Colligative Properties

A colligative property is a property of a solution that depends on the concentration of solute particles, but not on their chemical identity. We will study 4 colligative properties in this course: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

Vapor Pressure Lowering

When a non-volatile solute (one that does not vaporize) is dissolved in a volatile solvent (one that vaporizes), the vapor pressure of the resulting solution is lower than that of the pure solvent. This reduction in vapor pressure is known as vapor pressure lowering. We can explain this phenomena as follows:

Pure Solvent   Solution
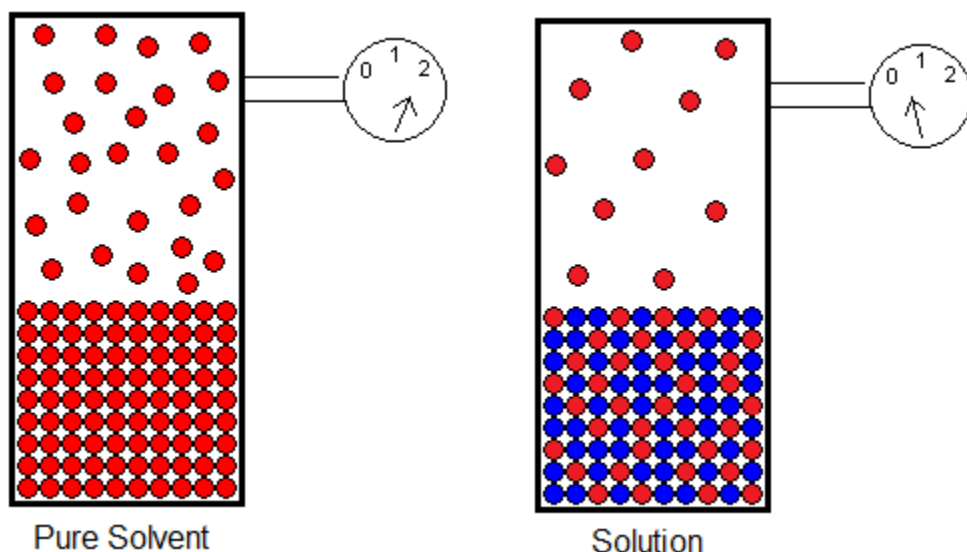
In the pure solvent, every surface molecule is a solvent molecule, and therefore, capable of vaporizing if it has enough energy. But in the solution, some of the surface molecules are solute molecules. Since the solute is non-volatile, these molecules will not vaporize. There are fewer surface molecules that are capable of vaporizing, so the rate of evaporation will be lower. This means that equilibrium will be established with a lower pressure of gas molecules above the liquid. The higher the concentration of non-volatile solute, the smaller the fraction of surface molecules that are solvent molecules. So the rate of evaporation – and therefore the equilibrium vapor pressure – decreases with increasing concentration of non-volatile solute.

Boiling Point Elevation

Boiling point elevation is a consequence of vapor pressure lowering. A liquid will boil when its equilibrium vapor pressure becomes equal to the external pressure. Imagine that you have water at 100 °C. At this temperature, water has a vapor pressure of 760 torr. Assuming the water is in an environment where the atmospheric pressure is 760 torr, the water can boil if heat is applied. Now suppose you dissolve a non-volatile solute in the water. This lowers the vapor pressure, as described above. Since the vapor pressure of the water will now be less than 760 torr, it will not boil, even if its temperature is still 100 °C. In order to boil, it will have to

be heated to a temperature above 100 ºC. When it gets hot enough to restore the equilibrium vapor pressure to 760 torr, the water can boil again if we continue to apply heat. The higher the concentration of non-volatile solute, the lower the vapor pressure will be, and therefore, the more the temperature will have to be increased to get the vapor pressure back to 760 torr. So the boiling point elevation increases with increasing concentration of non-volatile solute.

Freezing Point Depression

Like boiling point elevation, freezing point depression is also a consequence of vapor pressure lowering, though it is not as easy to explain. In the case of boiling point elevation, it was fairly obvious why lowering the vapor pressure should raise the boiling point. When the equilibrium vapor pressure of the liquid drops below the external pressure, the liquid can no longer boil. Since the equilibrium vapor pressure of a liquid increases with temperature, raising the temperature of the liquid will eventually get the equilibrium vapor pressure back to the external pressure, and the liquid can boil again. But now the liquid will be boiling at a higher temperature.

