

4.5: Colligative Properties

Learning Objectives

- Express concentrations of solution components using mole fraction and molality
- Describe the effect of solute concentration on various solution properties (vapor pressure, boiling point, freezing point, and osmotic pressure)
- Perform calculations using the mathematical equations that describe these various colligative effects
- Describe the process of distillation and its practical applications
- Explain the process of osmosis and describe how it is applied industrially and in nature

The properties of a solution are different from those of either the pure solute(s) or solvent. Many solution properties are dependent upon the chemical identity of the solute. Compared to pure water, a solution of hydrogen chloride is more acidic, a solution of ammonia is more basic, a solution of sodium chloride is more dense, and a solution of sucrose is more viscous. There are a few solution properties, however, that depend *only* upon the total concentration of solute species, regardless of their identities. These colligative properties include vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure. This small set of properties is of central importance to many natural phenomena and technological applications, as will be described in this module.

Mole Fraction and Molality

Several units commonly used to express the concentrations of solution components were introduced in an earlier chapter of this text, each providing certain benefits for use in different applications. For example, molarity (M) is a convenient unit for use in stoichiometric calculations, since it is defined in terms of the molar amounts of solute species:

$$M = \frac{\text{mol solute}}{\text{L solution}} \quad (4.5.1)$$

Because solution volumes vary with temperature, molar concentrations will likewise vary. When expressed as molarity, the concentration of a solution with identical numbers of solute and solvent species will be different at different temperatures, due to the contraction/expansion of the solution. More appropriate for calculations involving many colligative properties are mole-based concentration units whose values are not dependent on temperature. Two such units are *mole fraction* (introduced in the previous chapter on gases) and *molality*.

The mole fraction, χ , of a component is the ratio of its molar amount to the total number of moles of all solution components:

$$\chi_A = \frac{\text{mol A}}{\text{total mol of all components}} \quad (4.5.2)$$

Molality is a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms:

$$m = \frac{\text{mol solute}}{\text{kg solvent}} \quad (4.5.3)$$

Since these units are computed using only masses and molar amounts, they do not vary with temperature and, thus, are better suited for applications requiring temperature-independent concentrations, including several colligative properties, as will be described in this chapter module.

✓ Example 4.5.1: Calculating Mole Fraction and Molality

The antifreeze in most automobile radiators is a mixture of equal volumes of ethylene glycol and water, with minor amounts of other additives that prevent corrosion. What are the (a) mole fraction and (b) molality of ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$, in a solution prepared from 2.22×10^3 g of ethylene glycol and 2.00×10^3 g of water (approximately 2 L of glycol and 2 L of water)?

Solution

(a) The mole fraction of ethylene glycol may be computed by first deriving molar amounts of both solution components and then substituting these amounts into the unit definition.

$$\begin{aligned}\text{mol C}_2\text{H}_4(\text{OH})_2 &= 2220 \text{ g} \times \frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g C}_2\text{H}_4(\text{OH})_2} = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2 \\ \text{mol H}_2\text{O} &= 2000 \text{ g} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} = 111 \text{ mol H}_2\text{O} \\ \chi_{\text{ethylene glycol}} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{(35.8 + 111) \text{ mol total}} = 0.245\end{aligned}$$

Notice that mole fraction is a dimensionless property, being the ratio of properties with identical units (moles).

(b) To find molality, we need to know the moles of the solute and the mass of the solvent (in kg).

First, use the given mass of ethylene glycol and its molar mass to find the moles of solute:

$$2220 \text{ g C}_2\text{H}_4(\text{OH})_2 \left(\frac{1 \text{ mol C}_2\text{H}_4(\text{OH})_2}{62.07 \text{ g}} \right) = 35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2$$

Then, convert the mass of the water from grams to kilograms:

$$2000 \text{ g H}_2\text{O} \left(\frac{1 \text{ kg}}{1000 \text{ g}} \right) = 2 \text{ kg H}_2\text{O}$$

Finally, calculate molality per its definition:

$$\begin{aligned}\text{molality} &= \frac{\text{mol solute}}{\text{kg solvent}} \\ \text{molality} &= \frac{35.8 \text{ mol C}_2\text{H}_4(\text{OH})_2}{2 \text{ kg H}_2\text{O}} \\ \text{molality} &= 17.9 \text{ m}\end{aligned}$$

? Exercise 4.5.1

What are the mole fraction and molality of a solution that contains 0.850 g of ammonia, NH_3 , dissolved in 125 g of water?

Answer

$$7.14 \times 10^{-3}; 0.399 \text{ m}$$

✓ Example 4.5.2: Converting Mole Fraction and Molal Concentrations

Calculate the mole fraction of solute and solvent in a 3.0 *m* solution of sodium chloride.

Solution

Converting from one concentration unit to another is accomplished by first comparing the two unit definitions. In this case, both units have the same numerator (moles of solute) but different denominators. The provided molal concentration may be written as:

$$\frac{3.0 \text{ mol NaCl}}{1.0 \text{ kg H}_2\text{O}}$$

The numerator for this solution's mole fraction is, therefore, 3.0 mol NaCl. The denominator may be computed by deriving the molar amount of water corresponding to 1.0 kg

$$1.0 \text{ kg H}_2\text{O} \left(\frac{1000 \text{ g}}{1 \text{ kg}} \right) \left(\frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g}} \right) = 55 \text{ mol H}_2\text{O}$$

and then substituting these molar amounts into the definition for mole fraction.

$$X_{\text{H}_2\text{O}} = \frac{\text{mol H}_2\text{O}}{\text{mol NaCl} + \text{mol H}_2\text{O}}$$

$$X_{\text{H}_2\text{O}} = \frac{55 \text{ mol H}_2\text{O}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}}$$

$$X_{\text{H}_2\text{O}} = 0.95$$

$$X_{\text{NaCl}} = \frac{\text{mol NaCl}}{\text{mol NaCl} + \text{mol H}_2\text{O}}$$

$$X_{\text{NaCl}} = \frac{3.0 \text{ mol NaCl}}{3.0 \text{ mol NaCl} + 55 \text{ mol H}_2\text{O}}$$

$$X_{\text{NaCl}} = 0.052$$

? Exercise 4.5.2

The mole fraction of iodine, I_2 , dissolved in dichloromethane, CH_2Cl_2 , is 0.115. What is the molal concentration, m , of iodine in this solution?

