Chapter 14
Solutions and Their Behavior

PRACTICING SKILLS

Concentration

1. For 2.56 g of succinic acid in 500. mL of water:

The molality of the solution:

Molality = #mole solute/kg solvent:

With a density of water of 1.00 g/cm3, 500. mL = 0.500 kg

$$\text{Molality} = \frac{0.0217\ \text{mol}}{0.500\ \text{kg}} = 0.0434\ \text{molal}$$

The mole fraction of succinic acid in the solution:

For mole fraction we need *both* the # moles of solute *and* #moles of solvent.

$$\text{Moles of water} = 500.\ \text{g}\ H_2O \bullet \frac{1\ \text{mol}\ H_2O}{18.02\ \text{g}\ H_2O} = 27.7\ \text{mol}\ H_2O$$

$$\text{The mf of acid} = \frac{0.0217\ \text{mol}}{(0.0217\ \text{mol} + 27.7\ \text{mol})} = 7.81 \times 10^{-4}$$

The weight percentage of succinic acid in the solution:

The fraction of *total* mass of solute + solvent which is solute:

$$\text{Weight percentage} = \frac{2.56\ \text{g succinic acid}}{502.56\ \text{g acid + water}} \bullet 100 = 0.509\%\ \text{succinic acid}$$

3. Complete the following transformations for

NaI:

Weight percent:

$$\frac{0.15\ \text{mol NaI}}{1\ \text{kg solvent}} \bullet \frac{0.15\ \text{mol NaI}}{1\ \text{kg solvent}} = \frac{22.5\ \text{g NaI}}{1\ \text{kg solvent}}$$

$$\frac{22.5\ \text{g NaI}}{1000\ \text{g solvent} + 22.5\ \text{g NaI}} \bullet 100 = 2.2\ \%\ \text{NaI}$$

Mole fraction:

1000 g H_2O = 55.51 mol H_2O

$$X_{NaI} = \frac{0.15\ \text{mol NaI}}{55.51\ \text{mol}\ H_2O + 0.15\ \text{mol NaI}} = 2.7 \times 10^{-3}$$

C_2H_5OH:

Molality:

$$\frac{5.0\text{ g }C_2H_5OH}{100\text{ g solution}} \bullet \frac{1\text{ mol }C_2H_5OH}{46.07\text{ g }C_2H_5OH} \bullet \frac{100\text{ g solution}}{95\text{ g solvent}} \bullet \frac{1000\text{ g solvent}}{1\text{ kg solvent}} = 1.1\text{ molal}$$

Mole fraction:

$$\frac{5.0\text{ g }C_2H_5OH}{1} \bullet \frac{1\text{ mol }C_2H_5OH}{46.07\text{ g }C_2H_5OH} = 0.11\text{ mol }C_2H_5OH$$

and for water: $\frac{95\text{ g }H_2O}{1} \bullet \frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O} = 5.27\text{ mol }H_2O$

$$X_{C_2H_5OH} = \frac{0.11\text{ mol }C_2H_5OH}{5.27\text{ mol }H_2O + 0.11\text{ mol }C_2H_5OH} = 0.020$$

$C_{12}H_{22}O_{11}$:

Weight percent:

$$\frac{0.15\text{ mol }C_{12}H_{22}O_{11}}{1\text{ kg solvent}} \bullet \frac{342.3\text{ g }C_{12}H_{22}O_{11}}{1\text{ mol }C_{12}H_{22}O_{11}} = \frac{51.3\text{ g }C_{12}H_{22}O_{11}}{1\text{ kg solvent}}$$

$$\frac{51.3\text{ g }C_{12}H_{22}O_{11}}{1000\text{ g }H_2O + 51.3\text{ g }C_{12}H_{22}O_{11}} \times 100 = 4.9\ \%\ C_{12}H_{22}O_{11}$$

Mole fraction:

$$X_{C_{12}H_{22}O_{11}} = \frac{0.15\text{ mol }C_{12}H_{22}O_{11}}{55.51\text{ mol }H_2O + 0.15\text{ mol }C_{12}H_{22}O_{11}} = 2.7 \times 10^{-3}$$

