TOPIC

13

PROPERTIES OF SOLUTIONS

In preparation for the critical quantitative chapters coming up, it is important to have a fundamental understanding of how solution concentrations are expressed and inter-converted mathematically. The colligative properties of solutions, especially vapor pressure lowering, freezing point depression, and boiling point elevation, are often used to calculate the molar mass of compounds. Pay close attention to these sections:

13.4 **Ways of Expressing Concentration**

13.5 **Colligative Properties**

The Solution Process

Section 13.1

A **solution** is formed when one or more substances (the solutes) disperse uniformly throughout the solvent, normally the substance in greatest amount. All of the intermolecular attractive forces discussed in Topic 11 act between solute and solvent particles. For example, ion-dipole interactions are the most common forces of attraction when ionic compounds dissolve in water. The positive end of water dipoles surround anions and cations are attracted to the negative end of the water dipole as shown in Figure 13.1.

A few ionic compounds dissolve exothermically because the ion-dipole forces formed in the solution are greater than the forces required to overcome the ionic bonds of the solid substance. Thermodynamically, exothermic processes tend to be spontaneous.

However, most ionic compounds dissolve endothermically because the energy required to break the ionic bonds is greater than the energy released when the ion-dipole interactions are formed in the solution. The driving force of the solution process is the increase in entropy.

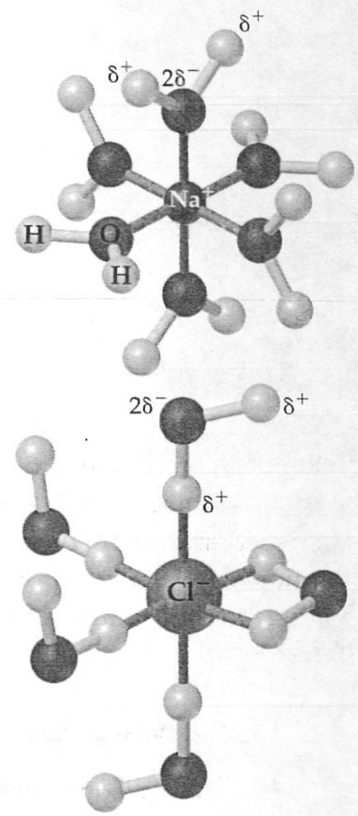

Figure 13.1. Hydrated Na+ and Cl− ions form ion-dipole interactions with water molecules.

Entropy is a state of randomness or disorder of a system. Formation of solutions is favored by the increase in entropy that accompanies mixing. Most processes occur with an increase in entropy.

Your Turn 13.1

Calcium chloride dissolves in water with an increase in temperature of the water. Is this process exothermic or endothermic? Use intermolecular forces to explain. Write your answer in the space provided.

Section 13.2 Saturated Solutions and Solubility

A saturated solution is one in which dissolved solute is in equilibrium with undissolved solute.

Solubility is the amount of solute needed to form a saturated solution in a given amount of solvent. The units of solubility for an aqueous solution are usually grams of solute per 100 milliliters of water, g solute/100 mL water.

An **unsaturated solution** contains less solute than a saturated solution.

A **supersaturated solution** contains more solute than a saturated solution. Supersaturation can be achieved because many substances are more soluble at high temperatures than they are at low temperatures. If a hot, saturated solution is slowly cooled, an unstable supersaturated solution often forms.

Factors Affecting Solubility

Section 13.3

Solubility increases with increasing strength of attractions between solvent and solute particles.

"Like dissolves like." Substances with similar intermolecular attractive forces tend to be soluble in one another. Polar solutes tend to dissolve in polar solvents. Nonpolar solutes tend to dissolve in nonpolar solvents. Polar solvents, because of their relatively strong attractive forces, tend to exclude nonpolar substances and their relatively weak attractive forces.

Miscible liquids are pairs of liquids that dissolve in all proportions.

Immiscible liquids are those that do not dissolve in each other.

Your Turn 13.2

Explain using intermolecular forces why gasoline and water don't mix. Write your answer in the space provided.

Gases tend to be more soluble in liquids at higher pressure and at lower temperature. The solubility of a gas increases in direct proportion to its partial pressure above the solution.

Your Turn 13.3

Why do bubbles appear in a plastic soda bottle when the cap is removed? Write your answer in the space provided.