Answer

1.50 m

Vapor Pressure Lowering

As described in the chapter on liquids and solids, the equilibrium vapor pressure of a liquid is the pressure exerted by its gaseous phase when vaporization and condensation are occurring at equal rates:



Dissolving a nonvolatile substance in a volatile liquid results in a lowering of the liquid's vapor pressure. This phenomenon can be rationalized by considering the effect of added solute molecules on the liquid's vaporization and condensation processes. To vaporize, solvent molecules must be present at the surface of the solution. The presence of solute decreases the surface area available to solvent molecules and thereby reduces the rate of solvent vaporization. Since the rate of condensation is unaffected by the presence of solute, the net result is that the vaporization-condensation equilibrium is achieved with fewer solvent molecules in the vapor phase (i.e., at a lower vapor pressure) (Figure 4.5.1). While this kinetic interpretation is useful, it does not account for several important aspects of the colligative nature of vapor pressure lowering. A more rigorous explanation involves the property of *entropy*, a topic of discussion in a later text chapter on thermodynamics. For purposes of understanding the lowering of a liquid's vapor pressure, it is adequate to note that the greater entropy of a solution in comparison to its separate solvent and solute serves to effectively stabilize the solvent molecules and hinder their vaporization. A lower vapor pressure results, and a correspondingly higher boiling point as described in the next section of this module.

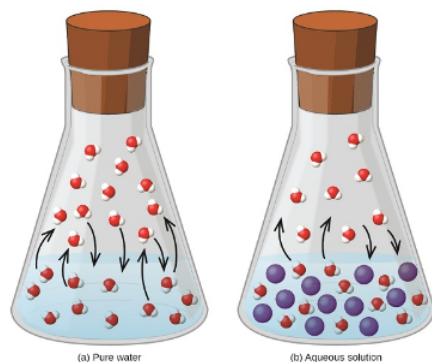


Figure 4.5.1: The presence of nonvolatile solutes lowers the vapor pressure of a solution by impeding the evaporation of solvent molecules.

This figure contains two images. Figure a is labeled “pure water.” It shows a beaker half-filled with liquid. In the liquid, eleven molecules are evenly dispersed in the liquid each consisting of one central red sphere and two slightly smaller white spheres are

shown. Four molecules near the surface of the liquid have curved arrows drawn from them pointing to the space above the liquid in the beaker. Above the liquid, twelve molecules are shown, with arrows pointing from three of them into the liquid below. Figure b is labeled “Aqueous solution.” It is similar to figure a except that eleven blue spheres, slightly larger in size than the molecules, are dispersed evenly in the liquid. Only four curved arrows appear in this diagram with two from the molecules in the liquid pointing to the space above and two from molecules in the space above the liquid pointing into the liquid below.

The relationship between the vapor pressures of solution components and the concentrations of those components is described by Raoult’s law: *The partial pressure exerted by any component of an ideal solution is equal to the vapor pressure of the pure component multiplied by its mole fraction in the solution.*

$$P_A = X_A P_A^\circ \quad (4.5.5)$$

where P_A is the partial pressure exerted by component A in the solution, P_A° is the vapor pressure of pure A, and X_A is the mole fraction of A in the solution. (Mole fraction is a concentration unit introduced in the chapter on gases.)

Recalling that the total pressure of a gaseous mixture is equal to the sum of partial pressures for all its components (Dalton’s law of partial pressures), the total vapor pressure exerted by a solution containing i components is

$$P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ \quad (4.5.6)$$

A nonvolatile substance is one whose vapor pressure is negligible ($P^\circ \approx 0$), and so the vapor pressure above a solution containing only nonvolatile solutes is due only to the solvent:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ \quad (4.5.7)$$

✓ Example 4.5.3: Calculation of a Vapor Pressure

Compute the vapor pressure of an ideal solution containing 92.1 g of glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$, and 184.4 g of ethanol, $\text{C}_2\text{H}_5\text{OH}$, at 40 °C. The vapor pressure of pure ethanol is 0.178 atm at 40 °C. Glycerin is essentially nonvolatile at this temperature.

Solution

Since the solvent is the only volatile component of this solution, its vapor pressure may be computed per Raoult’s law as:

$$P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$$

First, calculate the molar amounts of each solution component using the provided mass data.

$$92.1 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3 \times \frac{1 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3}{92.094 \text{ g } \text{C}_3\text{H}_5(\text{OH})_3} = 1.00 \text{ mol } \text{C}_3\text{H}_5(\text{OH})_3$$

$$184.4 \text{ g } \text{C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol } \text{C}_2\text{H}_5\text{OH}}{46.069 \text{ g } \text{C}_2\text{H}_5\text{OH}} = 4.000 \text{ mol } \text{C}_2\text{H}_5\text{OH}$$

Next, calculate the mole fraction of the solvent (ethanol) and use Raoult’s law to compute the solution’s vapor pressure.

$$X_{\text{C}_2\text{H}_5\text{OH}} = \frac{4.000 \text{ mol}}{(1.00 \text{ mol} + 4.000 \text{ mol})} = 0.800$$

$$P_{\text{solv}} = X_{\text{solv}} P_{\text{solv}}^\circ = 0.800 \times 0.178 \text{ atm} = 0.142 \text{ atm}$$

? Exercise 4.5.3

A solution contains 5.00 g of urea, $\text{CO}(\text{NH}_2)_2$ (a nonvolatile solute) and 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?

Answer

23.4 torr

Elevation of the Boiling Point of a Solvent

As described in the chapter on liquids and solids, the *boiling point* of a liquid is the temperature at which its vapor pressure is equal to ambient atmospheric pressure. Since the vapor pressure of a solution is lowered due to the presence of nonvolatile solutes, it stands to reason that the solution's boiling point will subsequently be increased. Compared to pure solvent, a solution, therefore, will require a higher temperature to achieve any given vapor pressure, including one equivalent to that of the surrounding atmosphere. The increase in boiling point observed when nonvolatile solute is dissolved in a solvent, ΔT_b , is called boiling point elevation and is directly proportional to the molal concentration of solute species:

$$\Delta T_b = K_b m \quad (4.5.8)$$

where

- K_b is the boiling point elevation constant, or the *ebullioscopic constant* and
- m is the molal concentration (molality) of all solute species.

Boiling point elevation constants are characteristic properties that depend on the identity of the solvent. Values of K_b for several solvents are listed in Table 4.5.1.

