

## Chapter 43

## COLLIGATIVES

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In this Chapter, we talk about colligative properties. "Colligative" is not a common word; think of it as "collective". Colligative properties are solution properties which depend on the collective concentrations of all solutes.

### 43.1 Preliminaries

Ideally, colligative properties are proportional to the total concentration of all solutes, regardless of identity. The solutes can be molecular or ionic. For ionic solutes, the assumed, ideal condition is full dissociation. Thus, a solution of one mol of NaCl dissolved in one kg H<sub>2</sub>O has a concentration of two molal for total ions.

Pure water boils at 100. °C and freezes at 0. °C. Salt water boils above 100. °C and freezes below 0. °C. These changes in boiling point and in freezing point are two examples of colligative properties. At higher concentrations of salt, the boiling point is higher and the freezing point is lower. That's the concentration effect: more concentration gives more effect. Identity doesn't matter. Ideally, a solution of NaCl(aq) and a solution of KBr(aq) will have the same boiling point and freezing point as long as their concentrations are the same.

Colligative properties follow mathematical relationships but, as we had seen for gases back in Chapter 17, there's ideal behavior and there's real behavior. The real behavior of colligative properties can easily deviate from ideality, depending on the type of solute. For neutral, molecular solutes, the colligative properties for solutions are reasonably ideal up to ~0.5 m. For ionic solutes, however, there are substantial departures from ideality even at 0.01 m for simple 1+/1- salts and the situation is even worse for salts with ions of higher charge. Thus, calculations for ionic solutes are not very meaningful. The primary reason for the greater nonideality of ionics is that the interactions of ions are so strong; they interact strongly with solvent and they even interact with other solvated ions nearby. Due to the large deviations from ideality for ionics, we will only do calculations for neutral, molecular solutes. Nevertheless, the general qualitative trend for ionics still applies: higher concentrations have greater effects.

Before getting into this, there is one thing which you must understand about this colligative business. Colligative properties are about the solvent and they are not about the solute. Much of our prior discussions focused on the solute. That won't be the case here: we shift our focus to the solvent of the solution. We are comparing the properties of a pure liquid to the properties of that liquid as a solvent in a solution. This is a subtle but important distinction. Be careful on this point. A pure liquid will have different thermodynamic properties from that same liquid acting as the solvent in some mixture. And, under ideal conditions, the identity of the solute will not matter.

Let me address some of the thermodynamic aspects. In general, all solutions have a natural preference to take up more solvent and to mix if they are able to do so. This can be manifested in several ways. For example, if you add pure H<sub>2</sub>O(l) carefully to a container of salt water without a lot of stirring, then the pure water and the solution will eventually diffuse and become fully mixed on their own. This is simple dilution. If you add a solution of 1 m NaCl(aq) to a container of 2 m NaCl(aq) without a lot of stirring, then the solutions will also mix (eventually) on their own and they will achieve some uniform, middle concentration. For all of these cases and under ideal conditions, the system gains entropy upon mixing and this then favors mixing. This gain in entropy is true regardless of solute identity.

Overall then, solution entropy favors mixing. Our emphasis here will be simple dilution: the scenario will be that of a pure liquid mixing into a solution which has that liquid as the solvent. We will not deal with the scenario of two solutions mixing together. For our purposes here, we can say that solution entropy favors gaining more solvent; conversely, solution entropy disfavors solvent loss. There will be a catch to this, however, depending on how the additional, pure solvent is accessible. In one variation, the solution can be in contact with the gas phase of the solvent; for example, a solution of sugar water can be in contact with H<sub>2</sub>O(g) in the air which is overhead. In another variation, the solution can be in contact with the solid phase of the solvent compound; for example, a solution of sugar water can be in contact with an ice cube of pure H<sub>2</sub>O(s). In a third variation, the solution can be in indirect contact with the liquid phase of the pure solvent; for example, a solution of sugar water can be in indirect contact with pure water by means of a membrane. Although solution entropy favors the solution to take up more solvent and to become more dilute, that must now be tempered by the entropy differences of all phases which are present. Thus, opposing factors will operate and an equilibrium will be involved.

We will consider four colligative properties here: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. The first two will receive only qualitative coverage; the latter two will receive both qualitative and quantitative coverage.