Section 13.4 Ways of Expressing Concentration

Concentration is the quantity of solute present in a given quantity of solvent or solution. Table 13.1 defines the various ways to express concentration.

Table 13.1. Ways of expressing concentration

Concentration	Abv.	Definition	Example
Mass percent	%	(mass of solute) ÷ (mass of solution) × 100	14.0% aqueous ethanol = 14.0 g ethanol/100 g solution
Parts per million	ppm	10^6 × (mass of solute) ÷ (mass of solution)	18 ppm Pb^{2+} in water = 18 mg Pb^{2+}/1000 g solution
Mole fraction	X	(moles of one component) ÷ (total moles of components)	$X_{NH_3} = 0.10$ (One tenth of all the moles in solution is ammonia.)
Molarity	M	(moles of solute) ÷ (liters of solution)	0.15 M HCl (aq) = 0.15 moles HCl per liter of solution.
Molality	m	(moles of solute) ÷ (kilograms of solvent)	0.20 m NaCl (aq) = 0.20 moles NaCl per kilogram of water.

Section 13.5 Colligative Properties

Colligative properties are physical properties of solutions that depend only on the quantity of solute particles present in the solution and not on the identity of the solute particles. Colligative properties apply to any solution consisting of a volatile solvent and a nonvolatile solute.

A **volatile** substance is one that has a measurable equilibrium vapor pressure. A nonvolatile substance has no measurable vapor pressure.

The colligative properties are:

1. **Vapor Pressure Lowering:** A solution has a lower vapor pressure than does the pure solvent. The vapor pressure is lower because the presence of the nonvolatile solute inhibits the escape of solvent molecules. Figure 13.2 compares the phase diagrams for a pure solvent and a solution.
2. **Boiling Point Elevation:** A solution boils at a higher temperature than a pure solvent. Notice that Figure 13.2 shows that a lower vapor pressure increases the boiling point, the temperature at which the equilibrium vapor pressure equals the external pressure.
3. **Freezing Point Lowering:** A solution freezes at a lower temperature than a pure solvent.

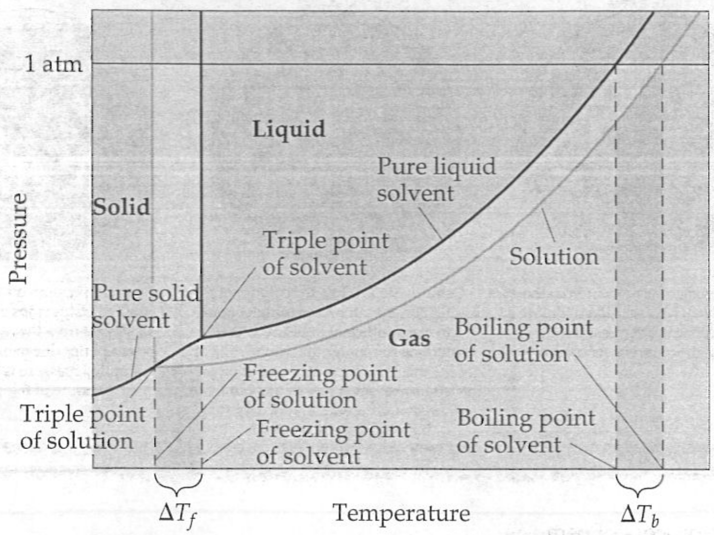

Figure 13.2. Phase diagram for a pure solvent and for a solution of a nonvolatile solute. Notice that the lower vapor pressure of the solution has the effect of increasing the boiling point and decreasing the freezing point.

4. **Osmotic Pressure:** the pressure required to prevent osmosis. Osmosis is the net movement of solvent through a semipermeable membrane toward a solution of higher concentration. See Figure 13.3.

The **Van't Hoff factor,** i, is a measure of the extent to which electrolytes dissociate. The ideal value for i is the number of ions per formula unit. For example, ideal solutions for the salts NaCl, $CaCl_2$, $Al(NO_3)_3$, and $Fe_2(SO_4)_3$ have van't Hoff factors of 2, 3, 4 and 5, respectively. Since colligative properties depend on the number of particles dissolved in a solution, the van't Hoff factor, which accounts for the number of ions in solution, must be considered in any colligative property calculations.