Table 4.5.1: Boiling Point Elevation and Freezing Point Depression Constants for Several Solvents

Solvent	Boiling Point (°C at 1 atm)	K_b (Cm ⁻¹)	Freezing Point (°C at 1 atm)	K_f (Cm ⁻¹)
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	-63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

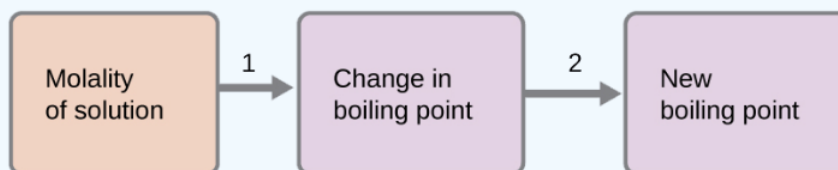
The extent to which the vapor pressure of a solvent is lowered and the boiling point is elevated depends on the total number of solute particles present in a given amount of solvent, not on the mass or size or chemical identities of the particles. A 1 *m* aqueous solution of sucrose (342 g/mol) and a 1 *m* aqueous solution of ethylene glycol (62 g/mol) will exhibit the same boiling point because each solution has one mole of solute particles (molecules) per kilogram of solvent.

✓ Example 4.5.4: Calculating the Boiling Point of a Solution

What is the boiling point of a 0.33 *m* solution of a nonvolatile solute in benzene?

Solution

Use the equation relating boiling point elevation to solute molality to solve this problem in two steps.



$$1. \Delta T_b = K_b m = 2.53 \text{ } ^\circ\text{C } m^{-1} \times 0.33 \text{ } m = 0.83 \text{ } ^\circ\text{C}$$

- Add the boiling point elevation to the pure solvent's boiling point.

$$\text{Boiling temperature} = 80.1 \text{ } ^\circ\text{C} + 0.83 \text{ } ^\circ\text{C} = 80.9 \text{ } ^\circ\text{C}$$

? Exercise 4.5.4

What is the boiling point of the antifreeze described in Example 4.5.4?

Answer

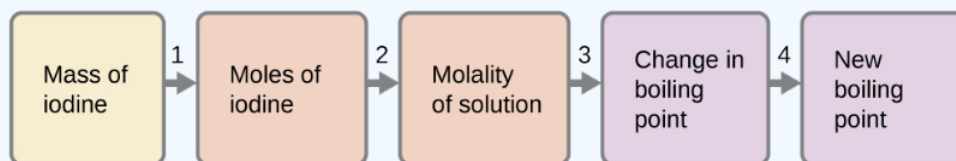
109.2 °C

✓ Example 4.5.5: The Boiling Point of an Iodine Solution

Find the boiling point of a solution of 92.1 g of iodine, I_2 , in 800.0 g of chloroform, $CHCl_3$, assuming that the iodine is nonvolatile and that the solution is ideal.

Solution

We can solve this problem using four steps.



1. Convert from grams to moles of I_2 using the molar mass of I_2 in the unit conversion factor.

Result: 0.363 mol

Determine the molality of the solution from the number of moles of solute and the mass of solvent, in kilograms.

Result: 0.454 m

Use the direct proportionality between the change in boiling point and molal concentration to determine how much the boiling point changes.

Result: 1.65 °C

Determine the new boiling point from the boiling point of the pure solvent and the change.

Result: 62.91 °C

Check each result as a self-assessment.

? Exercise 4.5.5: glycerin:Water Solution

What is the boiling point of a solution of 1.0 g of glycerin, $C_3H_5(OH)_3$, in 47.8 g of water? Assume an ideal solution.

Answer

100.12 °C

Distillation of Solutions

Distillation is a technique for separating the components of mixtures that is widely applied in both in the laboratory and in industrial settings. It is used to refine petroleum, to isolate fermentation products, and to purify water. This separation technique involves the controlled heating of a sample mixture to selectively vaporize, condense, and collect one or more components of interest. A typical apparatus for laboratory-scale distillations is shown in Figure 4.5.2.

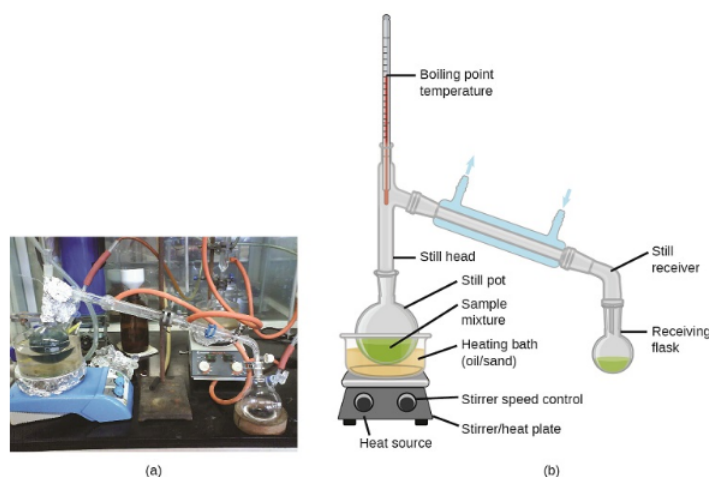


Figure 4.5.2: A typical laboratory distillation unit is shown in (a) a photograph and (b) a schematic diagram of the components. (credit a: modification of work by “Rifleman82”/Wikimedia commons; credit b: modification of work by “Slashme”/Wikimedia Commons) Figure a contains a photograph of a common laboratory distillation unit. Figure b provides a diagram labeling typical components of a laboratory distillation unit, including a stirrer/heat plate with heat and stirrer speed control, a heating bath of oil or sand, stirring means such as boiling chips, a still pot, a still head, a thermometer for boiling point temperature reading, a condenser with a cool water inlet and outlet, a still receiver with a vacuum or gas inlet, a receiving flask for holding distillate, and a cooling bath.

Oil refineries use large-scale *fractional distillation* to separate the components of crude oil. The crude oil is heated to high temperatures at the base of a tall *fractionating column*, vaporizing many of the components that rise within the column. As vaporized components reach adequately cool zones during their ascent, they condense and are collected. The collected liquids are simpler mixtures of hydrocarbons and other petroleum compounds that are of appropriate composition for various applications (e.g., diesel fuel, kerosene, gasoline), as depicted in Figure 4.5.3.

