Analyse
In distillation, lower-boiling components are separated from higher-boiling components (Figure 11.10).

Solve
The lower-boiling components are progressively removed from the distillation mixture during a distillation. This leaves higher-boiling-point components in the vessel yet to be separated and the temperature at which that mixture boils increases.

Think about it
We can understand the process of distillation through Raoult’s law, as described in Section 11.3 and in Figure 11.15.

11.25. Collect and Organize
To calculate the vapor pressure of a mixture of 25 g of methanol and 75 g of ethanol, we can use the knowledge that the total vapor pressure of a mixture of two volatile components is the sum of the products of the individual vapor pressures and the mole fraction of that component in the mixture. We are given the vapor pressures of pure methanol (92 torr) and pure ethanol (45 torr).

Analyze
The total pressure can be calculated by

\[ P_{\text{total}} = x_{\text{methanol}} P^*_{\text{methanol}} + x_{\text{ethanol}} P^*_{\text{ethanol}} \]

where \( P^* \) is the vapor pressure of the pure methanol or ethanol at standard temperature and \( x \) is the mole fraction of each component.

Solve
The moles of each component are

\[ 25 \text{ g} \times \frac{1 \text{ mol}}{32.04 \text{ g}} = 0.780 \text{ mol methanol} \]
\[ 75 \text{ g} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 1.63 \text{ mol ethanol} \]

Total moles = 1.63 + 0.780 = 2.41 mol

The mole fraction of each component is

\[ x_{\text{methanol}} = \frac{0.780 \text{ mol}}{2.41 \text{ mol}} = 0.324 \]
\[ x_{\text{ethanol}} = \frac{1.63 \text{ mol}}{2.41 \text{ mol}} = 0.676 \]

The vapor pressure of the mixture at 20°C is

\[ P_{\text{total}} = (0.324 \times 92 \text{ torr}) + (0.676 \times 45 \text{ torr}) = 60 \text{ torr} \]

Think about it
Because methanol is more volatile than ethanol, the proportion of methanol in the vapor state compared with that of ethanol is greater than the proportion of methanol to ethanol in the liquid state.

11.26. Collect and Organize
From the vapor pressures of octane and heptane at 25°C (11 and 31 torr, respectively) we are asked to calculate the mole ratio of heptane to octane in the vapor state above a 50:50 mixture (mole to mole) of these two volatile liquids.

Analyze
The pressure exerted by each gas in the mixture is calculated from

\[ P_{\text{gas}} = x_{\text{gas}} P^*_{\text{gas}} \]
Solve
The mole fraction of water in the solution is
\[ x = \frac{4.5 \text{ mol}}{4.5 \text{ mol} + 0.3 \text{ mol} + 0.20 \text{ mol}} = 0.90 \]
and the vapor pressure of the solution is
\[ P_{\text{solution}} = 0.90 \times 42.2 \text{ torr} = 38 \text{ torr} \]

Think about it
Because the solution is not pure water, the vapor pressure of the solution is less than that for pure water.

11.39. Collect and Organize
For each solution, we are to calculate the molality.

Analyze
Molality is the number of moles of solute present in 1 kg of solvent.

Solve
(a) \( \frac{0.875 \text{ mol}}{1.5 \text{ kg}} = 0.58 \text{ m glucose} \)
(b) \( \frac{11.5 \text{ mmol}}{65 \text{ g}} \times \frac{1 \text{ mol}}{1000 \text{ mmol}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 0.18 \text{ m acetic acid} \)
(c) \( \frac{0.325 \text{ mol}}{290.0 \text{ g}} \times \frac{1000 \text{ g}}{1 \text{ kg}} = 1.12 \text{ m NaHCO}_3 \)

Think about it
Be sure to express the mass of the solvent in kilograms when calculating molality.

11.40. Collect and Organize
We are to convert the molarities (moles per liter) of the ions in seawater in Table 8.1 to molalities (moles per kilogram), given that the density of seawater is 1.025 g/mL.