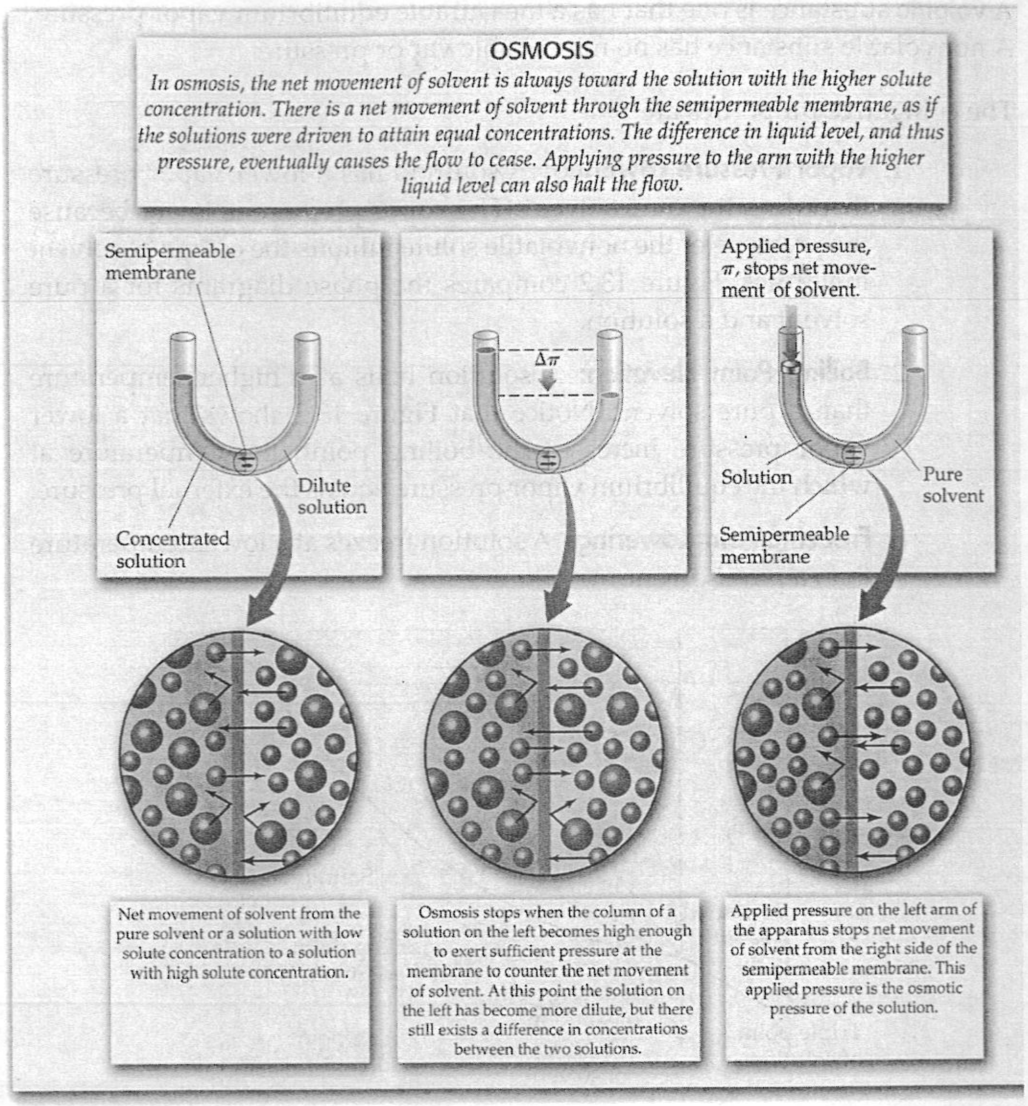

Figure 13.3. The process of osmosis.

Common misconception: The van't Hoff factor is usually less than the predicted factor for ideal solutions of ionic compounds due to ion pairing. Electrostatic forces of attraction between two ions of opposite charge cause them to adhere to one another and behave as a single particle. As a solution concentration decreases, the van't Hoff factor for its electrolytic solute approaches its ideal value.

Table 13.2 shows the quantitative relationships for colligative properties. Notice that each property is directly proportional to the number of moles of solvent or solute particles in the form of mole fraction, molality, or molarity.