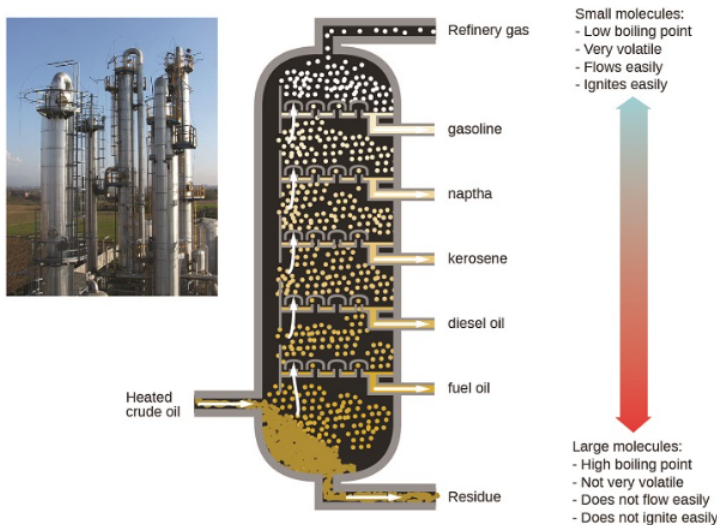


Figure 4.5.3: Crude oil is a complex mixture that is separated by large-scale fractional distillation to isolate various simpler mixtures. This figure contains a photo of a refinery, showing large columnar structures. A diagram of a fractional distillation column used in separating crude oil is also shown. Near the bottom of the column, an arrow pointing into the column shows a point of entry for heated crude oil. The column contains several layers at which different components are removed. At the very bottom, residue materials are removed as indicated by an arrow out of the column. At each successive level, different materials are removed proceeding from the bottom to the top of the column. The materials are fuel oil, followed by diesel oil, kerosene, naptha, gasoline, and refinery gas at the very top. To the right of the column diagram, a double sided arrow is shown that is blue at the top and gradually changes color to red moving downward. The blue top of the arrow is labeled, “small molecules: low boiling point, very

volatile, flows easily, ignites easily.” The red bottom of the arrow is labeled, “large molecules: high boiling point, not very volatile, does not flow easily, does not ignite easily.”

Depression of the Freezing Point of a Solvent

Solutions freeze at lower temperatures than pure liquids. This phenomenon is exploited in “de-icing” schemes that use salt (Figure 4.5.4), calcium chloride, or urea to melt ice on roads and sidewalks, and in the use of ethylene glycol as an “antifreeze” in automobile radiators. Seawater freezes at a lower temperature than fresh water, and so the Arctic and Antarctic oceans remain unfrozen even at temperatures below 0 °C (as do the body fluids of fish and other cold-blooded sea animals that live in these oceans).



Figure 4.5.4 Rock salt (NaCl), calcium chloride (CaCl₂), or a mixture of the two are used to melt ice. (credit: modification of work by Eddie Welker)

The decrease in freezing point of a dilute solution compared to that of the pure solvent, ΔT_f , is called the freezing point depression and is directly proportional to the molal concentration of the solute

$$\Delta T_f = K_f m \quad (4.5.9)$$

where

- m is the *molal* concentration of the solute in the solvent and
- K_f is called the freezing point depression constant (or *cryoscopic constant*).

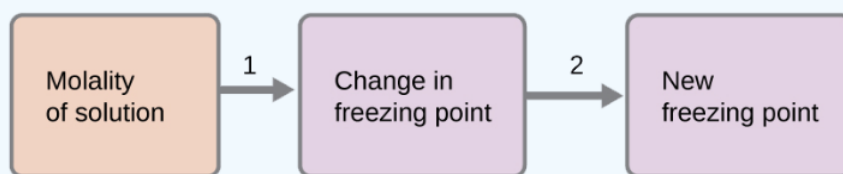
Just as for boiling point elevation constants, these are characteristic properties whose values depend on the chemical identity of the solvent. Values of K_f for several solvents are listed in Table 4.5.1.

✓ Example 4.5.5: Calculation of the Freezing Point of a Solution

What is the freezing point of the 0.33 m solution of a nonvolatile nonelectrolyte solute in benzene described in Example 4.5.4?

Solution

Use the equation relating freezing point depression to solute molality to solve this problem in two steps.



1. Calculate the change in freezing point. $\Delta T_f = K_f m = 5.12^\circ\text{C} \cdot m^{-1} \times 0.33\text{ } m = 1.7^\circ\text{C}$
2. Subtract the freezing point change observed from the pure solvent's freezing point.

$$\text{Freezing Temperature} = 5.5^\circ\text{C} - 1.7^\circ\text{C} = 3.8^\circ\text{C}$$

? Exercise 4.5.6

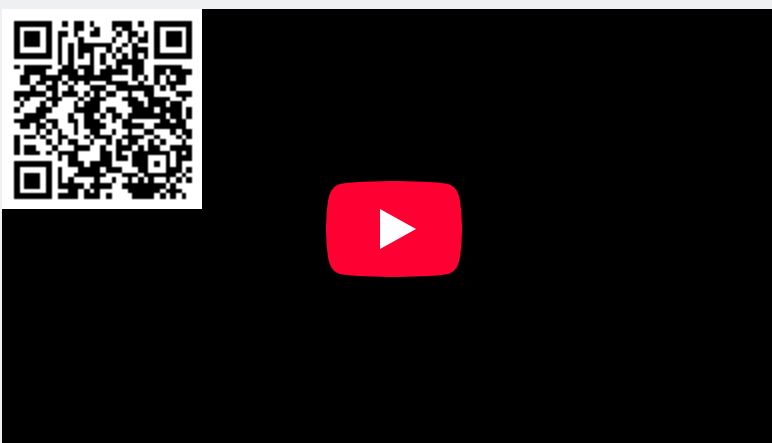
What is the freezing point of a 1.85 m solution of a nonvolatile nonelectrolyte solute in nitrobenzene?

Answer

Colligative Properties and De-Icing

Sodium chloride and its group 2 analogs calcium and magnesium chloride are often used to de-ice roadways and sidewalks, due to the fact that a solution of any one of these salts will have a freezing point lower than 0 °C, the freezing point of pure water. The group 2 metal salts are frequently mixed with the cheaper and more readily available sodium chloride ("rock salt") for use on roads, since they tend to be somewhat less corrosive than the NaCl, and they provide a larger depression of the freezing point, since they dissociate to yield three particles per formula unit, rather than two particles like the sodium chloride.

Because these ionic compounds tend to hasten the corrosion of metal, they would not be a wise choice to use in antifreeze for the radiator in your car or to de-ice a plane prior to takeoff. For these applications, covalent compounds, such as ethylene or propylene glycol, are often used. The glycols used in radiator fluid not only lower the freezing point of the liquid, but they elevate the boiling point, making the fluid useful in both winter and summer. Heated glycols are often sprayed onto the surface of airplanes prior to takeoff in inclement weather in the winter to remove ice that has already formed and prevent the formation of more ice, which would be particularly dangerous if formed on the control surfaces of the aircraft (Video 4.5.1).