5. To prepare a solution that is 0.200 m Na_2CO_3:

$$\frac{0.200\text{ mol }Na_2CO_3}{1\text{ kg }H_2O} \bullet \frac{0.125\text{ kg }H_2O}{1} \bullet \frac{106.0\text{ g }Na_2CO_3}{1\text{ mol }Na_2CO_3} = 2.65\text{ g }Na_2CO_3$$

$$\text{mol }Na_2CO_3 = \frac{0.200\text{ mol }Na_2CO_3}{1\text{ kg }H_2O} \bullet \frac{0.125\text{ kg }H_2O}{1} = 0.025\text{ mol}$$

The mole fraction of Na_2CO_3 in the resulting solution:

$$\frac{125.\text{ g }H_2O}{1} \bullet \frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O} = 6.94\text{ mol }H_2O$$

$$X_{Na_2CO_3} = \frac{0.025\text{ mol }Na_2CO_3}{0.025\text{ mol }Na_2CO_3 + 6.94\text{ mol }H_2O} = 3.59 \times 10^{-3}$$

7. To calculate the number of mol of $C_3H_5(OH)_3$:

$$0.093 = \frac{x\text{ mol }C_3H_5(OH)_3}{x\text{ mol }C_3H_5(OH)_3 + (425\text{ g }H_2O \bullet \frac{1\text{ mol }H_2O}{18.02\text{ g }H_2O})}$$

$$0.093 = \frac{\text{x mol } C_3H_5(OH)_3}{\text{x mol } C_3H_5(OH)_3 + 23.58 \text{ mol } H_2O}$$

0.093(x + 23.58) = x and solving for x we get 2.4 mol $C_3H_5(OH)_3$

Grams of glycerol needed: 2.4 mol $C_3H_5(OH)_3 \bullet \frac{92.1 \text{ g}}{1 \text{ mol}} = 220 \text{ g } C_3H_5(OH)_3$

The molality of the solution is (2.4 mol $C_3H_5(OH)_3$, 0.425 kg H_2O)= 5.7 m

9. Concentrated HCl is 12.0M and has a density of 1.18 g/cm^3.

(a) The molality of the solution:

Molality is defined as moles HCl/kg solvent, so begin by deciding the mass of 1 L, and the mass of water in that 1L. Since the density = 1.18g/mL, then 1 L (1000 mL) will have a mass of 1180g.

The mass of HCl present in 12.0 mol HCl =

$$12.0 \text{ mol HCl} \bullet \frac{36.46 \text{ g HCl}}{1 \text{ mol HCl}} = 437.52 \text{ g HCl}$$

Since 1 L has a mass of 1180 g and 437.52 g is HCl, the difference (1180-437.52) is solvent. So 1 L has 742.98 g water.

$$\frac{12.0 \text{ mol HCl}}{1 \text{ L}} \bullet \frac{1 \text{ L}}{742.98 \text{ g } H_2O} \bullet \frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O} = 16.2 \text{ m}$$

(b) Weight percentage of HCl:

12.0 mol HCl has a mass of 437.52 g, and the 1 L of solution has a mass of 1180 g.

$$\%HCl = \frac{437.52 \text{ g HCl}}{1180 \text{ g solution}} \bullet 100 = 37.1 \%$$

11. The concentration of ppm expressed in grams is:

$$0.18 \text{ ppm} = \frac{0.18 \text{ g solute}}{1.0 \text{x} 10^6 \text{ g solvent}} = \frac{0.18 \text{ g solute}}{1.0 \text{x} 10^3 \text{ kg solvent}} \text{ or } \frac{0.00018 \text{ g solute}}{1 \text{ kg water}}$$

$$\frac{0.00018 \text{ g } Li^+}{1 \text{ kg water}} \bullet \frac{1 \text{ mol } Li^+}{6.939 \text{ g } Li^+} = 2.6 \text{ x } 10^{-5} \text{ molal } Li^+$$

The Solution Process

13. Pairs of liquids that will be miscible:

(a) $H_2O/CH_3CH_2CH_2CH_3$

Will **not** be miscible. Water is a polar substance, while butane is nonpolar.

(b) C_6H_6/CCl_4

Will **be** miscible. Both liquids are nonpolar and are expected to be miscible.