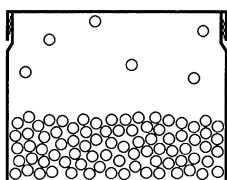
### 43.2 Vapor pressure lowering and boiling point elevation

Before describing these two properties, let me note that we will limit our discussion of all four colligative properties to solutions with nonvolatile solutes. "Nonvolatile" means not volatile. The adjective "volatile" applies to a compound which vaporizes readily. There is no quantitative definition for this term. "Vaporizes readily" can mean the compound has a high EVP at normal temperature or it can mean the compound has a fairly low nbp. It's pretty much a relative thing. For example, diethyl ether,  $C_2H_5OC_2H_5$ , is generally regarded as very volatile. Methanol,  $CH_3OH$ , is less volatile than diethyl ether but more volatile than water. Flip back to the end of Chapter 35 and look at the numbers for those compounds. The noun volatility refers to the property itself. Diethyl ether has high volatility; water's volatility is much less. On the other hand, the adjective nonvolatile means not vaporizing readily, which can be taken to mean not vaporizing to a significant extent. For example, food oils are nonvolatile. Solids can also be characterized in these terms but their volatility is much less than that of a liquid. Nevertheless, we can regard mothballs as volatile if compared to rocks which are nonvolatile.

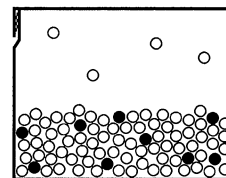
Why do we need this?

Limiting our coverage to nonvolatile solutes allows us to focus on the gas phase of the solvent only. The solutes do not vaporize, so they contribute no vapor pressure of their own. We focus only on the vaporization of the solvent and we do not worry about any vaporization of solute. On the other hand, your instructor may choose to include volatile solute cases. Heed if there's need.

I already mentioned one case of boiling point elevation when I said upstairs that salt water boils above 100. °C. Before we cover bp elevation, let me do vapor pressure lowering. They're related.



In Chapter 35, we talked extensively about the equilibrium of vaporization and about EVP. Vaporization was favored by entropy; condensation was favored by enthalpy (IFs). That discussion applied for a single compound by itself, as depicted at left. When that compound is the solvent in a solution, however, it already has a bit more entropy so the entropy gained by vaporization is slightly diminished. Vaporization is still favored, but now not as much. For this reason, the point of equilibrium balance for the system has a lower concentration (pressure) in the gas phase, as depicted at right. (The black circles are the solute again.) In other words, the EVP for the solvent in the solution is less than the EVP for the pure solvent by itself. With more and more solute dissolved in solution, the effect is greater and the EVP is even lower. For example, the EVP of  $H_2O(g)$  over pure  $H_2O(l)$  is 17.5 Torr at 20. °C. The EVP of  $H_2O(g)$  over a solution of 0.1 m sucrose,  $C_{12}H_{22}O_{11}(aq)$ , is less and the EVP over a solution of 0.2 m  $C_{12}H_{22}O_{11}(aq)$  is even lower. This is the colligative property known as vapor pressure lowering. All of this is a result of the diminished tendency of a solvent to escape from solution to the gas phase.



Our second colligative property, the elevation of the boiling point, is a natural consequence of the lowering of the vapor pressure. As also seen in Chapter 35 for a pure liquid, EVP increases with temperature and there will be some  $T$  for which EVP is one atm. That's the normal boiling point for the pure liquid. For a solution, the EVP is less to start with, so it takes even higher temperature to hit one atm. Thus, the temperature needed for boiling the solvent in a solution is higher. With more and more solute dissolved in solution, the effect is even greater. For example, the nbp of pure  $H_2O$  is 100. °C; the boiling point of a solution of 0.1 m  $NaCl(aq)$  is higher than this, and the boiling point of a solution of 0.2 m  $NaCl(aq)$  is even higher.

Although there are mathematical relationships for ideal conditions for vapor pressure lowering and for boiling point elevation, we will not cover those aspects. Your instructor may choose to add the math. As always, that is their prerogative. Here, we simply stick to qualitative coverage for these two colligative properties.