But why should vapor pressure lowering cause a decrease in the freezing point? This is best understood with the aid of phase diagram.
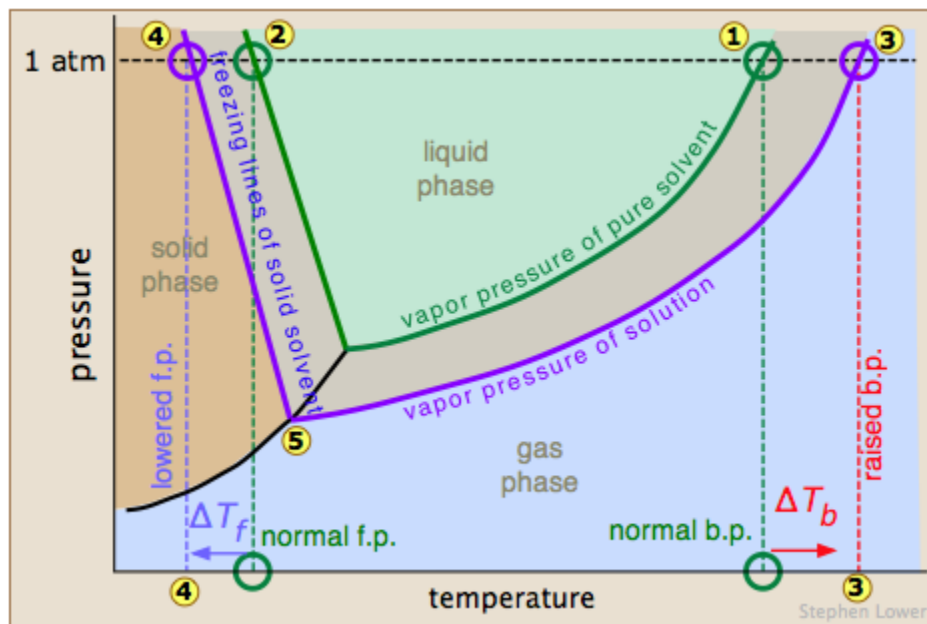
Shown above is a phase diagram for water. The green curves correspond to the pure solvent, and the purple curves are for an aqueous solution. Using the green curves, we can identify the freezing and boiling points for pure water. The freezing point of water is the temperature at which the solid and liquid phases of water can coexist in equilibrium. We usually quote freezing points at normal (1 atm or 760 torr) pressure, but the pressure is not as critical as the case of boiling points. The boundary that separates the solid and liquid regions on a phase diagram is very steep, so even large changes in pressure have only a small effect on the freezing point. On the above phase diagram, point number 2 is the temperature at which solid

and liquid water can coexist at a pressure of 1 atm. This occurs at 0 °C. Point number 1 is the temperature at which the liquid and gaseous phases of water can coexist in equilibrium at a pressure of 1 atm. This occurs at 100 °C. Notice that the slope of the liquid vapor pressure curve is not anywhere near as steep as that of the solid / liquid boundary. Therefore, boiling points are far more pressure dependent than freezing points. If you go to the top of a mountain (where the pressure is lower), you will find that water boils significantly cooler than 100 °C, but the freezing point of water is still about 0 °C.