(c) H_2O/CH_3CO_2H

Will **be** miscible. Both substances can hydrogen bond, and we know that they mix—since a 5% aqueous solution of acetic acid is sold as "vinegar"

15. The enthalpy of solution for LiCl:

The process can be represented as LiCl (s) $\rightarrow$ LiCl (aq)

The $\Delta_rH = \Sigma\Delta_fH$ (product) - $\Sigma\Delta_fH$ (reactant)

$= (-445.6 \text{ kJ/mol})(1\text{mol}) - (-408.7 \text{ kJ/mol})(1\text{mol}) = -36.9 \text{ kJ}$

The similar calculation for NaCl is + 3.9 kJ. Note that the enthalpy of solution for NaCl is endothermic while that for LiCl is exothermic.

Note the data (-408.7 kJ/mol) is from Table 14.1.

17. Raising the temperature of the solution will increase the solubility of NaCl in water. To increase the amount of dissolved NaCl in solution one must **(c) raise the temperature of the solution and add some NaCl**.

Henry's Law

19. Solubility of $O_2 = k \bullet P_{O_2}$

$= (1.66\text{x } 10^{-6} \frac{\text{M}}{\text{mm Hg}}) \bullet 40 \text{ mm Hg} = 6.6 \text{ x } 10^{-5} \text{ M } O_2$

and $6.6 \text{ x } 10^{-5} \frac{\text{mol}}{\text{L}} \bullet \frac{32.0 \text{ g } O_2}{1 \text{ mol } O_2} = 2 \text{ x } 10^{-3} \frac{\text{g } O_2}{\text{L}}$

21. Solubility $= k \bullet P_{CO_2}$;$0.0506 \text{ M} = (4.48 \text{ x } 10^{-5} \frac{\text{M}}{\text{mm Hg}}) \bullet P_{CO_2}$

$1130 \text{ mm Hg} = P_{CO_2}$ or expressed in units of atmospheres:

$1130 \text{ mm Hg} \bullet \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 1.49$ atm and given the relationship of atm to bar: 1.49 bar

Raoult's Law

23. Since $P_{water} = X_{water} P^\circ_{water}$, to determine the vapor pressure of the solution (P_{water}), we need the mf of water.

$35.0 \text{ g glycol} \bullet \frac{1 \text{ mol glycol}}{62.07 \text{ g glycol}} = 0.564 \text{ mol glycol}$ and

$500.0 \text{ g } H_2O \bullet \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} = 27.75 \text{ mol } H_2O$. The mf of water is then:

$\frac{27.75 \text{ mol } H_2O}{(27.75 \text{ mol } + 0.564 \text{ mol})} = 0.9801$ and

$P_{water} = X_{water} P^\circ_{water} = 0.9801 \bullet 35.7 \text{ mm Hg} = 35.0 \text{ mm Hg}$

25. Using Raoult's Law, we know that the vapor pressure of pure water (P°) multiplied by the mole fraction (X) of the solute gives the vapor pressure of the solvent above the solution (P).

$$P_{water} = X_{water} P°_{water}$$

The vapor pressure of pure water at 90 ˚C is 525.8 mmHg (from Appendix G).

Since the P_{water} is given as 457 mmHg, the mole fraction of the water is:

$$\frac{457 \text{ mmHg}}{525.8 \text{ mmHg}} = 0.869$$

The 2.00 kg of water correspond to a mf of 0.869. This mass of water corresponds to:

$$2.00 \times 10^3 \text{ g } H_2O \bullet \frac{1 \text{mol} H_2O}{18.02 \text{g} H_2O} = 111 \text{ mol water.}$$

Representing moles of ethylene glycol as x we can write:

$$\frac{\text{mol } H_2O}{\text{mol } H_2O + \text{mol } C_2H_4(OH_2)} = \frac{111}{111+x} = 0.869$$

$$\frac{111}{0.869} = 111 + x;\ 16.7 = x \text{ (mol of ethylene glycol)}$$

$$16.7 \text{ mol } C_2H_4(OH)_2 \bullet \frac{111}{111+x} = 1.04 \times 10^3 \text{ g } C_2H_4(OH)_2$$

Boiling Point Elevation

27. Benzene normally boils at a temperature of 80.10 °C. If the solution boils at a temperature of 84.2 °C, the change in temperature is (84.2 - 80.10 °C) or 4.1 °C.

Calculate the Δt, using the equation $\Delta t = K_{bp} \bullet m_{solute}$:

The molality of the solution is $\frac{0.200 \text{ mol}}{0.125 \text{ kg solvent}}$ or 1.60 m

The K_{bp} for benzene is +2.53 °C/m

So $\Delta t = K_{bp} \bullet m_{solute} = +2.53\ °C/m \bullet 1.60 \text{ m} = +4.1\ °C$.