Video 4.5.1: Freezing point depression is exploited to remove ice from the control surfaces of aircraft.

Phase Diagram for an Aqueous Solution of a Nonelectrolyte

The colligative effects on vapor pressure, boiling point, and freezing point described in the previous section are conveniently summarized by comparing the phase diagrams for a pure liquid and a solution derived from that liquid. Phase diagrams for water and an aqueous solution are shown in Figure 4.5.5.

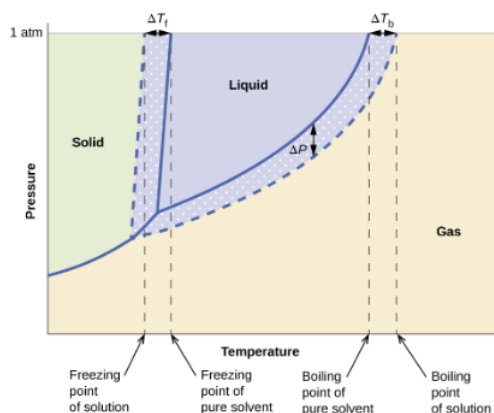


Figure 4.5.5: These phase diagrams show water (solid curves) and an aqueous solution of nonelectrolyte (dashed curves). This phase diagram indicates the pressure in atmospheres of water and a solution at various temperatures. The graph shows the freezing point of water and the freezing point of the solution, with the difference between these two values identified as ΔT_f .

The graph shows the boiling point of water and the boiling point of the solution, with the difference between these two values identified as ΔT_b . Similarly, the difference in the pressure of water and the solution at the boiling point of water is shown and identified as ΔP . This difference in pressure is labeled vapor pressure lowering. The lower level of the vapor pressure curve for the solution as opposed to that of pure water shows vapor pressure lowering in the solution. Background colors on the diagram indicate the presence of water and the solution in the solid state to the left, liquid state in the central upper region, and gas to the right.

The liquid-vapor curve for the solution is located *beneath* the corresponding curve for the solvent, depicting the vapor pressure lowering, ΔP , that results from the dissolution of nonvolatile solute. Consequently, at any given pressure, the solution's boiling point is observed at a higher temperature than that for the pure solvent, reflecting the boiling point elevation, ΔT_b , associated with the presence of nonvolatile solute. The solid-liquid curve for the solution is displaced left of that for the pure solvent, representing the freezing point depression, ΔT_f , that accompanies solution formation. Finally, notice that the solid-gas curves for the solvent and its solution are identical. This is the case for many solutions comprising liquid solvents and nonvolatile solutes. Just as for vaporization, when a solution of this sort is frozen, it is actually just the *solvent* molecules that undergo the liquid-to-solid transition, forming pure solid solvent that excludes solute species. The solid and gaseous phases, therefore, are composed solvent only, and so transitions between these phases are not subject to colligative effects.

Osmosis and Osmotic Pressure of Solutions

A number of natural and synthetic materials exhibit *selective permeation*, meaning that only molecules or ions of a certain size, shape, polarity, charge, and so forth, are capable of passing through (permeating) the material. Biological cell membranes provide elegant examples of selective permeation in nature, while dialysis tubing used to remove metabolic wastes from blood is a more simplistic technological example. Regardless of how they may be fabricated, these materials are generally referred to as semipermeable membranes.

Consider the apparatus illustrated in Figure 4.5.6, in which samples of pure solvent and a solution are separated by a membrane that only solvent molecules may permeate. Solvent molecules will diffuse across the membrane in both directions. Since the concentration of *solvent* is greater in the pure solvent than the solution, these molecules will diffuse from the solvent side of the membrane to the solution side at a faster rate than they will in the reverse direction. The result is a net transfer of solvent molecules from the pure solvent to the solution. Diffusion-driven transfer of solvent molecules through a semipermeable membrane is a process known as osmosis.

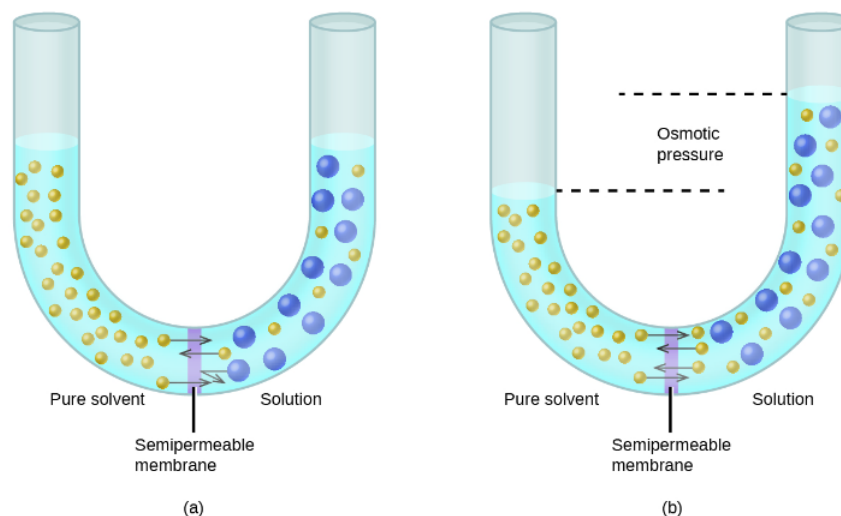


Figure 4.5.6: Osmosis results in the transfer of solvent molecules from a sample of low (or zero) solute concentration to a sample of higher solute concentration. The figure shows two U shaped tubes with a semi permeable membrane placed at the base of the U. In figure a, pure solvent is present and indicated by small yellow spheres to the left of the membrane. To the right, a solution exists with larger blue spheres intermingled with some small yellow spheres. At the membrane, arrows pointing from three small yellow spheres on both sides of the membrane cross over the membrane. An arrow drawn from one of the large blue spheres does not cross the membrane, but rather is reflected back from the surface of the membrane. The levels of liquid in both sides of the U shaped

tube are equal. In figure b, arrows again point from small yellow spheres across the semipermeable membrane from both sides. This diagram shows the level of liquid in the left, pure solvent, side to be significantly lower than the liquid level on the right. Dashed lines are drawn from these two liquid levels into the middle of the U-shaped tube and between them is the term osmotic pressure.