Analyze
To convert from molarity to molality, we first need to determine the mass of 1 L of seawater:
\[ 1 \text{ L} \times \frac{1.025 \text{ g}}{\text{mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1025 \text{ g/L}, \text{ or } 1.025 \text{ kg/L} \]
Because molality is the moles of solute divided by the mass (in kilograms) of pure solvent, we have to subtract from the mass of the seawater the total mass of dissolved solids in the seawater. This can be obtained using the data (millimolar) in Table 8.1 to calculate the mass of each ion present in 1 L (1.025 kg) of seawater. The sum of all the masses of the ions in 1 kg of seawater then can be subtracted from the mass of 1 L of seawater to get the mass of pure water in 1 L of seawater. From there we can calculate the molality of each ion by dividing the moles of the ion present in 1 L of seawater (from the millimolar concentrations given) by the mass of pure water in that 1 L of seawater.

Solve
The mass of dissolved solids in 1 L of seawater is as follows:
\[ \text{Na}^+: \frac{0.48057 \text{ mol}}{\text{L}} \times \frac{22.990 \text{ g}}{\text{mol}} = 11.048 \text{ g/L} \]
\[ \text{K}^+: \frac{0.01046 \text{ mol}}{\text{L}} \times \frac{39.098 \text{ g}}{\text{mol}} = 0.4090 \text{ g/L} \]
\[ \text{Mg}^{2+}: \frac{0.05414 \text{ mol}}{\text{L}} \times \frac{24.305 \text{ g}}{\text{mol}} = 1.316 \text{ g/L} \]
\[ \text{Ca}^{2+}: \frac{0.01053 \text{ mol}}{\text{L}} \times \frac{40.078 \text{ g}}{\text{mol}} = 0.4220 \text{ g/L} \]
11.41. Collect and Organize

For each solution of a given molality listed, we are to calculate the mass of the solution that contains 0.100 mol of the solute.

**Analyze**
Because molality is expressed as moles per kilogram, we can calculate the mass of solution required to give 0.100 mol by dividing 0.100 mol by the molality of the solution (or multiplying by the inverse of the molality). This gives the mass of solvent in the solution that also contains 0.100 mol of the solute. For the total solution mass, we have to add the mass of the solute to the mass of the solvent.

**Solve**

(a) \[ 0.100 \text{ mol} \times \frac{1 \text{ kg}}{0.334 \text{ mol}} = 0.299 \text{ kg, or 299 g solvent} \]

\[ 0.100 \text{ mol} \times \frac{80.04 \text{ g}}{1 \text{ mol}} = 8.004 \text{ g NH}_4\text{NO}_3 \]

Total mass of solution = 299 g + 8.004 g = 307 g NH\textsubscript{4}NO\textsubscript{3} solution

(b) \[ 0.100 \text{ mol} \times \frac{1 \text{ kg}}{1.24 \text{ mol}} = 0.0806 \text{ kg, or 80.6 g solvent} \]

\[ 0.100 \text{ mol} \times \frac{62.07 \text{ g}}{1 \text{ mol}} = 6.207 \text{ g ethylene glycol (HOCH}_2\text{CH}_2\text{OH)} \]

Total mass of solution = 80.6 g + 6.207 g = 86.8 g ethylene glycol solution

(c) \[ 0.100 \text{ mol} \times \frac{1 \text{ kg}}{5.65 \text{ mol}} = 0.0177 \text{ kg, or 17.7 g solvent} \]

\[ 0.100 \text{ mol} \times \frac{110.98 \text{ g}}{1 \text{ mol}} = 11.098 \text{ g CaCl}_2 \]

Total mass = 17.7 g + 11.098 g = 28.8 g CaCl\textsubscript{2} solution

**Think about It**
Remember that in molality, the mass of the solvent is used and that the mass of solute must be added to determine the mass of the solution needed.

11.42. Collect and Organize

Using the definition of molality (m) and the mass of the solvent, we can calculate the moles of solute present in each of three solutions.

**Analyze**
The moles of solute can be calculated by multiplying the mass of solvent (in comparable units, kilograms) by the molality of the solution.