To proceed further in our analysis of how vapor pressure lowering causes a decrease in the freezing point, we need to understand what happens when a solution freezes. It is important to know that when a solution freezes, the first solid that forms is essentially pure solvent. That is, the solute does not begin to appear in the frozen solution until late in the freezing process, when the solution is almost frozen solid. You can illustrate this by putting sugar water in your ice cube trays, and then breaking off the first ice that forms when the sugar water begins to freeze. You will find that the ice that forms early in the freezing process has hardly any sweetness to it. It contains very little sugar. Almost all of the sugar has remained in the still unfrozen solution.
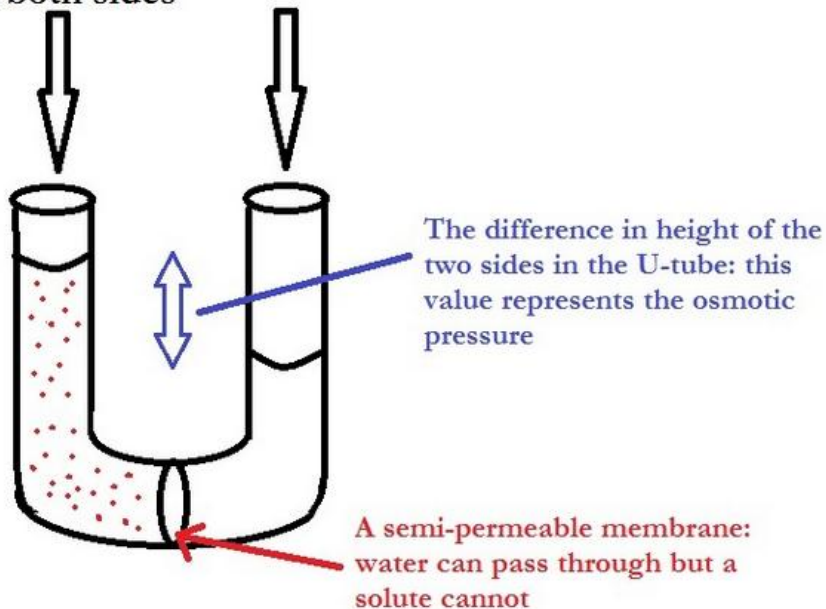
Now refer to the purple curves on the graph shown on the previous page of this paper. Because of the vapor pressure lowering, the vapor pressure curve of the solution (purple curve) is lower than that of the pure solvent (green curve). However, the sublimation curve for the solid (black curve) is unaffected, because it is the boundary between the solid and the gas, and neither of these phases contain the solute. The gas does not contain the solute, because we are dealing with a non-volatile solute – that is, one that does not vaporize. The solid (frozen) solvent does not contain the solute either, because the solvent tends to crystalize out of solution before the solute does. Notice that sublimation curve and the liquid vapor pressure curve meet each other at a particular temperature. That temperature becomes a 3-way intersection, because that's where the solid / liquid boundary originates from, forming what is known as the triple point. Since the vapor pressure curve of the liquid is lowered, but the sublimation pressure curve remains in the same place, the intersection of the two curves will occur at a lower temperature. Since the solid / liquid boundary extends from this point, the freezing point will be lower for the solution than for the pure solvent. The more the vapor pressure is lowered, the lower the temperature at which the vapor pressure curve will intersect the sublimation curve. Therefore, as we make the concentration of non-volatile solute higher and higher, we push the solid / liquid boundary to lower and lower temperatures. This means that the magnitude of the freezing point depression increases with the concentration of non-volatile solute.

Osmotic Pressure

Osmosis is the movement of molecules across a membrane from a region of higher concentration to a region of lower concentration. Osmosis is of interest when we have a semi-permeable membrane – that is, one that lets some molecules pass through but not others. Generally, this is governed by the size of the molecules. Sufficiently large molecules will not be able to pass through the pores in the membrane, whereas small molecules will. In this

course, we consider aqueous solutions, in which the water molecules can pass through the membrane but the solute molecules can not. Aqueous solutions of proteins will establish an osmotic pressure across a semipermeable membrane, because the protein molecules can not cross the membrane.

The pressure of the atomosphere is the same on both sides

The difference in height of the two sides in the U-tube: this value represents the osmotic pressure

A semi-permeable membrane: water can pass through but a solute cannot

The above illustration shows a U-shaped tube with a semipermeable membrane in the middle. The liquid on the left side of the membrane is an aqueous solution containing a solute composed of molecules that are too large to pass through the pores in the membrane. The liquid on the right side of the membrane is pure water (the solvent in this example). Initially, the liquid levels in the two sides of the tube were the same. However, because of the higher concentration of water on the right side of the membrane, more water molecules were striking the membrane on the right side than on the left side. Because of this, there was a net flow of water from the right side to the left side of the tube, resulting in a build-up of liquid on the left side. But this extra height of liquid on the left side of the tube exerts a pressure on the membrane which tends to push water molecules back to the right side. As you can imagine, if the pressure becomes large enough, it will push solvent (water) molecules back to pure solvent side of the tube just as fast as the solvent molecules are entering the solution. When this happens, we have osmotic equilibrium, and the pure solvent no longer dilutes the solution on the other side of the membrane. The pressure that must be supplied to establish this equilibrium is known as the osmotic pressure of the solution. Since the difference in solvent flow rates across the membrane will be proportional to the concentration of solute, a solution with a higher solute concentration will require a greater pressure to establish osmotic equilibrium.   If you supply a pressure *higher* that that needed to establish osmotic equilibrium, you can make the solvent flow from the solution side of the membrane to the pure solvent side. This is known as reverse osmosis, and can be used to purify a water sample.