When osmosis is carried out in an apparatus like that shown in Figure 4.5.6, the volume of the solution increases as it becomes diluted by accumulation of solvent. This causes the level of the solution to rise, increasing its hydrostatic pressure (due to the weight of the column of solution in the tube) and resulting in a faster transfer of solvent molecules back to the pure solvent side. When the pressure reaches a value that yields a reverse solvent transfer rate equal to the osmosis rate, bulk transfer of solvent ceases. This pressure is called the osmotic pressure (Π) of the solution. The osmotic pressure of a dilute solution is related to its solute molarity, M , and absolute temperature, T , according to the equation

$$\Pi = MRT \quad (4.5.10)$$

where R is the universal gas constant.

✓ Example 4.5.7: Calculation of Osmotic Pressure

What is the osmotic pressure (atm) of a 0.30 M solution of glucose in water that is used for intravenous infusion at body temperature, 37 °C?

Solution

We can find the osmotic pressure, Π , using Equation 4.5.10, where T is on the Kelvin scale (310 K) and the value of R is expressed in appropriate units (0.08206 L atm/mol K).

$$\begin{aligned} \Pi &= MRT \\ &= 0.30 \text{ mol/L} \times 0.08206 \text{ L atm/mol K} \times 310 \text{ K} \\ &= 7.6 \text{ atm} \end{aligned}$$

? Exercise 4.5.7

What is the osmotic pressure (atm) a solution with a volume of 0.750 L that contains 5.0 g of methanol, CH_3OH , in water at 37 °C?

Answer

5.3 atm

If a solution is placed in an apparatus like the one shown in Figure 4.5.7, applying pressure greater than the osmotic pressure of the solution reverses the osmosis and pushes solvent molecules from the solution into the pure solvent. This technique of reverse osmosis is used for large-scale desalination of seawater and on smaller scales to produce high-purity tap water for drinking.

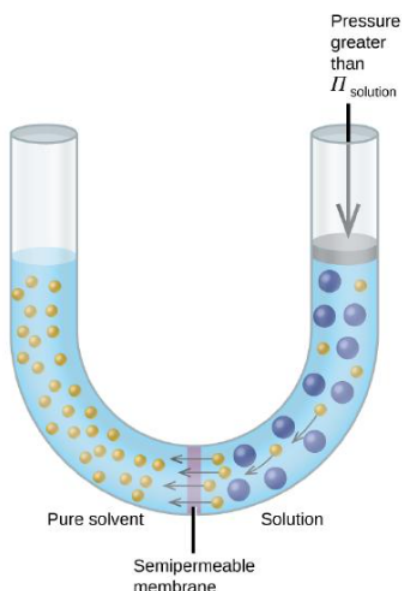


Figure 4.5.7: Applying a pressure greater than the osmotic pressure of a solution will reverse osmosis. Solvent molecules from the solution are pushed into the pure solvent. The figure shows a U shaped tube with a semi permeable membrane placed at the base of the U. Pure solvent is present and indicated by small yellow spheres to the left of the membrane. To the right, a solution exists with larger blue spheres intermingled with some small yellow spheres. At the membrane, arrows point from four small yellow spheres to the left of the membrane. On the right side of the U, there is a disk that is the same width of the tube and appears to block it. The disk is at the same level as the solution. An arrow points down from the top of the tube to the disk and is labeled, “Pressure greater than Π subscript solution.”

Examples of osmosis are evident in many biological systems because cells are surrounded by semipermeable membranes. Carrots and celery that have become limp because they have lost water can be made crisp again by placing them in water. Water moves into the carrot or celery cells by osmosis. A cucumber placed in a concentrated salt solution loses water by osmosis and absorbs some salt to become a pickle. Osmosis can also affect animal cells. Solute concentrations are particularly important when solutions are injected into the body. Solute concentrations in body cell fluids and blood serum give these solutions an osmotic pressure of approximately 7.7 atm. Solutions injected into the body must have the same osmotic pressure as blood serum; that is, they should be isotonic with blood serum. If a less concentrated solution, a hypotonic solution, is injected in sufficient quantity to dilute the blood serum, water from the diluted serum passes into the blood cells by osmosis, causing the cells to expand and rupture. This process is called hemolysis. When a more concentrated solution, a hypertonic solution, is injected, the cells lose water to the more concentrated solution, shrivel, and possibly die in a process called *crenation* (Figure 11.5.8).

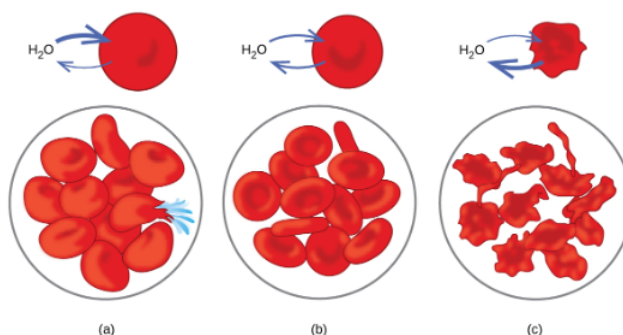


Figure 4.5.8: Red blood cell membranes are water permeable and will (a) swell and possibly rupture in a hypotonic solution; (b) maintain normal volume and shape in an isotonic solution; and (c) shrivel and possibly die in a hypertonic solution. (credit a/b/c: modifications of work by “LadyofHats”/Wikimedia commons) This figure shows three scenarios relating to red blood cell membranes. In a, H_2O has two arrows drawn from it pointing into a red disk. Beneath it in a circle are eleven similar disks with a bulging appearance, one of which appears to have burst with blue liquid erupting from it. In b, the image is similar except that rather than having two arrows pointing into the red disk, one points in and a second points out toward the H_2O

O. In the circle beneath, twelve of the red disks are present. In c, both arrows are drawn from a red shriveled disk toward the H subscript 2 O. In the circle below, twelve shriveled disks are shown.

