mathbf{0.524}$$

Since this is a two component solution, the mole fraction of B is: $x_B = 1 - 0.524 = \mathbf{0.476}$

(b) We can use Equation 9.8 of the text and the mole fractions calculated in part (a) to calculate the partial pressures of A and B over the solution.

$$P_A = x_A P_A^O = (0.524)(95 \text{ mmHg}) = \mathbf{50 \text{ mmHg}}$$

$$P_B = x_B P_B^O = (0.476)(42 \text{ mmHg}) = \mathbf{20 \text{ mmHg}}$$

(c) Recall that pressure of a gas is directly proportional to moles of gas ($P \propto n$). The ratio of the partial pressures calculated in part (b) is 50 : 20, and therefore the ratio of moles will also be 50 : 20. Let's assume that we have 50 moles of A and 20 moles of B. We can solve for the mole fraction of each component and then solve for the vapor pressures using Equation 9.8 of the text.

The mole fraction of A is:

$$x_A = \frac{n_A}{n_A + n_B} = \frac{50}{50 + 20} = \mathbf{0.71}$$

Since this is a two component solution, the mole fraction of B is: $x_B = 1 - 0.71 = \mathbf{0.29}$

The vapor pressures of each component above the solution are:

$$P_A = x_A P_A^O = (0.71)(95 \text{ mmHg}) = \mathbf{67 \text{ mmHg}}$$

$$P_B = x_B P_B^O = (0.29)(42 \text{ mmHg}) = \mathbf{12 \text{ mmHg}}$$