Table 13.2. Quantitative relationships for colligative properties

Property	Equation	Explanation of terms
Vapor pressure lowering	$P_{A'} = X_A P°_A$ Raoult's law	$P_{A'}$ = vapor pressure of solution X_A = mole fraction of solvent $P°_A$ = vapor pressure of pure solvent
Freezing point lowering	$\Delta T_f = K_f\, m\, i$	ΔT_f = change in freezing point, °C K_f = freezing point constant, °C/m m = molality of solute, mol solute/kg solvent i = the van't Hoff factor
Boiling point elevation	$\Delta Tb = Kb\, m\, i$	ΔT_b = change in boiling point, °C K_b = boiling point constant, °C/m m = molality of solute, mol solute/kg solvent i = the van't Hoff factor
Osmotic pressure	$\Pi = (n/V)RT$ or $\Pi = MRT$	Π = osmotic pressure in atm (n/V) = M = molarity of solution in mol/L R = 0.0821 L atm/mol K T = absolute temperature in K

Example:

175 grams of calcium chloride are dissolved in 975 g of water. The density of the resulting solution is 1.10 g per milliliter.

a. *What is the vapor pressure of the solution at 25°C? The vapor pressure of pure water at 25°C is 23.76 torr.*

b. *At what temperature will the solution freeze? The freezing point constant for water is 1.86°C/m.*

c. *At what temperature will the solution boil? The boiling point constant for water is 0.51°C/m.*

d. *What will be the osmotic pressure at 27.0°C?*

Solution:

a. *moles of* $CaCl_2 = 175\ g/111\ g/mol = 1.58\ mol\ CaCl_2$.

However, $CaCl_2$ *dissociates into three moles of ions per mole of* $CaCl_2$: $CaCl_2(s) \dashrightarrow Ca^{2+}(aq) + 2Cl^-(aq)$.

The number of moles of ions in solution is three times the number of moles of $CaCl_2$.

Moles ions $= 3 \times 1.58\ mol = 4.74\ mol$.

moles of water $= 975\ g/\ 18.0\ g/mol = 54.2\ mol\ H_2O$.

mole fraction of water = moles of water/total moles $= 54.2\ mol/(54.2 + 4.74)\ mol = 0.920$.

This means that the vapor pressure of this solution is only 92% of the vapor pressure of water.

$P_{A'} = X_A P°_A = 0.920 \times 23.76\ torr = 21.9\ torr$.

b. *The solvent molality, m = moles of ions/kg water* $= 4.74\ mol/0.975\ kg = 4.86\ m$.

(Notice that in Part a, we already have taken into account the van't Hoff factor of 3 for $CaCl_2$.*)*

$\Delta T_f = K_f\ m\ i = (1.86°C/m)(4.86\ m) = 9.04°C$.

The solution will freeze at 9.04°C lower than the freezing point of water: $0.00°C - 9.04°C = -9.04°C$.

c. $\Delta T_b = K_b\ m\ i = (0.51°C/m)(4.86\ m) = 2.48°C$.

The solution will boil at 2.48°C higher than the boiling point of water: $100.00°C + 2.48°C = 102.48°C$.

d. *Total mass of the solution* $= 175\ g\ CaCl_2 + 975\ g\ H_2O = 1150\ g$ *solution.*

The liters of solution = (1150 g solution/1.10 g/mL solution)(1 L /1000 mL) $= 1.05\ L$.

The molarity, M, of the solution = moles of ions/liters of solution $= 4.74/1.05 = 4.51\ M$.

$\Pi = MRT = (4.51\ mol/L)(0.0821\ L\ atm/mol\ K)(273 + 27\ K)$
$\Pi = 111\ atm$.

Note: We have assumed an ideal solution where the van't Hoff factor is three in all cases. The concentration of this solution is such that the true value of the van't Hoff factor is considerably less than three.

Molar Mass Determination

Any of the four colligative properties of solutions can be used to experimentally determine the molar mass of an unknown compound.

Example:

An unknown compound contains only carbon, hydrogen, and oxygen. Combustion analysis of the compound gives mass percents of 31.57% C and 5.30% H. A solution made by dissolving 10.56 g of the compound in 25.0 mL of water freezes at −5.20°C. Determine the empirical formula, molar mass, and molecular formula of the compound. Assume the compound is a nonelectrolyte. The freezing point constant for water is 1.86°C/m.