Determination of Molar Masses

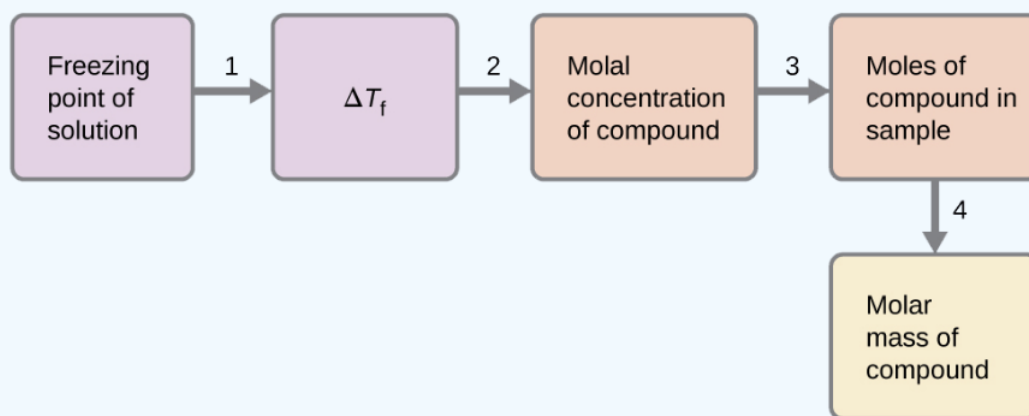
Osmotic pressure and changes in freezing point, boiling point, and vapor pressure are directly proportional to the concentration of solute present. Consequently, we can use a measurement of one of these properties to determine the molar mass of the solute from the measurements.

✓ Example 4.5.8: Determining Molar Mass from Freezing Point Depression

A solution of 4.00 g of a nonelectrolyte dissolved in 55.0 g of benzene is found to freeze at 2.32 °C. What is the molar mass of this compound?

Solution

We can solve this problem using the following steps.



1. Determine the change in freezing point from the observed freezing point and the freezing point of pure benzene (Table 11.5.1). $\Delta T_f = 5.5\text{ }^\circ\text{C} - 2.32\text{ }^\circ\text{C} = 3.2\text{ }^\circ\text{C}$
2. Determine the molal concentration from K_f , the freezing point depression constant for benzene (Table 11.5.1), and ΔT_f .
$$(\Delta T_f = K_f m) m = \frac{\Delta T_f}{K_f} = \frac{3.2\text{ }^\circ\text{C}}{5.12\text{ }^\circ\text{C} m^{-1}} = 0.63\text{ } m$$
3. Determine the number of moles of compound in the solution from the molal concentration and the mass of solvent used to make the solution. $(\text{Moles of solute} = \frac{0.62\text{ mol solute}}{1.00\text{ kg solvent}} \times 0.0550\text{ kg solvent} = 0.034\text{ mol})$
4. Determine the molar mass from the mass of the solute and the number of moles in that mass. $(\text{Molar mass} = \frac{4.00\text{ g}}{0.034\text{ mol}} = 1.2 \times 10^2\text{ g/mol})$

? Exercise 4.5.8

A solution of 35.7 g of a nonelectrolyte in 220.0 g of chloroform has a boiling point of 64.5 °C. What is the molar mass of this compound?

Answer

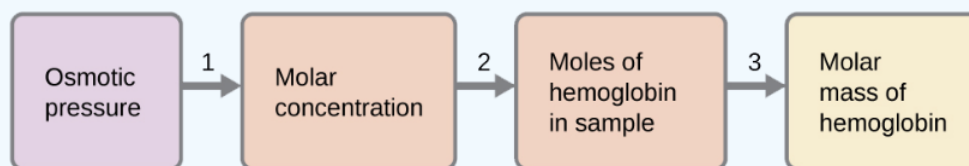
$$1.8 \times 10^2\text{ g/mol}$$

✓ Example 4.5.9: Determination of a Molar Mass from Osmotic Pressure

A 0.500 L sample of an aqueous solution containing 10.0 g of hemoglobin has an osmotic pressure of 5.9 torr at 22 °C. What is the molar mass of hemoglobin?

Solution

Here is one set of steps that can be used to solve the problem:



1. $\Pi = \frac{n}{V}RT$
 $\Pi = \frac{7.8 \times 10^{-3} \text{ atm}}{0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}(295 \text{ K})} = 3.2 \times 10^{-4} \text{ M}$
 $\text{moles of hemoglobin} = 3.2 \times 10^{-4} \text{ mol/L} \times 0.500 \text{ L} = 1.6 \times 10^{-4} \text{ mol}$

2. Determine the molar mass from the mass of hemoglobin and the number of moles in that mass

$$\text{molar mass} = \frac{10.0 \text{ g}}{1.6 \times 10^{-4} \text{ mol}} = 6.2 \times 10^4 \text{ g/mol}$$

? Exercise 4.5.9

What is the molar mass of a protein if a solution of 0.02 g of the protein in 25.0 mL of solution has an osmotic pressure of 0.56 torr at 25 °C?

Answer

$$2.7 \times 10^4 \text{ g/mol}$$

Colligative Properties of Electrolytes

As noted previously in this module, the colligative properties of a solution depend only on the number, not on the kind, of solute species dissolved. For example, 1 mole of any nonelectrolyte dissolved in 1 kilogram of solvent produces the same lowering of the freezing point as does 1 mole of any other nonelectrolyte. However, 1 mole of sodium chloride (an electrolyte) forms 2 moles of ions when dissolved in solution. Each individual ion produces the same effect on the freezing point as a single molecule does.

✓ Example 4.5.10: The Freezing Point of a Solution of an Electrolyte

The concentration of ions in seawater is approximately the same as that in a solution containing 4.2 g of NaCl dissolved in 125 g of water. Assume that each of the ions in the NaCl solution has the same effect on the freezing point of water as a nonelectrolyte molecule, and determine the freezing temperature the solution (which is approximately equal to the freezing temperature of seawater).

Solution

We can solve this problem using the following series of steps.

- Convert from grams to moles of NaCl using the molar mass of NaCl in the unit conversion factor. Result: 0.072 mol NaCl
- Determine the number of moles of ions present in the solution using the number of moles of ions in 1 mole of NaCl as the conversion factor (2 mol ions/1 mol NaCl). Result: 0.14 mol ions
- Determine the molality of the ions in the solution from the number of moles of ions and the mass of solvent, in kilograms. Result: 1.1 m
- Use the direct proportionality between the change in freezing point and molal concentration to determine how much the freezing point changes. Result: 2.0 °C
- Determine the new freezing point from the freezing point of the pure solvent and the change. Result: -2.0 °C

Check each result as a self-assessment.

? Exercise 4.5.10

Assume that each of the ions in calcium chloride, CaCl_2 , has the same effect on the freezing point of water as a nonelectrolyte molecule. Calculate the freezing point of a solution of 0.724 g of CaCl_2 in 175 g of water.