**Solve**

(a) \[ 100.0 \text{ kg} \times \frac{0.150 \text{ mol}}{1.00 \text{ kg}} = 15.0 \text{ mol glucose} \]

(b) \[ 1000.0 \text{ g} \times \frac{1.00 \text{ kg}}{1000 \text{ g}} \times \frac{0.028 \text{ mol}}{1.00 \text{ kg}} = 0.028 \text{ mol Na}_2\text{CrO}_4 \]

(c) \[ 500.0 \text{ g} \times \frac{1.00 \text{ kg}}{1000 \text{ g}} \times \frac{0.100 \text{ mol}}{1.00 \text{ kg}} = 0.0500 \text{ mol urea} \]

**Think about It**
Be sure to always convert the mass of the solvent to kilograms before using molality values for calculations.
Think about It
Dissolved elements are often expressed as mass/mass or mass/volume, but the numbers of particles in a mixture are best expressed as moles/mass or moles/volume.

11.45. Collect and Organize
Using the equation for freezing point depression, we can determine the freezing point of a benzene solution of cinnamaldehyde.

Analyze
The change in freezing point of a solution is
\[ \Delta T_f = K_f m \]
where \( K_f \) is the boiling point elevation constant for the solvent and \( m \) is the molality of the solute in the solution. We are given that 75 mg of cinnamaldehyde \((C_9H_{10}O, 132.16 \text{ g/mol})\) is dissolved in 1.00 g \((1.00 \times 10^{-3} \text{ kg})\) of benzene \((K_f = 4.3^\circ C/m\) and normal \( T_b = 5.5^\circ C\)). We have to convert the mass of the cinnamaldehyde to moles by dividing by the molar mass before calculating the molality.

Solve
Molality of cinnamaldehyde solution:
\[
\frac{0.075 \text{ g} \times \frac{1 \text{ mol}}{132.16 \text{ g}}}{1.00 \times 10^{-3} \text{ kg}} = 0.567 \text{ m}
\]
Freezing point depression due to the presence of cinnamaldehyde in the benzene solution is
\[
\Delta T_f = \frac{4.3^\circ C}{m} \times 0.567 \text{ m} = 2.44^\circ C
\]
The freezing point of the solution is
\[
T_{f, \text{solution}} = 5.5^\circ C - 2.44^\circ C = 3.1^\circ C
\]

Think about It
The boiling point of pure CCl₄ is 76.7°C. The boiling point of this cinnamaldehyde solution will be 80.5°C.

11.46. Collect and Organize
Using the equation for boiling point elevation, we can determine the boiling point of a CS₂ solution of oil of spearmint (carvone).

Analyze
The change in boiling point of a solution is
\[ \Delta T_b = K_b m \]
where \( K_b \) is the boiling point elevation constant for the solvent and \( m \) is the molality of the solute in the solution. We are given that 125 mg of carvone \((C_{10}H_{14}O, 150.22 \text{ g/mol})\) is dissolved in 1.50 g \((1.50 \times 10^{-3} \text{ kg})\) of CS₂. We have to convert the mass of the carvone to moles by dividing by the molar mass before calculating the molality.

Solve
Molality of carvone solution:
\[
\frac{0.125 \text{ g} \times \frac{1 \text{ mol}}{150.22 \text{ g}}}{1.50 \times 10^{-3} \text{ kg}} = 0.555 \text{ m}
\]
Boiling point elevation:
\[
\Delta T_b = \frac{2.34^\circ C}{m} \times 0.555 \text{ m} = 1.30^\circ C
\]

Think about It
The boiling point of pure CS₂ is 46°C. The boiling point of this solution of carvone is 47°C.
Solve
The molality of the solution is
\[ 0.186 \, \text{g} \times \frac{1 \, \text{mol}}{183.19 \, \text{g}} = 1.015 \times 10^{-3} \, \text{mol saccharin} \]

The mass of water in solution = 1.00 g, or \( 1.00 \times 10^{-3} \, \text{kg} \)

\[ \text{molality of solution} = \frac{1.015 \times 10^{-3} \, \text{mol}}{1.00 \times 10^{-3} \, \text{kg}} = 1.015 \, \text{m} \]

The freezing point depression of the solution is
\[ \Delta T_f = \frac{1.86 \, ^\circ \text{C}}{m} \times 1.015 \, \text{m} = 1.89 \, ^\circ \text{C} \]

The freezing point of this solution is \( 0.00 \, ^\circ \text{C} - 1.89 \, ^\circ \text{C} = -1.89 \, ^\circ \text{C} \)

Think about it
The freezing point of this solution is noticeably lower than that of pure water.