29. Calculate the molality of acenaphthene, $C_{12}H_{10}$, in the solution.

$$0.515 \text{ g } C_{12}H_{10} \bullet \frac{1 \text{ mol } C_{12}H_{10}}{154.2 \text{ g } C_{12}H_{10}} = 3.34 \times 10^{-3} \text{ mol } C_{12}H_{10}$$

and the molality is: $\frac{3.34 \times 10^{-3} \text{mol acenaphthene}}{0.0150 \text{ kg } CHCl_3} = 0.223$ molal

the boiling point *elevation* is: $\Delta t = m \bullet K_{bp} = 0.223 \bullet \frac{+3.63˚C}{\text{molal}} = 0.808$ ˚C

and the boiling point will be 61.70 + 0.808 = 62.51 ˚C

Freezing Point Depression

31. The solution freezes 16.0 ˚C lower than pure water.

(a) We can calculate the molality of the ethanol:

$$\Delta t = mK_{fp}$$

$$-16.0\ ˚C = m\ (-1.86\ ˚C/\text{molal})$$

$$8.60 = \text{molality of the alcohol}$$

(b) If the molality is 8.60 then there are 8.60 moles of C_2H_5OH

(8.60 x 46.07 g/mol = 396 g) in 1000 g of H_2O.

The weight percent of alcohol is $\frac{396g}{1396g}$ x 100 = 28.4 % ethanol

33. Freezing point of a solution containing 15.0 g sucrose in 225 g water:

(1) Calculate the molality of sucrose in the solution:

$$15.0\text{ g } C_{12}H_{22}O_{11} \bullet \frac{1\text{ mol } C_{12}H_{22}O_{11}}{342.30\text{ g } C_{12}H_{22}O_{11}} = 0.0438\text{ mol}$$

$$\frac{0.0438\text{ mol } C_{12}H_{22}O_{11}}{0.225\text{ kg } H_2O} = 0.195\text{ molal}$$

(2) Use the Δt equation to calculate the freezing point change:

$$\Delta t = mK_{fp} = 0.195\text{ molal} \bullet (-1.86\ ˚C/\text{molal}) = -\ 0.362\ ˚C$$

The solution is expected to begin freezing at – 0.362 ˚C.

Colligative Properties and Molar Mass Determination

35. The change in the temperature of the boiling point is (80.26 - 80.10)˚C or 0.16 ˚C.

Using the equation $\Delta t = m \bullet K_{bp}$; 0.16 ˚C = m • +2.53 °C/m, and the molality is: $\frac{0.16\ ˚C}{+2.53\ °C/m} = m = 0.063$ molal

The solution contains 11.12 g of solvent (or 0.01112 kg solvent). We can calculate the # of moles of the orange compound, since we know the molality:

$$0.063\text{ molal} = \frac{x\text{ mol compound}}{0.01112\text{ kg solvent}}$$ or 7.0×10^{-4} mol compound.

This number of moles of compound has a mass of 0.255 g, so 1 mol of compound is:

$$\frac{0.255\text{ g compound}}{7.0 \times 10^{-4}\text{ mol}} = 360\text{ g/mol.}$$

The empirical formula, $C_{10}H_8Fe$, has a mass of 184 g, so the # of "empirical formula units" in one molecular formula is: $\frac{360\text{g/mol}}{184\text{ g/empirical formula}}$ = 2 mol/empirical formulas or a molecular formula of $C_{20}H_{16}Fe_2$.

37. The change in the temperature of the boiling point is (61.82 - 61.70)˚C or 0.12 ˚C.

Using the equation $\Delta t = m \bullet K_{bp}$; 0.12 ˚C = m • +3.63 °C/m, and the molality is:

$$\frac{0.12\ ^\circ\text{C}}{+3.63\ ^\circ\text{C/m}} = \text{m} = 0.033 \text{ molal}$$

The solution contains 25.0 g of solvent (or 0.0250 kg solvent). We can calculate the # of moles of benzyl acetate:

$$0.033 \text{ molal} = \frac{\text{x mol compound}}{0.01112 \text{ kg solvent}} \text{ or } 8.3 \times 10^{-4} \text{ mol compound.}$$