### 43.3 Freezing point depression

Freezing point depression is the lowering of the freezing point of the solvent in a solution, relative to the freezing point of the pure solvent compound. Pure water freezes at 0. °C but salt water freezes below 0. °C. This is freezing point depression. This is also the reason for salting roads in the winter time.

Roads are salted so that water on the road stays liquid below 0. °C. If temperatures drop too far, then the water still freezes. That's life in the colder climes.

We limit our discussion here to solutes which are solids as pure compounds. Under these conditions, as the solution freezes, it is the solvent (not the solute) which is freezing. There are some subtleties to this process which need elaboration. Let me describe some of this.

If you chill an aqueous solution of whatever solute to 0.000 °C, ice will not form. The reason is that the formation of ice removes some solvent from the solution because  $\text{H}_2\text{O}(l)$  is changing to  $\text{H}_2\text{O}(s)$ , and solution entropy opposes the loss of solvent. If you start dropping the temperature below 0.000 °C, however, you will hit a point at which some water will start to freeze to ice. How cold does it have to be to start freezing? That depends on the concentration of dissolved solute. For example, pure  $\text{H}_2\text{O}(l)$  freezes at 0.000 °C, but the water in 0.1 m  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$  freezes below this and the water in 0.2 m  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(aq)$  freezes even lower. As you freeze any aqueous solution, some water freezes to ice and, if you stopped there, you would have an equilibrium system of an ice cube sitting in a solution at some temperature below 0.000 °C. Now there's a catch: since freezing removes solvent from the solution, the concentration of the remaining solution has increased. Since the concentration has increased, then further freezing requires dropping the temperature even more. In other words, the temperature must continue dropping in order to freeze more and more solvent. Here's an important point about freezing a solution: you don't get a single freezing point like you get for a pure liquid by itself. For a solution, the freezing point itself is changing; it's going down as the solution gets more and more concentrated. You get a freezing range instead of a single freezing point.

But that only goes so far. Eventually, the solution gets so concentrated that the solute reaches saturation. Now, as more solvent is removed by freezing, the solute crystallizes as its own solid phase. Note the distinction: the solute never "freezes"; it crystallizes to a solid. If you chill the whole mixture to a solid, then you have a heterogeneous, solid mixture of frozen solvent and portions of crystallized, solid solute.

For our colligative coverage here, we won't be going that far. We're just covering the start of the freezing process of the pure solvent. We regard the freezing point for a solution to be the first temperature at which freezing begins.

Let's take a look at some of the mathematics involved in this process. The solution first starts to freeze at some  $T$  lower than the usual fp of pure solvent. The difference in those temperatures is called the freezing point depression, designated  $\Delta T_f$ .

$$\Delta T_f = \text{fp of pure solvent} - \text{fp of actual solution}$$

Note that  $\Delta$  here is not your usual final-minus-initial thing.  $\Delta T_f$  is just the drop in freezing point in °C (or K) for the solution relative to the pure solvent compound, expressed as a positive number.

This freezing point depression is proportional to the molal concentration of the solute. We can write this proportionality as the following.

$$\Delta T_f \propto m$$

Now, we introduce a proportionality constant which is labeled  $K_f$ ; this is called the freezing point constant or the cryoscopic constant.

$$\Delta T_f = K_f \times m$$

The units of  $K_f$  are °C/m or K/m. It doesn't matter if you use °C or K because a  $\Delta T$  is the same in both scales (as noted in Section 18.5).

Different solvents behave differently in this regard, so different solvents all have different values of  $K_f$ . Here are cryoscopic constants and freezing points for four compounds.

	water $\text{H}_2\text{O}$	benzene $\text{C}_6\text{H}_6$	cyclohexane $\text{C}_6\text{H}_{12}$	naphthalene $\text{C}_{10}\text{H}_8$
fp	0.00 °C	5.49 °C	6.59 °C	80.26 °C
$K_f$	1.86 °C/m	5.07 °C/m	20.8 °C/m	7.45 °C/m

Naphthalene is a solid at room temperature, so we don't usually think of it as a solvent. Nevertheless, it does find use in these applications above its melting point.

Let's illustrate a sample calculation. Let's take the aqueous sugar solution from the last Chapter and find its freezing point depression and its actual freezing point.