11.50. Collect and Organize
We are given the molality of an aqueous ethylene glycol solution and the \( K_b \) for water and asked to determine the boiling point of the solution.

Analyze
The boiling point elevation of the solution can be calculated by using
\[ \Delta T_b = K_b m \]

where \( m = 2.50 \, \text{m} \) and \( K_b = 0.52 \, ^\circ \text{C/m} \). Once we know how much the boiling point is elevated, we can add that value to 100.00°C to calculate the new boiling point of the ethylene glycol solution.

Solve
\[ \Delta T_b = 0.52 \, ^\circ \text{C/m} \times 2.50 \, \text{m} = 1.30 \, ^\circ \text{C} \]

The new boiling point of the solution will be 101.3°C.

Think about it
Ethylene glycol is used in car radiators. Its function is to act both as an antifreeze and raise the boiling point of the water in the radiator so it does not boil away as it takes heat away from the engine.

11.51. Collect and Organize
Of the aqueous solutions named, we are to determine which has the lowest freezing point.

Analyze
Freezing point depression is a colligative property and, as such, depends not on the identity of the solute but on the number of particles dissolved in the solution. Molecular substances dissolve as single molecules, so their particle molality is equal to the molality of the solution. Ionic substances, by contrast, dissolve to form two or more particles (ions) in solution; therefore, the molality of particles in solution is a multiple (two times, three times, etc.) of the molality of the salt in the solution.

Solve
Glucose is a molecular solid, so its particle molality in the solution is 0.5 m. Sodium chloride forms \( \text{Na}^+ \) and \( \text{Cl}^- \) in solution, so its particle molality is \( 0.50 \, \text{m} \times 2 = 1.0 \, \text{m} \). Calcium chloride forms \( \text{Ca}^{2+} \) and 2 \( \text{Cl}^- \) in solution, so its particle molality is \( 0.5 \, \text{m} \times 3 = 1.5 \, \text{m} \). The greater the particle molality, the larger the freezing point depression. Therefore, the aqueous solution that has the lowest freezing point is 0.5 m \( \text{CaCl}_2 \).

Think about it
We have to compare not only the molality of the solutions but also the behavior of the substance in the solvent (does it break into ions when dissolved, and how many?) in comparing colligative properties.
11.74. Collect and Organize

From the osmotic pressure of a 75.0 mL aqueous solution prepared from 152 mg of a nonelectrolyte at 27°C, we are to calculate the molarity of the solution and the molar mass of the solute. With the elemental analysis data given, we can then determine the molecular formula.

**Analyze**

We can calculate the molarity from the osmotic pressure by using

\[ M = \frac{\Pi}{iRT} \]

where \( i = 1, \) \( R = 0.0821 \text{ L} \cdot \text{atm/ mol} \cdot \text{K} , \) \( \Pi = 0.328 \text{ atm} , \) and \( T = 300 \text{ K} \). From the molarity, we can calculate the molar mass of the solute:

\[ \text{molar mass of solute (g/mol)} = \frac{\text{mass of solute (g)}}{\text{mol/L of solute} \times \text{volume of solution (L)}} \]

where the mass of solute is 0.152 g and the volume of solute is 0.0750 L. From the elemental analysis, we can determine the empirical formula for the solute, which we can then relate to the molar mass just calculated and therefore write the molecular formula.