This number of moles of benzyl acetate has a mass of 0.125 g, so 1 mol of benzyl acetate is:

$$\frac{0.125 \text{ g compound}}{8.3\text{x}10^{-4} \text{ mol}} = 150 \text{ g/mol. (2 sf)}$$

39. To determine the molar mass, first determine the molality of the solution

$$-0.040\ ^\circ\text{C} = \text{m} \bullet -1.86\ ^\circ\text{C/molal} = 0.0215 \text{ molal (or 0.022 to 2 sf)}$$

$$\text{and} \quad 0.022 \text{ molal} = \frac{\frac{0.180 \text{ g solute}}{\text{MM}}}{0.0500 \text{ kg water}}$$

$$\text{MM} = 167 \text{ or } 170 \text{ (to 2 sf)}$$

Colligative Properties of Ionic Compounds

41 The number of moles of LiF is: $52.5 \text{ g LiF} \bullet \frac{1 \text{ mol LiF}}{25.94 \text{ g LiF}} = 2.02 \text{ mol LiF}$

$$\text{So } \Delta t_{fp} = \frac{2.02 \text{ mol LiF}}{0.306 \text{ kg H}_2\text{O}} \bullet -1.86\ ^\circ\text{C/molal} \bullet 2 = -24.6\ ^\circ\text{C}$$

The anticipated freezing point is then 24.6 ˚C lower than pure water (0.0˚C) or -24.6 ˚C

43. Solutions given in order of increasing freezing point (lowest freezing point listed first):

The solution with the **greatest number** of particles will have the lowest freezing point.

The total molality of solutions is:

	Solution	Particles / formula unit	Identity of particles	Total molality
(a)	0.1 m sugar	1	covalently bonded molecules	0.1 m • 1 = 0.1 m
(b)	0.1 m NaCl	2	Na^+, Cl^-	0.2 m • 1 = 0.2 m
(c)	0.08 m $CaCl_2$	3	Ca^{2+}, 2 Cl^-	0.08 m • 3 = 0.24 m
(d)	0.04 m Na_2SO_4	3	2 Na^+, SO_4^{2-}	0.04 m • 3 = 0.12 m

The freezing points would increase in the order: $CaCl_2$ < NaCl < Na_2SO_4 < sugar

Osmosis

45. Assume we have 100 g of this solution, the number of moles of phenylalanine is

$$3.00\text{ g phenylalanine} \bullet \frac{1\text{ mol phenylalanine}}{165.2\text{ g phenylalanine}} = 0.0182\text{ mol phenylalanine}$$

The molality of the solution is: $\frac{0.0182\text{ mol phenylalanine}}{0.09700\text{ kg water}} = 0.187$ molal

(a) The freezing point:

$\Delta t = 0.187\text{ molal} \bullet -1.86\ ^\circ\text{C/molal} = -0.348\ ^\circ\text{C}$

The new freezing point is 0.0 - 0.348 ˚C = - 0.348 ˚C.

(b) The boiling point of the solution

$\Delta t = m\,K_{bp} = 0.187\text{ molal} \bullet 0.5121^\circ\text{C/molal} = +0.0959\ ^\circ\text{C}$

The new boiling point is 100.000 + 0.0959 = +100.0959 ˚C

(c) The osmotic pressure of the solution:

If we assume that the **Molarity** of the solution is equal to the **molality**, then the osmotic pressure should be:

$$\Pi = (0.187\text{ mol/L})(0.0821\,\frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}})(298\text{ K}) = 4.58\text{ atm}$$

The osmotic pressure will be most easily measured, since the magnitudes of osmotic pressures (large values) result in decreased experimental error.

47. The molar mass of bovine insulin with a solution having an osmotic pressure of 3.1 mm Hg:

$$3.1\text{ mm Hg} \bullet \frac{1\text{ atm}}{760\text{ mm Hg}} = (\text{M})(0.08205\,\frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}})(298\text{ K})$$

$$1.67 \times 10^{-4} = \text{Molarity or } 1.7 \times 10^{-4}\text{ (to 2 sf)}$$

The definition of molarity is #mol/L. Substituting into the definition we obtain:

$$1.7 \times 10^{-4}\,\frac{\text{mol bovine insulin}}{\text{L}} = \frac{\frac{1.00\text{ g bovine insulin}}{\text{MM}}}{1\text{ L}}$$; Solving for MM = 6.0×10^3 g/mol

Colloids

49. (a) $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,NaCl(aq)$

(b) The $BaSO_4$ initially formed is of a colloidal size — not large enough to precipitate fully.