“ Consider a sugar solution which contains 7.43 g sucrose (table sugar),  $C_{12}H_{22}O_{11}$ , in 100.0 g water. Calculate the molality of the sugar in the solution. ”

You need that molality from Chapter 42 and you will need  $K_f$  for water from the above list. Your setup for the molality from last Chapter should have come out in the end to be the following.

$$\frac{7.43/342.30}{0.1000} \text{ m}$$

We enter this into the equation for the freezing point depression.

$$\Delta T_f = K_f \times m$$

$$\Delta T_f = \frac{1.86 \text{ }^\circ\text{C}}{\text{m}} \times \frac{7.43/342.30}{0.1000} \text{ m} = 0.404 \text{ }^\circ\text{C}$$

Now, that's how much the freezing point went down. The actual freezing point for the solution is calculated from that. Since

$$\Delta T_f = \text{fp of pure solvent} - \text{fp of actual solution}$$

then

$$\text{fp of actual solution} = \text{fp of pure solvent} - \Delta T_f$$

so that

$$\text{fp of actual solution} = 0.000 \text{ }^\circ\text{C} - 0.404 \text{ }^\circ\text{C} = -0.404 \text{ }^\circ\text{C}$$

and that is your answer. The solution of 7.43 g sucrose in 100.0 g water would start freezing at  $-0.404 \text{ }^\circ\text{C}$ .

By the way, since the fp of pure water is set to  $0 \text{ }^\circ\text{C}$ , it can be taken as  $0.0 \text{ }^\circ\text{C}$ ,  $0.00 \text{ }^\circ\text{C}$ ,  $0.000 \text{ }^\circ\text{C}$ , etc. The other solvents above are restricted to the two decimals as listed.

As noted upstairs, salting roads is a huge, common, current application of freezing point depression. Historically, there was also a laboratory use for this colligative property associated with the determination of molar masses. Look above at the sucrose calculation. Look at the numbers which went into the calculation. 1.86 is from the given  $K_f$ . 7.43 is from the known sample size. 0.1000 is from the known amount of solvent. What does that leave? It leaves the molar mass. Sure, we knew that was 342.30 g/mol for sucrose, but what if you didn't know that the solute was sucrose? What if you had some unknown compound? Well, you could measure the actual  $\Delta T_f$  and use that to find the molar mass. Let's see an example.

You have some mystery compound and you decide to measure its molar mass by freezing point depression. You dissolve 0.887 g of the unknown into 20.0 g benzene,  $C_6H_6$ . You measure the freezing point of this solution to be  $3.83 \text{ }^\circ\text{C}$ . What is the molar mass of your mystery compound?

Keep in mind that colligative properties are concentration properties; here, the colligative property of freezing point depression will give us a concentration in terms of a molality. The  $3.83 \text{ }^\circ\text{C}$  is the actual freezing point; we need the depression.

$$\Delta T_f = \text{fp of pure solvent} - \text{fp of actual solution}$$

From the list above, the fp of pure benzene is  $5.49 \text{ }^\circ\text{C}$ .

$$\Delta T_f = 5.49 \text{ }^\circ\text{C} - 3.83 \text{ }^\circ\text{C}$$

Solving gives  $\Delta T_f = 1.66 \text{ }^\circ\text{C}$ . That goes into the colligative equation.

$$\Delta T_f = K_f \times m$$

From the list,  $K_f = 5.07 \text{ }^\circ\text{C/m}$ . Now we can find the molality of the solution.

$$m = \frac{\Delta T_f}{K_f} = \frac{1.66 \text{ }^\circ\text{C}}{5.07 \text{ }^\circ\text{C/m}} = 0.327416... \text{ m}$$

I didn't round off yet because I'm not done with the whole thing. Right now, we have the molality of the solute as measured experimentally from the freezing point depression itself.

$$m = 0.327416... \text{ m} = \frac{0.327416... \text{ mol solute}}{\text{kg C}_6\text{H}_6}$$

From the wording of the problem, we can also set up the molality as the following although we don't yet know the moles of solute used in the measurement.

$$m = \frac{??? \text{ mol solute}}{0.0200 \text{ kg C}_6\text{H}_6}$$

These two equations are equal.