**Solve**

\[ M = \frac{0.328 \text{ atm}}{1 \times 0.0821 \text{ L} \cdot \text{atm/ mol} \cdot \text{K} \times 300 \text{ K}} = 0.01332 \text{ M} \]

\[ \text{molar mass} = \frac{0.152 \text{ g}}{0.01332 \text{ mol/L} \times 0.075 \text{ L}} = 152 \text{ g/mol} \]

If we assume 100 g of solute,

\[ 78.90 \text{ g} \times \frac{1 \text{ mol}}{12.011 \text{ g}} = 6.569 \text{ mol C} \]

\[ 10.59 \text{ g} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 10.51 \text{ mol H} \]

\[ 10.51 \text{ g} \times \frac{1 \text{ mol}}{15.999 \text{ g}} = 0.6569 \text{ mol O} \]

This gives a carbon–hydrogen–oxygen molar ratio of 10:16:1 for an empirical formula of C_{10}H_{16}O, with a formula mass of 152.2 g/mol. This matches the measured molar mass as determined from osmotic pressure, so the molecular formula is C_{10}H_{16}O.

**Think about It**

Osmotic pressure is the best colligative property to use to measure molar mass because it is the most sensitive technique.

11.75. Collect and Organize

From the boiling point elevation (2.45°C) of a solution prepared by dissolving 0.111 g of eugenol (a nonelectrolyte) in 1.00 \times 10^{-3} \text{ kg of chloroform (with } K_b = 3.63°C/m), we are to calculate the molar mass of eugenol. With the elemental analysis data provided, we can then determine the molecular formula.

**Analyze**

We can calculate the molality of the solution from the measured boiling point elevation:

\[ m = \frac{\Delta T_b}{K_b} \]

From the molality, we can calculate the molar mass:

\[ \frac{\text{g of eugenol}}{\text{kg of chloroform} \times \text{molality of solution (mol/kg)}} = \frac{\text{g}}{\text{mol}} \]
From the elemental analysis, we can determine the empirical formula of eugenol, which we can then relate to the molar mass to write the molecular formula.

**Solve**

\[
m = \frac{2.45 \degree C}{3.63 \degree C/mol} = 0.6749 \text{ mol/kg}
\]

Molar mass = \( \frac{0.111 \text{ g}}{1.00 \times 10^{-3} \text{ kg} \times 0.6749 \text{ mol/kg}} = 164 \text{ g/mol} \)

From the elemental analysis, if we assume 100 g,

\[
73.17 \text{ g C} \times \frac{1 \text{ mol}}{12.011 \text{ g}} = 6.092 \text{ mol C}
\]

\[
7.32 \text{ g H} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 7.26 \text{ mol H}
\]

\[
19.51 \text{ g O} \times \frac{1 \text{ mol}}{15.999 \text{ g}} = 1.219 \text{ mol O}
\]

This gives a molar ratio of 5C:6H:1O, for an empirical formula of C₅H₆O with a formula mass of 82.10 g/mol. This is one-half the measured molar mass, so the molecular formula of eugenol is C₁₀H₁₅O₂.

**Think about It**
The formula for eugenol is indeed C₁₀H₁₅O₂, and this compound has the following structure:

![Structure of eugenol](image)

11.76. **Collect and Organize**

From the measured freezing point depression of a solution of 0.150 g of caffeine (a nonelectrolyte molecular compound) in 10.0 g of camphor, we are to calculate the molar mass of caffeine. Then, given the mass ratios of C, H, N, and O in caffeine, we can write the molecular formula.

**Analyze**
We can calculate the molality of the caffeine solution by using

\[
m = \frac{\Delta T_f}{iK_f}
\]

where \( i = 1 \), \( \Delta T_f = 3.07 \degree C \), and \( K_f = 39.7 \degree C/mol \). From the molality of the solution, we can calculate the molar mass of caffeine:

\[
\text{molar mass of caffeine (g/mol)} = \frac{\text{mass of caffeine (g)}}{\text{molality of solution (mol/kg)} \times \text{mass of solvent (kg)}}
\]

where the mass of caffeine is 0.150 g and the mass of solvent is 0.0100 kg. From the elemental analysis, we can determine the empirical formula for caffeine, which we can then relate to the molar mass derived from the freezing point depression measurement and then write the molecular formula.