Answer

−0.208 °C

Assuming complete dissociation, a 1.0 *m* aqueous solution of NaCl contains 2.0 mole of ions (1.0 mol Na^+ and 1.0 mol Cl^-) per each kilogram of water, and its freezing point depression is expected to be

$$\Delta T_f = 2.0 \text{ mol ions/kg water} \times 1.86^\circ\text{C kg water/mol ion} = 3.7^\circ\text{C}. \quad (4.5.11)$$

When this solution is actually prepared and its freezing point depression measured, however, a value of 3.4 °C is obtained. Similar discrepancies are observed for other ionic compounds, and the differences between the measured and expected colligative property values typically become more significant as solute concentrations increase. These observations suggest that the ions of sodium chloride (and other strong electrolytes) are not completely dissociated in solution.

To account for this and avoid the errors accompanying the assumption of total dissociation, an experimentally measured parameter named in honor of Nobel Prize-winning German chemist Jacobus Henricus van't Hoff is used. The van't Hoff factor (*i*) is defined as the ratio of solute particles in solution to the number of formula units dissolved:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of formula units dissolved}} \quad (4.5.12)$$

Values for measured van't Hoff factors for several solutes, along with predicted values assuming complete dissociation, are shown in Table 4.5.2.

Table 4.5.2: Expected and Observed van't Hoff Factors for Several 0.050 *m* Aqueous Electrolyte Solutions

Electrolyte	Particles in Solution	<i>i</i> (Predicted)	<i>i</i> (Measured)
HCl	H^+, Cl^-	2	1.9
NaCl	Na^+, Cl^-	2	1.9
MgSO_4	$\text{Mg}^{2+}, \text{SO}_4^{2-}$	2	1.3
MgCl_2	$\text{Mg}^{2+}, 2\text{Cl}^-$	3	2.7
FeCl_3	$\text{Fe}^{3+}, 3\text{Cl}^-$	4	3.4
glucose (a non-electrolyte)	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1	1.0

In 1923, the chemists Peter Debye and Erich Hückel proposed a theory to explain the apparent incomplete ionization of strong electrolytes. They suggested that although interionic attraction in an aqueous solution is very greatly reduced by solvation of the ions and the insulating action of the polar solvent, it is not completely nullified. The residual attractions prevent the ions from behaving as totally independent particles (Figure 4.5.9). In some cases, a positive and negative ion may actually touch, giving a solvated unit called an ion pair. Thus, the activity, or the effective concentration, of any particular kind of ion is less than that indicated by the actual concentration. Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less and less. Thus, in extremely dilute solutions, the effective concentrations of the ions (their activities) are essentially equal to the actual concentrations. Note that the van't Hoff factors for the electrolytes in Table 4.5.2 are for 0.05 *m* solutions, at which concentration the value of *i* for NaCl is 1.9, as opposed to an ideal value of 2.

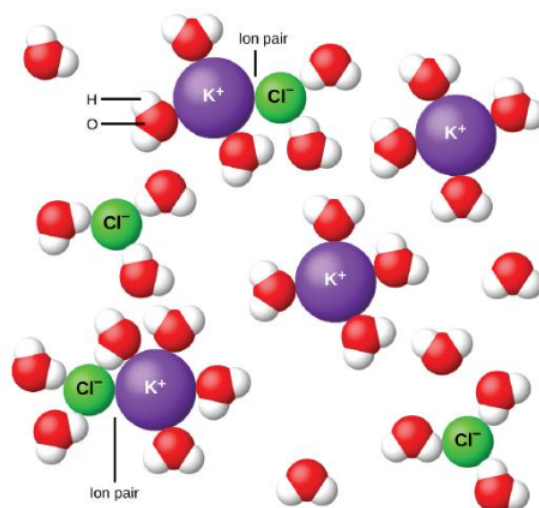


Figure 4.5.9: Ions become more and more widely separated the more dilute the solution, and the residual interionic attractions become less. The diagram shows four purple spheres labeled K^+ and four green spheres labeled Cl^- dispersed in H_2O as shown by clusters of single red spheres with two white spheres attached. Red spheres represent oxygen and white represent hydrogen. In two locations, the purple and green spheres are touching. In these two locations, the diagram is labeled ion pair. All red and green spheres are surrounded by the white and red H_2O clusters. The white spheres are attracted to the purple spheres and the red spheres are attracted to the green spheres.

Summary

Properties of a solution that depend only on the concentration of solute particles are called colligative properties. They include changes in the vapor pressure, boiling point, and freezing point of the solvent in the solution. The magnitudes of these properties depend only on the total concentration of solute particles in solution, not on the type of particles. The total concentration of solute particles in a solution also determines its osmotic pressure. This is the pressure that must be applied to the solution to prevent diffusion of molecules of pure solvent through a semipermeable membrane into the solution. Ionic compounds may not completely dissociate in solution due to activity effects, in which case observed colligative effects may be less than predicted.

Key Equations

- $(P_A = X_A P_A^\circ)$
- $P_{\text{solution}} = \sum_i P_i = \sum_i X_i P_i^\circ$
- $P_{\text{solution}} = X_{\text{solvent}} P_{\text{solvent}}^\circ$
- $\Delta T_b = K_b m$
- $\Delta T_f = K_f m$
- $\Pi = MRT$

Footnotes

1. A nonelectrolyte shown for comparison.

Glossary

boiling point elevation

elevation of the boiling point of a liquid by addition of a solute

boiling point elevation constant

the proportionality constant in the equation relating boiling point elevation to solute molality; also known as the ebullioscopic constant

colligative property

property of a solution that depends only on the concentration of a solute species

crenation

process whereby biological cells become shriveled due to loss of water by osmosis

freezing point depression

lowering of the freezing point of a liquid by addition of a solute

freezing point depression constant

(also, cryoscopic constant) proportionality constant in the equation relating freezing point depression to solute molality

hemolysis

rupture of red blood cells due to the accumulation of excess water by osmosis

hypertonic

of greater osmotic pressure

hypotonic

of less osmotic pressure

ion pair

solvated anion/cation pair held together by moderate electrostatic attraction

isotonic

of equal osmotic pressure

molality (m)

a concentration unit defined as the ratio of the numbers of moles of solute to the mass of the solvent in kilograms

osmosis

diffusion of solvent molecules through a semipermeable membrane

osmotic pressure (Π)

opposing pressure required to prevent bulk transfer of solvent molecules through a semipermeable membrane

Raoult's law

the partial pressure exerted by a solution component is equal to the product of the component's mole fraction in the solution and its equilibrium vapor pressure in the pure state

semipermeable membrane

a membrane that selectively permits passage of certain ions or molecules

van't Hoff factor (i)

the ratio of the number of moles of particles in a solution to the number of moles of formula units dissolved in the solution

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