$$m = \frac{0.327416... \text{ mol solute}}{\text{kg C}_6\text{H}_6} = \frac{??? \text{ mol solute}}{0.0200 \text{ kg C}_6\text{H}_6}$$

Solve for the ??? moles of solute; that's how many moles of solute were actually dissolved.

$$(0.0200)(0.327416...) \text{ mol solute} = 0.00654832... \text{ mol solute}$$

Now, we take this number for moles of solute and connect it to the grams of solute as given in the problem. We put these together to get the molar mass.

$$\text{molar mass} = \frac{0.887 \text{ g}}{0.00654832... \text{ mol}} = 135 \frac{\text{g}}{\text{mol}}$$

So there's your final answer. The molar mass of the mystery compound is 135 g/mol.

Now do one on your own. We'll even add a step to it.

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**Example 1.** You have an allotrope of sulfur and you wish to know which one it is. You dissolve 1.21 g into 50.0 g benzene and you measure the solution freezing point to be 4.86 °C. What is the molar mass of this allotrope? Which allotrope of sulfur is it?  
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Here are three clues and some space.

First clue: You need the molar mass again; follow the same path as above.

Second clue: As first done way back in Section 5.4, you must relate the true molar mass to the empirical formula mass. The empirical formula for every allotrope of sulfur is just S.

Third clue: This allotrope was one of several mentioned at the very end of Chapter 2.

OK, now we'll chill out on freezing point depression. It is time to turn to our final colligative property.

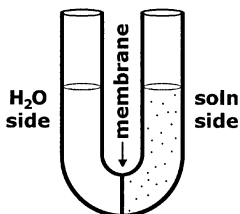
#### 43.4 Osmotic pressure

Osmotic pressure is based on osmosis. This colligative is a bit more involved than the prior colligatives so let me do some explaining. We need to bring in the notion of a semipermeable membrane. A semipermeable membrane is one which is only partly permeable. Permeable here is used in the usual dictionary sense related to permeate which means to pass through. A semipermeable membrane is a membrane which allows some things to pass through but not others. In other words, it leaks but it leaks selectively. Membranes can be chosen which allow solvent to pass through but block other things from permeating. For example, some membranes can block ions while some other membranes can block large solute molecules while letting small water molecules through.

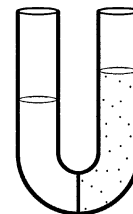
Osmosis involves the passage of solvent from one solution into another solution through such a semipermeable membrane. Due to entropy, the solutions naturally want to mix but solute cannot pass

through the membrane. Solvent can pass through, however, so there is a net flow of solvent from the solution of low concentration to the solution of high concentration. One "solution" is often chosen to be just plain solvent, so its solute concentration is zero. In this application, pure solvent will pass through the semipermeable membrane into the solution on the other side. Thus, the solution gains solvent and this constitutes dilution of the solution. As more solvent passes through the semipermeable membrane, the solution gets more dilute but this continues only to a certain point as we shall see.

There are numerous physical setups which can be used for an osmotic pressure experiment. I'm going to keep it basic here and consider a simple U-tube setup. We will also work only with water as solvent. We will use a U-tube with a semipermeable membrane which prevents bulk contact between the left compartment and the right compartment. Although the membrane prevents bulk contact, the membrane does allow water molecules to slowly pass through, either way. As shown at left, we will start the process with pure water in the left compartment and with a solution whose concentration is to be measured in the right compartment. For purposes of this illustration, we start with both sides at the same liquid height. Gravity prefers equal heights for the two sides. (This assumes the density of the solution is the same density as the water, which is a good assumption for very dilute solutions, as in our application here.)



Although water can pass either way through the membrane, more will pass from left to right than will pass from right to left. This will give a net transfer of water from left to right, thus fulfilling the entropy preference for the solution to gain solvent. This causes the levels of the two sides to become unequal, as shown at right. That introduces a conflict, however, because that opposes gravity. Gravity wants equal heights. Entropy wants more water on the right side but that makes the heights unequal. Thus, we have opposing processes operating and we have an equilibrium system. The system will go to a point of equilibrium. At equilibrium, the two opposing processes are in dynamic balance; water still flows through the membrane, but now equally in both directions.