**Solve**

\[
m = \frac{3.07 \degree C}{1 \times 39.7 \degree C/mol} = 0.07733 \text{ mol}
\]

Molar mass = \( \frac{0.150 \text{ g}}{0.07733 \text{ mol/kg} \times 0.0100 \text{ kg}} = 194 \text{ g/mol} \)
If we assume 100 g of caffeine,

\[
49.49 \text{ g} \times \frac{1 \text{ mol}}{12.011 \text{ g}} = 4.120 \text{ mol C}
\]

\[
5.15 \text{ g} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 5.11 \text{ mol H}
\]

\[
28.87 \text{ g} \times \frac{1 \text{ mol}}{14.007 \text{ g}} = 2.061 \text{ mol N}
\]

\[
16.49 \text{ g} \times \frac{1 \text{ mol}}{15.999 \text{ g}} = 1.031 \text{ mol O}
\]

This gives a molar ratio of 4C:5H:2N:10O, for an empirical formula of \( \text{C}_4\text{H}_5\text{N}_2\text{O} \) with a formula mass of 97.1 g/mol. The measured molar mass is 194 g/mol, so the molar mass is twice the formula mass. Therefore, the molecular formula for caffeine is \( \text{C}_8\text{H}_{10}\text{N}_4\text{O}_2 \).

**Think about it**
Given careful measurement of any of the colligative properties of a solution of a solute, we can accurately determine the molar mass of a substance. When that information is coupled with the results of elemental analysis, we can then write the molecular formula. This a powerful technique to characterize new substances prepared or isolated in the laboratory.

11.77. **Collect and Organize**
We consider whether \( \text{CaCl}_2 \) would melt ice at \(-20^\circ\text{C}\). We are given that 70.1 g of \( \text{CaCl}_2 \) (\( i = 2.5 \)) is dissolved in 100.0 g of water at this temperature.

**Analyze**
From the mass of \( \text{CaCl}_2 \) that dissolves in 100.0 g of water, we can compute the molality of the \( \text{CaCl}_2 \) solution. We can then use the freezing point depression equation

\[
\Delta T_f = i K_f m
\]

to calculate \( \Delta T_f \). The \( K_f \) for water is 1.86°C/m. If \( \Delta T_f \) is greater than 20°C, then \( \text{CaCl}_2 \) would melt ice at \(-20^\circ\text{C}\).

**Solve**

\[
\text{molality of CaCl}_2 \text{ solution} = \frac{70.1 \text{ g} \times \frac{1 \text{ mol}}{110.98 \text{ g}}}{0.1000 \text{ kg}} = 6.316 m
\]

Freezing point depression is \( \Delta T_f = 2.5 \times 1.86^\circ\text{C/m} \times 6.316 m = 29^\circ\text{C} \).

The freezing point of the \( \text{CaCl}_2 \) solution would be \(-29^\circ\text{C}\). This is lower than \(-20^\circ\text{C}\). Yes, the \( \text{CaCl}_2 \) could melt ice at \(-20^\circ\text{C}\).

**Think about it**
\( \text{CaCl}_2 \) is an excellent deicer. It gives three particles, ideally, when it dissolves and is very soluble in water, so the \( \Delta T_f \) for a saturated solution of \( \text{CaCl}_2 \) is very large.

11.78. **Collect and Organize**
Using the equation for freezing point depression, we can determine the melting (freezing) point of 12.00 pounds of ice (water) when 2.00 lb of NaCl is dissolved in 6.00 lb of melted ice water. We are also given that the van 't Hoff factor for the solution is 1.44.

**Analyze**
To apply the freezing point depression equation

\[
\Delta T_f = i K_f m
\]

we have to calculate the concentration of NaCl in moles of NaCl per kilogram of melted ice. We need the conversion that 0.454 kg = 1 lb along with the molar mass of NaCl (58.44 g/mol). The \( K_f \) for water is 1.86°C/m.