Solution:

First calculate the empirical formula by converting the percent in grams of each element to moles. The mass % of oxygen = 100% − 31.57% − 5.30% = 63.13% *O.*

$$C_{(31.57\,g)/1(2.0\,g/mol)}H_{(5.30\,g)/(1.00\,g/mol)}O_{(63.13\,g/16.0\,g/mol)} =$$

$$C_{2.63}\,H_{5.30}\,O_{3.95} = C_{(2.63)/(2.63)}\,H_{(5.30)/(2.63)}\,O_{(3.95)/(2.53)}$$

$$= C_1\,H_{2.01}\,O_{1.50} = C_2\,H_4\,O_3$$

Calculate the number of moles by first determining the molality of the solution using the freezing point depression expression.

$$\Delta T_f = K_f\, m\, i$$

$$5.20°C = (1.86°C/m)\, m\, (1)$$

(The value for i is always 1 for nonelectrolytes.)
$m = (5.20°C)/(1.86°C/m) = 2.80$ *moles unknown/Kg water*
Convert molality to moles by multiplying by the number of kilograms of water.
Moles unknown = (2.80 *moles unknown/kg* H_2O)(0.0250 *kg* H_2O) = 0.0700 *mol unknown.*
(The density of water is 1.00 g / mL so 25.0 mL = 25 *g* = 0.0250 *kg.)*
Molar mass = *grams unknown / moles unknown* = 10.56 *g*/0.0700 *mol* = 151 *g/mol*
151 grams per mole is, within significant figures, twice the mass of $C_2H_4O_3$ *so the molecular formula is* $C_4H_8O_6$.

Multiple Choice Questions

1. *Compared to a 1.0 M aqueous solution of glucose, a 1.0 M aqueous solution of calcium chloride will have:*

   A) *The same freezing and boiling points.*

   B) *A lower freezing point and a lower boiling point.*

   C) *A lower freezing point and a higher boiling point.*

   D) *A higher freezing point and a higher boiling point.*

   E) *A higher freezing point and a lower boiling point.*

2. *What is the mass percent of methanol in a solution prepared by adding 32.0 g of methanol to 18.0 grams of water?*

   A) 16.0%

   B) 32.0%

   C) 36.0%

   D) 50.0%

   E) 64.0%

3. *What is the relative order of freezing points of these three substances?*

   I. *water*

   II. *0.1 M aqueous ammonia solution*

   III. *0.1 M aqueous ammonium chloride*

   A) $III < II < I$

   B) $II < III < I$

   C) $II = III < I$

   D) $II < III = I$

   E) $I < II < III$

4. *A one thousand liter sample of water contains one gram of iron (III) ions. What is the concentration of $Fe^{3+}(aq)$ in parts per million?*

   A) 0.001

   B) 0.01

   C) 0.1

   D) 1

   E) 10

5. *Consider a 0.50 M solution of each of the following salts. Which will have the lowest freezing point?*

   A) $NaCl$

   B) $MgCl_2$

   C) K_2SO_4

   D) $Cr(NO_3)_3$

   E) $CaSO_4$

6. *Enough water is added to 11.5 grams of ethanol to make 2.00 liters of solution. What is the molarity of the ethanol?*

   A) 0.125

   B) 0.250

   C) 0.500

   D) 5.75

   E) 0.333

7. *Which pairs of substances will dissolve in each other?*

   I. CH_3OH

   II. C_6H_6

   III. CH_3CH_3

   A) I and II only

   B) II and III only

   C) I and II, I and III, II and III.