The difference in liquid heights causes a small pressure difference between the two sides due to gravity. That pressure difference is the colligative property known as osmotic pressure. Osmotic pressure is given by capital, Greek pi,  $\Pi$ .

For ideal solutions, the extent of the pressure difference depends on the concentration of the solute in the solution at equilibrium. We use the concentration unit of molarity in this application. Arithmetically, the colligative relationship is

$$\Pi = M \times R \times T$$

where  $R$  is once again the gas constant in the same version as used back in Chapter 16. In fact, this equation looks hauntingly like the concentration expression for the ideal gas equation in Chapter 16 but there is no simple direct connection. By the way, this equation is good for any solvent and not just for water.

Osmotic pressure is much more sensitive as a colligative property than those discussed earlier. The greater sensitivity allows for the use of very dilute solutions. Let's see how this goes with a sample calculation.

We'll refer back to the sucrose solution which we've used twice now since Chapter 42.

“ Consider a sugar solution which contains 7.43 g sucrose (table sugar),  $C_{12}H_{22}O_{11}$ , in 100.0 g water. Calculate the molality of the sugar in the solution. ”

But now we modify this with two changes. Instead of 7.43 g sucrose, we'll use one-thousand times less: 7.43 mg. We'll also specify 100. mL of solution, since we need molarity in this calculation. So here's the question: what is the osmotic pressure (at equilibrium) at 25 °C for 100. mL of solution which contains 7.43 mg  $C_{12}H_{22}O_{11}$ ?

Set it up.

$$\Pi = M \times R \times T$$

For molarity, you need the mass of the sucrose as 0.00743 g, you need its molar mass (342.30 g/mol) and you need the solution volume as 0.100 L soln.

$$\Pi = \frac{\overbrace{\frac{0.00743}{342.30} \text{ mol}}^M}{0.100 \text{ L}} \times \overbrace{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}}_R \times \overbrace{298 \text{ K}}^T$$

Plug in, punch out, round off. You get 0.00531 atm. That may not sound like much pressure, but it would give a difference in height of ~55 mm for the two sides of the U-tube, which is easily measurable. When you punched out the numbers for the molarity, you may have noticed that the solution concentration was 0.000217 M. That's very dilute compared to typical circumstances. Thus, osmotic pressure provides an easily measured result for a very dilute solution. You could not easily do freezing point depression on a solution which is this dilute.

As in the case for freezing point depression, osmotic pressure was also used historically for molar mass determinations. Due to its enhanced sensitivity, it could handle solutes of huge molar mass, well into many thousands of g/mol. This gets into the sizes of many proteins and polymers, many of which are over 100,000 g/mol. To go that large, however, requires another version of the osmotic pressure equation which we won't do. We'll back off from that a little bit. For illustration purposes, we'll work a sample problem for a protein of more modest size.

Here's the problem. You need to find the molar mass of an unknown protein. You measure the osmotic pressure to be 0.00162 atm at 20. °C for a solution which contains 0.0414 g in 50.0 mL solution. What is the molar mass?

Set it up.

$$\Pi = M \times R \times T$$

The problem gives you  $\Pi$ ,  $R$  and  $T$ . That gives you  $M$ .

$$M = \frac{\Pi}{R \times T} = \frac{0.00162 \text{ atm}}{0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 293 \text{ K}} = 6.7377... \times 10^{-5} \text{ M}$$

That's your concentration as found experimentally. From the wording of the problem, we can set up the molarity as mol solute per L soln, although we don't have moles of solute yet.

$$M = \frac{??? \text{ mol solute}}{0.0500 \text{ L soln}}$$

These two equations for the molarity are equal.

$$M = \frac{6.7377... \times 10^{-5} \text{ mol solute}}{\text{L soln}} = \frac{??? \text{ mol solute}}{0.0500 \text{ L soln}}$$

Re-arrange and solve.

$$(0.0500)(6.7377... \times 10^{-5}) \text{ mol solute} = 3.3688... \times 10^{-5} \text{ mol solute}$$

That's the moles of solute in the solution. The problem seeks molar mass. We know the mass of the solute in the solution, 0.0414 g, from the given information. Together, these give the molar mass.

$$\text{molar mass} = \frac{0.0414 \text{ g}}{3.3688... \times 10^{-5} \text{ mol}} = 12,300 \frac{\text{g}}{\text{mol}}$$

This is the final result.