Calculations Involving Colligative Properties

The preceding sections have described some colligative properties in a semi-quantitative way. We have seen that (as compared to a pure solvent) vapor pressure decreases, boiling point increases, and freezing point decrease as solute concentration increases. We have also seen that a solution separated from the pure solvent by a semipermeable membrane has a property we call osmotic pressure, and this osmotic pressure increases with solute concentration. But we have not yet seen any specific mathematical formulas describing these relationships. That is the subject of this section.

A Formula for Vapor Pressure Lowering

To calculate the vapor pressure of a solution, we can use Raoult's law. This law actually only holds for ideal solutions, or for solutions which are sufficiently dilute. It is a very simplistic equation, and assumes that all molecules at the surface of a liquid are equally likely to escape into the gas phase. This is true only for an ideal solution, since the attractive forces are all equal in such a solution. For a solution in which only the solvent is volatile, we can write Raoult's law as follows:

$$P_{solution} = X_{solvent} \cdot P^o_{solvent} \qquad\qquad \text{(Equation 1)}$$

In Equation 1, $X_{solvent}$ is the mole fraction of the solvent in the solution, and $P^o_{solvent}$ is the vapor pressure of the pure solvent. Since the solute does not vaporize in the case we are considering here (since it is non-volatile), the vapor above the solution is just the solvent vapor, but the solvent vapor pressure is lower than it would be above the pure solvent, because the presence of non-volatile solute molecules slows the rate of evaporation, resulting in the establishment of equilibrium at a lower pressure.

The vapor pressure lowering is simply the difference between vapor pressure of the pure solvent and that of the solution. Although the pressure decreases, "vapor pressure lowering" is usually reported as a positive number. Since ΔP is actually a negative quantity, I will use absolute value signs and write the equation as

$$\lvert\Delta P\rvert = P^o_{solvent} - P_{solution} \qquad\qquad \text{(Equation 2)}$$

Since vapor pressure lowering is a colligative property, it should depend on the solute concentration. We want to show that the higher the solute concentration, the greater the vapor pressure lowering. Substituting Equation 1 into Equation 2 gives

$$\lvert\Delta P\rvert = P^o_{solvent} - X_{solvent} \cdot P^o_{solvent} \qquad\qquad \text{(Equation 3)}$$

Factoring out $P^o_{solvent}$ on the right hand side of Equation 3, we can write

$$\lvert\Delta P\rvert = P^o_{sollvent} (1 - X_{solvent}) \qquad\qquad \text{(Equation 4)}$$

The sum of all mole fractions in any mixture must add up to 1. If we assume a solution containing a single solvent and a single solute, we can write

$$X_{solvent} + X_{solute} = 1 \qquad \text{(Equation 5)}$$

Solving Equation 5 for X_{solute} gives

$$X_{solute} = 1 - X_{solvent} \qquad \text{(Equation 6)}$$

But this quantity, $1 - X_{solvent}$ is exactly what appears in the parentheses on the right hand side of Equation 4. Therefore, we can substitute Equation 6 into Equation 4 to get

$$\left| \Delta P \right| = X_{solute} \cdot P^o_{solvent} \qquad \text{(Equation 7)}$$

Equation 7 shows that vapor pressure lowering is indeed a colligative property. For a given solvent at any given temperature, $P^o_{solvent}$ will be a constant. Therefore, as X_{solute} increases, $\left| \Delta P \right|$ must also increase.

A Formula for Freezing Point Depression

Since vapor pressure lowering was cast in terms of mole fraction of solute, and vapor pressure in turn, leads to freezing point depression and boiling point elevation, you might have expected these quantities to also be related to the mole fraction of solute. However, it has been customary to express these quantities in terms of the molality of the solute rather than its mole fraction. We can rationalize the validity of doing this my noting that all of the concentration scales must be related. If the concentration is higher on one scale, it should be higher on the others as well.