(c) The particles of $BaSO_4$ grow with time, owing to a gradual loss of charge and become large enough to have gravity affect them—and settle to the bottom.

GENERAL QUESTIONS

51. A solution of 0.52g of phenylcarbinol in 25.0 g of water melts at – 0.36 °C.

$\Delta t = m \bullet -1.86\ ^\circ\text{C/molal}$

$$-0.36\ ^\circ\text{C} = m \bullet -1.86\ ^\circ\text{C/molal so } \frac{-0.36^\circ\text{C}}{-1.86\ ^\circ\text{C/molal}} = m = 0.19\text{molal (0.194 to 3sf)}$$

$$0.19\ \frac{\text{mol phenylcarbinol}}{\text{kg}} = \frac{\text{mol phenylcarbinol}}{0.025\text{ kg}} \text{ and } (0.19 \bullet 0.025) = 4.8 \times 10^{-3}\text{ mol}$$

$$\text{The molar mass of phenylcarbinol is } \frac{0.52\text{ g phenylcarbinol}}{4.8 \times 10^{-3}\text{ mol}} = 110\text{ g/mol (2 sf)}$$

53. Arranged the solutions in order of (i) increasing vapor pressure of water and (ii) increasing boiling points:

(i) The solution with the highest water vapor pressure would have the **lowest particle concentration**, since according to Raoult's Law, the vapor pressure of the water in the solution is directly proportional to the mole fraction of the water. The lower the number of particles, the greater the mf of water, and the greater the vapor pressure. Hence the order of *increasing* vapor pressure is:

Na_2SO_4 < sugar < KBr < glycol

(See part (ii) for particle concentrations—(m•i))

(ii) Recall that $\Delta t = m \bullet Kfp \bullet i$. The difference in these four solutions will be in the product (m • i). The products for these solutions are:

glycol = 0.35 • 1 = 0.35
sugar = 0.50 • 1 = 0.50
KBr = 0.20 • 2 = 0.40
Na_2SO_4 = 0.20 • 3 = 0.60

Arranged in *increasing* boiling points: glycol < KBr < sugar < Na_2SO_4

55. For DMG, $(CH_3CNOH)_2$, the MM is 116.1 g/mol

$$\text{So 53.0 g is: } 53.0\text{ g} \bullet \frac{1\text{ mol DMG}}{116.1\text{ g DMG}} = 0.456\text{ mol DMG}$$

$$525.\text{ g of } C_2H_5OH\text{ is: } 525.\text{ g} \bullet \frac{1\text{ mol } C_2H_5OH}{46.07\text{ g } C_2H_5OH} = 11.4\text{ mol } C_2H_5OH$$

$$\text{(a) the mole fraction of DMG: } \frac{0.456\text{ mol}}{(11.4 + 0.456)\text{ mol}} = 0.0385\text{ mf DMG}$$

$$\text{(b) The molality of the solution: } \frac{0.456\text{ mol DMG}}{0.525\text{ kg}} = 0.869\text{ molal DMG}$$

(c) $P_{\text{alcohol}} = P^\circ_{\text{alcohol}} \bullet X_{\text{alcohol}}$

$= (760.\text{ mm Hg})(1 - 0.0385) = 730.7\text{ mm Hg}$

(d) The boiling point of the solution:

$\Delta t = m \bullet K_{bp} \bullet i = (0.870)(+1.22\ ^\circ\text{C/molal})(1) = 1.06\ ^\circ\text{C}$

The new boiling point is 78.4 ˚C + 1.06 ˚C = 79.46 ˚C or 79.5 ˚C

57. Concentrated NH_3 is 14.8 M and has a density of 0.90 g/cm^3.

(1) The molality of the solution:

Molality is defined as moles NH_3/kg solvent, so begin by deciding the mass of 1 L, and the mass of water in that 1L. Since the density = 0.90g/mL, then 1 L (1000 mL) will have a mass of 900g.