Your turn.

Polyvinyl alcohol (PVA) is a polymer used in a variety of applications including plastics and foods. Like many industrial polymers, its molar mass can vary over a considerable range, depending on the method of preparation. The empirical formula is  $\text{C}_2\text{H}_4\text{O}$  but the true molecular formulas can vary from 200 to 4,000 times the empirical formula unit. Typically, for any particular batch, a mixture of large molecules of somewhat different sizes is obtained. Thus, the measurement of molar mass is for the average of the batch.

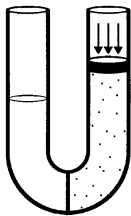
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**Example 2.** You have a batch of PVA and you wish to measure its average molar mass by osmotic pressure. For a solution of 65.4 mg in 35.0 mL solution, you find the osmotic pressure to be 1.6 Torr at 27 °C. What is the molar mass of the batch?  
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Be sure to convert Torr to atm.

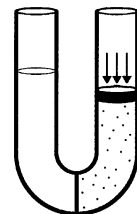
If you're having troubles, follow the method for the prior protein problem.

Like freezing point depression, osmotic pressure is not just a laboratory process. It, too, has important impacts on your world. The greatest impacts are extremely big and extremely small.

The extremely big impact is potability, as applied to water for drinking purposes. This aspect utilizes the process of reverse osmosis, which means running osmosis backwards relative to its natural direction. As seen above, the natural direction in osmosis is for net transfer of pure water through the membrane into the solution side. This sets up a pressure, imposed by gravity, which opposes further dilution. Now, what if we add to that opposing pressure?



As depicted at left, if we place a movable plug atop the solution and press down with extra, sufficient pressure, then this added pressure works against the natural dilution. Pure water is forced back through the membrane into the left side. The solution gets more concentrated, while the left side increases in the volume of pure water, as shown at right. As the solution gets more concentrated, it takes more added pressure to have an effect. Nevertheless, this method provides more water on the left side. As a result, this constitutes a purification of water: solvent water from the solution is forced through the membrane as pure water.



This process is operated on huge scales to provide drinkable water from a nondrinkable source. Reverse osmosis is one desalination method which is used to purify brackish water and seawater. Historically, evaporation methods accounted for most global desalination efforts but reverse osmosis has been growing in use tremendously. In these applications, the goal is "pure enough", which means reducing the concentration of salts down to potable and palatable levels. In many arid lands which are located near seawater, large desalination plants provide drinking water. There are also applications such as submarines which use reverse osmosis.

So why can't you drink seawater by itself? It will dry you out. This relates to the impact of osmosis on the extremely small scales. Small in size, but huge in consequences.

Cell membranes are actually semipermeable; they are permeable to a variety of substances (but not all), either directly through the bilayer or through the various channels which are built into the bilayer (as mentioned in Chapter 40). The water inside your cells exchanges with water outside your cells. The water inside your cells has a wide variety of salts, sugars, proteins, etc. dissolved in it. Likewise, the water outside your cells, such as in your blood, also has a wide variety of salts, sugars, proteins, etc. dissolved in it, although they may not be the same salts, sugars, proteins, etc. or they may be at different concentrations of the individual components. In order to keep things in osmotic balance, the total concentrations of all solutes must be reasonably close inside and outside the cell.

In biological or physiological applications, the term "tonicity" is used to indicate osmotic balance across a cell membrane. If a cell is placed into an "isotonic" solution, then that solution and the solution inside the cell are in osmotic balance and there will be equal flow of water both ways between them. (The prefix "iso-" again means equal or same, as seen for isoelectronic in Section 24.2.) If a cell is placed into a "hypotonic" solution, then that solution is of lower total solute concentration than the solution inside the