The freezing point depression is defined as the difference between the freezing point of the pure solvent and that of the solution. If we want to render this as a positive number, we can write

$$\left| \Delta T_f \right| = T^o_f - T_f \qquad \text{(Equation 8)}$$

where T^o_f is the freezing point of the pure solvent and T_f is the freezing point of the solution. Each solvent has a characteristic constant known as the freezing point depression constant, symbolized by K_f. This constant, when multiplied by the molality of the solute in the solution, gives the expected freezing point depression. That is,

$$\left| \Delta T_f \right| = K_f \cdot c_m \qquad \text{(Equation 9)}$$

where c_m is the concentration expressed in molality units. Due to the large number of solvents, you are not expected to memorize then. Instead, the values you need will either be quoted to you in the problems, or a table will be provided in which you can look up the necessary values. The freezing point depression constant for water, for example, is 1.858 ^{o}C / m. That is, the units are "degrees C per molal". This means that the freezing point becomes 1.858 ^{o}C colder for every 1 molal increase in solute concentration. It should be noted that at this stage we are dealing with a solute that does not ionize in solution. If the solute ionizes, the number of solute particles is larger than the solution's molality would suggest. We will see how to correct for ionization is a later section of these notes.

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A Formula for Boiling Point Elevation

Analogous to Equations 8 and 9 for freezing point depression, we can write the following for boiling point elevation:

$$\Delta T_b = T_b - T^o_b \qquad \text{(Equation 10)}$$

$$\Delta T_b = K_b \cdot c_m \qquad \text{(Equation 11)}$$

The absolute value signs are not used here, because the Δ function (normally defined as "final value minus initial value") is a positive number in its own right. We take the solution to be the "final state" and the pure solvent to be the "initial state". Since boiling point goes up with the addition of a non-volatile solute, calculating "final value minus initial value" will naturally result in a positive number.

The K_b in Equation 11 is known as the boiling point elevation constant. Each solvent will have its own boiling point elevation constant. As in the case freezing point depression constants, you are not expected to memorize them. The values you need will either be quoted in the problems, or you will be provided with a table in which you can look them up. As an example, the boiling point elevation constant for water is 0.512 °C / m. That is, the boiling point increases by 0.512 °C for every molal of non-volatile solute concentration.

A Formula for Osmotic Pressure

Although osmotic pressure is not the same thing as gas pressure, it can be approximately represented by an equation that is very similar to the ideal gas law that you learned about in General Chemistry I. As you may recall, the equation known as the ideal gas law is

$$PV = nRT \qquad \text{(Equation 12)}$$

If you were asked to solve this for pressure, you would probably write

$$P = (nRT) / V \qquad \text{(Equation 13)}$$

but it would be equally valid to write

$$P = (n / V) \cdot RT \qquad \text{(Equation 14)}$$

Because of the units that are conventionally given for the gas constant R, we have to express the volume in liters (R = 0.08206 L atm / K mol). Since n represents the number of moles, the quantity in parentheses in Equation 14 is "moles per liter", which is molarity. Symbolizing molarity as M, Equation 14 becomes

$$P = MRT \qquad \text{(Equation 15)}$$

Equation 15 is known as the Morse equation. We can rationalize its validity by noting that just as gas pressure is determined by the number of gas molecules that are present in a particular volume of gas, so too would osmotic pressure be expected to be determined by the number of solute molecules in a particular volume of solution. If more gas molecules are present in a

given volume, the gas pressure is higher, and referring to the U-tube illustration on page 4, if more solute molecules are present in a given volume of solution, the osmotic pressure will be higher. This is because a greater concentration of solute results in a greater disparity of solvent flow rates across the membrane. As a result, a higher pressure is needed to equalize the flow rates.

Some Representative Problems Involving Colligative Properties

1. At 70 °C, the equilibrium vapor pressure of water is 233.7 torr. At that same temperature, what is the equilibrium vapor pressure of an aqueous sugar solution in which the mole fraction of sugar is 0.200? What is the vapor pressure lowering for this solution? Assume that sugar is non-volatile, and note that sugar is a molecular compound and does not ionize in water. Assume that the solution obeys Raoult's law.