The mass of NH_3 present in 14.8 mol NH_3=

$$14.8\text{ mol NH}_3 \bullet \frac{17.03\text{ g NH}_3}{1\text{ mol NH}_3} = 252\text{ g NH}_3$$

Since 1 L has a mass of 900 g and 252 g is NH_3, the difference (900-252) is solvent. So 1 L has 648 g water.

$$\frac{14.8\text{ mol NH}_3}{1\text{ L}} \bullet \frac{1\text{ L}}{648\text{ g H}_2\text{O}} \bullet \frac{1000\text{ g H}_2\text{O}}{1\text{ kg H}_2\text{O}} = 22.8\text{ m or 23 m (2sf)}$$

(2) The mole fraction of ammonia is:

Calculate the # of moles of water present:

$$648\text{ g H}_2\text{O} \bullet \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} = 35.96\text{ mol H}_2\text{O (retaining 1 extra sf)}$$

The mf NH_3 is: $\dfrac{14.8\text{ mol NH}_3}{(14.8\text{ mol} + 35.96\text{ mol})} = 0.29$

(3) Weight percentage of NH_3:

14.8 mol NH_3 has a mass of 252.0 g, and 1 L of the solution has a mass of 900 g.

$$\%\ \text{NH}_3 = \frac{252.0\text{ g NH}_3}{900\text{ g solution}} \bullet 100 = 28\ \%\ \text{(2sf)}$$

59. To make a 0.100 m solution, we need a ratio of #moles of ions/kg solvent that is 0.100.

$0.100\text{ m} = \dfrac{\#\text{ mol ions}}{0.125\text{ kg solvent}}$ and solving for # mol ions: 0.0125 mol ions

The salt will dissociate into 3 ions per formula unit (2 Na^+ and 1 SO_4^{2-}).

The amount of Na_2SO_4 is:

$$0.0125\text{ mol ions} \bullet \frac{1\text{ mol Na}_2\text{SO}_4}{3\text{ mol ions}} \bullet \frac{142.04\text{ g Na}_2\text{SO}_4}{1\text{ mol Na}_2\text{SO}_4} = 0.592\text{ g Na}_2\text{SO}_4$$

61. Solution properties:

(a) The solution with the higher boiling point:

Recall that $\Delta t = m \bullet K_{fp} \bullet i$. The difference in these solutions will be in the product (m • i).

The products for these solutions are:

sugar = 0.30 • 1 = 0.30 (the sugar molecule remains as one unit)

KBr = 0.20 • 2 = 0.40 (KBr dissociates into K^+ and Br^- ions)

KBr will provide the larger Δt.

(b) The solution with the lower freezing point:

Using the same logic as in part (a), NH_4NO_3 provides 2 ions/formula unit while Na_2CO_3 provides 3. The product, (m • i), is larger for Na_2CO_3, so **Na_2CO_3** gives the greater Δt and the lower freezing point.

63. The change in temperature of the freezing point is: $\Delta t = m \bullet K_{fp} \bullet i$

Calculate the molality:

$$35.0 \text{ g } CaCl_2 \bullet \frac{1 \text{ mol } CaCl_2}{111.0 \text{ g } CaCl_2} = 0.315 \text{ mol } CaCl_2 \text{ in } 0.150 \text{ kg water.}$$

$$m = \frac{0.315 \text{ mol } CaCl_2}{0.150 \text{ kg}} = 2.10 \text{ molal } CaCl_2$$

$\Delta t = m \bullet K_{fp} \bullet i = (2.10 \text{ molal} \bullet -1.86 \text{ °C/molal} \bullet 2.7) = -10.6$ °C.(-11 to 2sf)

The freezing point of the solution is 0.0˚C - 11 ˚C = -11 ˚C

65. The molar mass of hexachlorophene if 0.640 g of the compound in 25.0 g of $CHCl_3$ boils at 61.93 ˚C:

Recalling the Δt equation: $\Delta t = m \bullet K_{bp} = m \bullet \frac{+3.63 \text{ °C}}{\text{molal}} = (61.93 - 61.70) \text{ °C}$

Solving for m: $\frac{0.23 \text{ °C}}{3.63 \text{ °C/m}} = 0.0634 \text{ m}$

Substitute into the definition for molality: m = #mol/kg solvent

$$0.0634 \text{ molal} = \frac{\frac{0.640 \text{ g hexachloraphene}}{\text{MM}}}{0.025 \text{ kg}} \text{ and solving for MM; } 4.0 \times 10^2 \text{ g/mol} = \text{MM}$$