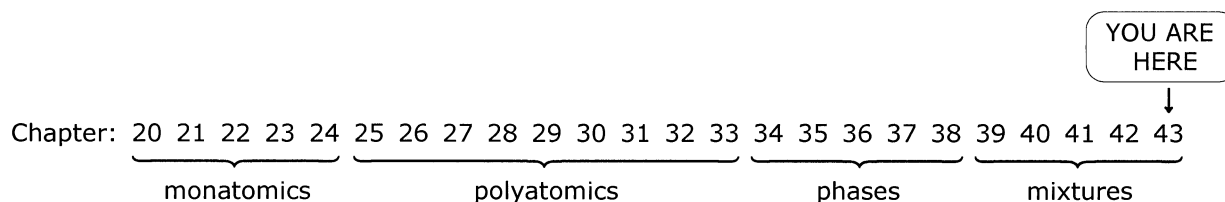
cell. (The "hypo-" prefix means below or less than.) Under these conditions, the natural tendency is for water to flow from the outside solution (lower concentration of solutes) into the cell (higher concentration of solutes). If excessive, the additional water inside the cell can kill the cell and can cause it to burst open. Conversely, if a cell is placed into a "hypertonic" solution, then that solution is of higher total concentration than the solution inside the cell. (The prefix "hyper-" means over or beyond.) The natural tendency is for water to flow out of the cell, and the cell shrivels. If excessive, the cell can die.

As you can see, osmotic pressure can be a life or death situation. For humans, water balance is very important. Human blood plasma and cellular fluids are in the range of 0.3 M for total solutes. By far, most of the solutes in blood plasma are  $\text{Na}^+$  and  $\text{Cl}^-$  ions (which are counted as dissociated, separate solutes). If you ever receive intravenous fluids in a hospital, then those fluids should be isotonic with blood plasma. Commonly these fluids are NaCl and/or glucose solutions, possibly with some nutrients and some medications thrown in. Even if you're seriously dehydrated, you cannot receive much pure water intravenously because it would dilute your plasma and render it hypotonic. That could rupture your blood cells which could kill you. As an opposite effect, this is why drinking a lot of seawater can be harmful. The ionic solutes in seawater (mostly  $\text{Na}^+$  and  $\text{Cl}^-$  again) exceed 1 M, far too hypertonic for your system. Your cells and body fluids would lose water and you dehydrate. That's somewhat of an irony: you dehydrate by drinking seawater.

With this we close out on colligatives. In fact, we close out on a tremendous journey.

### 43.5 The journey never really ends.

After 24 chapters, we reach the end of this particular journey which has dealt with the study of matter itself.



It has been a long journey. We began with the single atom, starting with humble H and its one electron, and then progressing into multi-electron systems. Then we bonded, forming the wide diversity of polyatomic things covalent, ionic and metallic, and which range from simple linears through octahedral, all with their various hybrid (or not) orbitals or with their bonding and antibonding MOs. Then we came up to the observable scale by allowing IFs to kick in between molecules, thus resulting in liquid and solid phases. Finally, we saw why different compounds mix and we saw why some compounds refuse to mix. This journey has been all about matter. Your matter. My matter. The matter of the universe. From the simplest atom to some of the basics of life itself.

But the travels are not over. As noted at the end of Chapter 40, the next journey has already started. The trails have overlapped since Chapter 34 when we addressed entropy and its role alongside that of enthalpy in determining phases and then mixtures. The continuation of this journey takes us further into aspects dealing with enthalpy and entropy, applying these now to any process, including chemical reactions. We have some fundamental questions to address along the way.

### Problems

- True or false.
  - The EVP of 1 m  $\text{KBr}(aq)$  is greater than the EVP of pure water.
  - A solution of sugar water has a lower boiling point than pure water.
  - When salt water freezes, only the water actually freezes.
  - Reverse osmosis can be used to purify water.
- What is the freezing point depression for a solution of 3.87 g of urea,  $(\text{NH}_2)_2\text{CO}$ , in 100. g  $\text{H}_2\text{O}$ ?

3. The molar mass of an unknown is determined by the following. 0.749 g of the unknown is dissolved in 15.0 g benzene,  $C_6H_6$ . This solution freezes at 2.83 °C. What is the molar mass (in g/mol) of the unknown?
4. An osmotic pressure measurement was done on a solution of a protein in order to determine its molar mass. The solution contained 47.0 mg of protein in 24.0 mL solution; the osmotic pressure was 2.1 Torr at 27 °C. What is the molar mass (in g/mol)?