Discussion and Answers:

Since only the water is volatile, the vapor above the solution consists of water vapor only. No sugar will be present in the gaseous state. If the solution obeys Raoult's law, we can apply Equation 1 on page 5.

$$P_{solution} = X_{water} \cdot P^{o}_{water}$$

The sum of the mole fractions must be 1, so if the mole fraction of sugar is 0.200, then the mole fraction of water must be 0.800.

$$X_{sugar} + X_{water} = 1 \rightarrow X_{water} = 1 - X_{sugar} = 1.000 - 0.200 = 0.800$$

Therefore,

$$P_{solution} = X_{water} \cdot P^{o}_{water} = (0.800)(233.7 \text{ torr}) = 187 \text{ torr}$$

We can get the vapor pressure lowering by finding the difference between the vapor pressure of the pure solvent and that of the solution (Equation 2 on page 5)

$$\left| \Delta P \right| = P^{o}_{water} - P_{solution} = 233.7 \text{ torr} - 187 \text{ torr} \approx 47 \text{ torr}$$

We can also calculate the vapor pressure lowering from the mole fraction of the solute, using Equation 7 on page 6.

$$\left| \Delta P \right| = X_{sugar} \cdot P^{o}_{water} = (0.200)(233.7 \text{ torr}) = 46.74 \text{ torr} \approx 47 \text{ torr}$$

2. At 80 °C, the equilibrium vapor pressure of water is 355.1 torr. At that same temperature, what is the equilibrium vapor pressure of an aqueous solution containing 99.50 g of sucrose, $C_{12}H_{22}O_{11}$ dissolved in 450.0 g of water? Assume that sucrose is non-volatile, and note that sucrose is a molecular compound and will not ionize in water. Assume that the solution obeys Raoult's law.

Discussion and Answers:

In the previous problem, we were given the mole factions directly.
Here, we have the masses in grams, so we must convert them to moles
and then use the moles to find the mole fractions.

Find the number of moles of sucrose:

$$99.50 \text{ g} \times \frac{1 \text{ mol}}{342.3 \text{ g}} = 0.290\underline{6}81 \text{ mol}$$

Find the moles of water:

$$450.0 \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 24.9\underline{7}23 \text{ mol}$$

Only the water is volatile, so we need the mole fraction of water to
find the pressure of water vapor above the solution. There will be
no sugar vapor above the solution.

$$X_{water} = \frac{24.9\underline{7}23 \text{ mol}}{24.9\underline{7}23 \text{ mol} + 0.290\underline{6}81 \text{ mol}} = \frac{24.9\underline{7}23 \text{ mol}}{25.2\underline{6}2981 \text{ mol}} = 0.988\underline{4}94$$

The mole fraction of any substance in a mixture is the number of
moles of that substance divided by the total number of moles of all
substances in the mixture. Here, we have a mixture of sugar and
water, so the mole fraction of water was calculated by dividing the
number of moles of water by the sum of the number of moles of water
and the number of moles of sugar.

Now calculate the vapor pressure of water above the solution using
Raoult's law:

$$P_{solution} = X_{water} \cdot P^{o}_{water} = (0.988\underline{4}94)(355.1 \text{ torr}) = 351.0 \text{ torr}$$

The vapor pressure lowering can be calculated as the difference
between the vapor pressure of pure water and that of the solution:

$$|\Delta P| = P^{o}_{water} - P_{solution} = 355.1 \text{ torr} - 351.0 \text{ torr} = 4.1 \text{ torr}$$

The vapor pressure lowering can also be calculated from the mole
fraction of sugar, using Equation 7 on page 6, but first we will have
to find the mole fraction of sugar:

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$$X_{sugar} = \frac{0.290\underline{6}81 \text{ mol}}{24.9723 \text{ mol} + 0.290681 \text{ mol}} = \frac{0.290\underline{6}81 \text{ mol}}{25.2\underline{6}2981 \text{ mol}} = 0.0115\underline{0}62$$

Now that we have the mole fraction of sugar, we can proceed to apply Equation 7:

$$\left|\Delta P\right| = X_{sugar} \cdot P^{o}_{water} = (0.0115\underline{0}62)(355.1 \text{ torr}) = 4.086 \text{ torr} \approx 4.1 \text{ torr}$$

This is consistent with the answer we obtained in the previous calculation.

Note also, that instead of calculating the mole fraction of sugar "from scratch" as we did above, we could also have obtained it from the mole fraction of water (which we had already calculated) since the mole fractions must add up to 1.

$$X_{water} + X_{sugar} = 1 \;\; \rightarrow \;\; X_{sugar} = 1 - X_{water} = 1 - 0.988\underline{4}94 = 0.011\underline{5}06$$

This mole fraction is consistent with the one calculated "from scratch". However, the "from scratch" calculation is the better way to go, because if you have an error in the mole fraction of water, and you use that mole fraction as the basis for calculating the mole fraction of sugar, you will also have an error in the mole fraction of sugar.