   D) I and III only

   E) I and II, II and III only

8. *For a solution containing a nonvolatile solute dissolved in a volatile solvent what is true of the vapor pressure, boiling point, and freezing point of the solution compared to the pure solvent?*

	Vapor pressure	*boiling point*	*freezing point*
A)	increases	increases	increases
B)	decreases	decreases	decreases
C)	increases	decreases	increases
D)	decreases	decreases	increases
E)	decreases	increases	decreases

9. *The freezing point of a 1.0 m aqueous solution of a substance is approximately −5.6°C. Which of these is the most likely substance dissolved in the solution? The molal freezing point constant for water is $-1.86°C\ m^{-1}$.*

   A) CH_3CH_2OH

   B) NaCl

   C) $Ca(NO_3)_2$

   D) C_6H_6

   E) $Al_2(SO_4)_3$

10. *What is the mole fraction of water in a solution that contains 32 grams of methanol in 36 grams of water?*

    A) O.33

    B) 0.50

    C) 0.67

    D) 1.0

    E) 1.1

Free Response Questions

1. *Answer the following questions about these laboratory observations.*

   Solid ammonium chloride dissolves in water with a marked decrease in temperature. Calcium chloride solid dissolves in water with a marked increase in temperature. Little or no temperature change is observed when solid sodium chloride dissolves in water.

   a. *Write an equation that describes the dissolving process of ammonium chloride.*

   b. *Is the dissolving of calcium chloride endothermic or exothermic? Explain.*

   c. *Describe the opposing forces of attraction that are at work in the dissolution of calcium chloride. Which are greater? Why?*

   d. *What can be said about opposing forces of attraction when sodium chloride dissolves in water. Why?*

   e. *Use the observation for ammonium chloride to discuss these seemingly contradictory statements:*

   Thermodynamically, exothermic processes tend to be spontaneous.

   Most processes occur spontaneously when there is an increase in entropy.

2. *The molecular formula of an unknown compound is determined by combustion analysis and freezing point depression. A solution containing 0.496 g of benzoic acid, C_6H_5COOH, and 25.0 g of camphor, $C_{10}H_{16}O$, freezes at 173.3°C. The freezing point of pure camphor is 179.8°C. An unknown molecular compound is found to contain 80.77% C, 3.846% hydrogen and 15.38% oxygen. A solution consisting of 0.243 g of unknown compound and 15.1 grams of camphor melts at 176.7°C.*

   a. *What is the empirical formula of the unknown compound?*
   b. *What is the freezing point constant for camphor? Specify the units.*
   c. *What is the concentration of the unknown compound in camphor in units of molality?*
   d. *What is the molar mass of the unknown compound?*
   e. *What is the molecular formula of the unknown compound?*

Additional Practice in *Chemistry the Central Science*

For more practice answering questions in preparation for the Advanced Placement examination, try these Problems in Chapter 13 of Chemistry the Central Science.

Additional Exercises: 13.93, 13.94, 13.99, 13.101, 13.102

Integrative Exercises: 13.104 a–c, 13.106, 13.107, 13.109 a–b, 13.112.

Multiple Choice Answers and Explanations

1. *C. Solutions freeze at lower temperatures and boil at higher temperatures than their pure solutes. Upon dissolving $CaCl_2$ dissociates into three ions giving it effectively a 3.0 M concentration of ions, whereas glucose is a molecular substance and dissolves intact. Because there are more particles in the $CaCl_2$ solution, it will freeze at a lower temperature and boil at a higher temperature than the glucose solution.*

2. *E. Percent by mass = grams of one substance divided by total grams of solution* = 32.0 *g methanol*/(32.0 *g methanol* + 18.0 *g water*) = 64.0%

3. *A. The freezing point will be the lowest for the solution with the most dissolved particles. Water has no dissolved solute particles. Ammonia, a molecular weak electrolyte, remains 99% intact when it dissolves. Ammonium chloride is a strong electrolyte, which dissociates into two ions per mole when it dissolves.*

4. D. *A part per million is one milligram of solute per liter of solution. One gram of Fe^{3+} is 1000 milligrams of Fe^{3+}. 1000 mg $Fe^{3+}/1000$ L water = 1 mg/L = 1 ppm Fe^{3+}.*

5. D. *The freezing point lowering is proportional to the number of particles dissolved in solution. All of these ionic compounds are strong electrolytes. However, chromium(III) nitrate dissociates into four ion per mole, the most of any of the choices.*

6. A. *Molarity is moles of solute per liter of solution. Ethanol is CH_3CH_2OH and has a molar mass of 46.0 g/mol which is four times 11.5. M = (11.5 g ethanol)/(46.0 g/mol) ÷ 2 L = 0.125 M.*

7. B. *Substances with similar intermolecular attractive forces will dissolve in each other. CH_3OH is polar and forms hydrogen bonds. C_6H_6 and CH_3CH_3 are nonpolar molecules and only form London dispersion forces.*

8. E. *A solution's vapor pressure is lower than the pure solvent which increases the temperature at which the vapor pressure will equal the atmospheric pressure (boiling point). The freezing point is also lower.*

9. C. *5.6°C is roughly three times the molecular freezing point constant so the compound that dissociates into three ions is the most likely substance that forms the solution.*

10. C. *The mole fraction of water is the number of moles of water divided by the total number of moles of substances.*
Moles of water = 36 g/18 g/mol = 2 mol.
Moles of CH_3OH = 32 g/32 g/mol = 1 mol.
Mole fraction of water = 2 moles/(2 + 1) mol = 0.67.

Free Response Answers

1. a. $NH_4Cl(s) \dashrightarrow NH_4^+(aq) + Cl^-(aq)$

   b. *The dissolving of calcium chloride in water is exothermic as evidenced by the increase in temperature of the water. In the dissolving process, heat flows out of the system (ammonium chloride) and into the surroundings (water).*

   c. *Ionic bonds are electrostatic forces of attraction between ions of opposite charge. These ionic bonds are broken when calcium chloride dissolves in water. When calcium chloride dissolves in water, ion-dipole forces exist between a Ca^{2+} ion and the negative end of a water molecule, and between a Cl^- ion and the positive end of a water molecule. Forming the ion-dipole interactions releases more energy than it takes* *to break the ionic bonds in calcium chloride. As a result a net amount of heat is released into the system.*

d. *Because NaCl dissolves with no apparent change in temperature it can be said that the ion-dipole forces between water molecules and sodium and chloride ions are about equal to the ionic bonds in NaCl.*

e. *The process of ammonium chloride dissolving in water is endothermic based on the observed decrease in temperature. However, the dissolving process occurs with an increase in entropy or randomness of the system. In the case of ammonium chloride and most ionic salts that dissolve in water, the drive toward increasing entropy outweighs the drive toward minimum enthalpy. As a result, the endothermic process is spontaneous.*

2. a. $C_{(80.77\,g)/(12.0\,g/mol)}H_{(3.846\,g)/(1.00\,g/mol)}O_{(15.38\,g/16.0\,g/mol)} =$
$C_{6.73}H_{3.846}\,O_{0.961} = C_{(6.73/.961)}H_{(3.84/0.961)}O_{(0.961/0.961)} = C_7H_4O$

b. $m = (0.496\,g\ benzoic\ acid/122\,g/mol)/(0.025\,kg\ camphor)$
$= 0.163\ m.$

$\Delta T_f = K_f\, m\, i$

$(179.8 - 173.3°C) = K_f(0.163\,m)(1)$

$Kf = 39.9°C/m$

c. $(179.8 - 176.7°C) = (39.9°C/m)\ m\ (1)$

$m = 0.0777\ m$

d. $moles\ of\ unknown = (0.0777\ mol\ unknown/kg\ camphor)$
$(0.0151\ kg\ camphor) = 0.00117\ moles\ unknown.$

$molar\ mass\ of\ unknown = grams\ unknown/moles\ of\ unknown$
$= 0.243\,g/0.00117\ mol = 208\,g/mol.$

e. *C_7H_4O has a mass of 104 g/mol. 208 is double 104 so the molecular formula is $C_{14}H_8O_2$.*

Your Turn Answers

13.1. *Calcium chloride dissolving with an increase in temperature is an exothermic process, releasing heat into the water. The ion-dipole forces in the solution release more energy than is required to break the ionic bonds of calcium chloride. The excess heat goes to warm the water.*

13.2. *Gasoline is a nonpolar liquid that has only dispersion forces holding its molecules together. Water molecules are tightly held together by hydrogen bonding. Water molecules have greater attractions for each* *other than they do for molecules in gasoline and so they exclude the gasoline molecules.*

13.3. *Soda is an aqueous solution of carbon dioxide. A sealed soda bottle contains an equilibrium vapor pressure of carbon dioxide above the liquid. When the cap is removed, the* CO_2 *above the liquid escapes to the environment, lowering the partial pressure. Gases are less soluble at lower partial pressures above the solution and bubbles form and begin to escape the solution. Nonpolar carbon dioxide is not very soluble in polar water at lower pressure.*