67. Solubility of $N_2 = k \bullet P_{N_2}$

$$= (6.0 \times 10^{-4} \frac{\text{mol}}{\text{kg} \bullet \text{bar}}) \bullet 585 \text{ mmHg} \bullet \frac{1.01325 \text{ bar}}{760 \text{ mmHg}} = 4.7 \times 10^{-4} \text{ mol/kg } N_2$$

69. (a) *Average* MM of starch if 10.0 g starch/L has an osmotic pressure = 3.8 mm Hg at 25 ˚C.

$$3.8 \text{ mm Hg} \bullet \frac{1 \text{ atm}}{760 \text{ mm Hg}} = (M)(0.08205 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}})(298 \text{ K})$$

2.045×10^{-4} = Molarity or 2.0×10^{-4} (to 2 sf)

The definition of molarity is #mol/L. Substituting into the definition we obtain:

$$2.0 \times 10^{-4}\ \frac{\text{mol bovine insulin}}{\text{L}} = \frac{\frac{10.0\text{ g starch}}{\text{MM}}}{1\text{L}}$$;Solving for MM = 4.9×10^{4} g/mol

(b) Freezing point of the solution:

$\Delta t = m \bullet K_{fp} \bullet i$ (assume that i=1and that Molarity = molality)

$\Delta t = m \bullet (-1.86\ ^\circ\text{C/molal})$

and the $M = \dfrac{\frac{10.0\text{ g starch}}{4.9 \times 10^{4}\text{ g/mol}}}{1\text{ L}} = 2.0 \times 10^{-4}$

so the $\Delta t = 2.0 \times 10^{-4} \bullet (-1.86\ ^\circ\text{C/molal}) = -3.8 \times 10^{-4}\ ^\circ\text{C}$. In essence the starch will boil at the temperature of pure water. From this data we can assume that *it will NOT be easy* to measure the molecular weight of starch using this technique.

71. The enthalpies of solution for Li_2SO_4 and K_2SO_4:

The process is MX(s) →MX(aq)

Using the data for **Li_2SO_4**:

$\Delta_{solution}H = \Delta_fH_{(aq)} - \Delta_fH_{(s)}$ = (-1464.4 kJ/mol) - (-1436.4 kJ/mol) = - 28.0 kJ/mol

Using the data for **K_2SO_4**:

$\Delta_{solution}H = \Delta_fH_{(aq)} - \Delta_fH_{(s)}$ = (-1414.0 kJ/mol) - (-1437.7 kJ/mol) = 23.7 kJ/mol

Note that for Li_2SO_4 *the process is **exothermic** while for* K_2SO_4 *the process is endothermic.*

Similar data for LiCl and KCl:

For LiCl: $\Delta_fH_{(aq)} - \Delta_fH_{(s)}$ = (-445.6 kJ/mol) - (-408.7 kJ/mol) = - 36.9 kJ/mol and

for KCl: $\Delta_fH_{(aq)} - \Delta_fH_{(s)}$ = (-419.5 kJ/mol) - (-436.7 kJ/mol) = 17.2 kJ/mol

*Note the similarities of the chloride salts, with the lithium salt being **exothermic** while the potassium salt is **endothermic**.*

73. Graham's law says that the pressure of a mixture of gases (benzene and toluene) is the sum of the partial pressures. So, using Raoult's Law $P_{benzene} = mf_{\ benzene} \bullet P^\circ_{benzene}$ and similarly for toluene.

The total pressure is:

$$P_{total} = P_{benzene} + P_{toluene}$$

$$= \left(\frac{2\text{ mol benzene}}{3\text{ mol}} \bullet 75\text{ mm Hg}\right) + \left(\frac{1\text{ mol toluene}}{3\text{ mol}} \bullet 22\text{ mm Hg}\right) = 57\text{mm Hg}$$

What is the mole fraction of each component in the liquid and in the vapor?

The **mf of the components in the liquid** are: benzene: 2/3 and toluene: 1/3

The **mf of the components in the vapor** are proportional to their pressures in the vapor state.

The mf of benzene is: $\frac{50 \text{ mm Hg}}{57 \text{ mm Hg}} = 0.87$; the mf of toluene would be (1 - 0.87) or 0.13.

75. A 2.0 % aqueous solution of novocainium chloride(NC) is also 98.0 % in water. Assume that we begin with 100 g of solution. The molality of the solution is:

$$\frac{2.0 \text{ g} \bullet \frac{1 \text{mol NC}}{272.8 \text{ g NC}}}{0.0980 \text{ kg water}} = 0.075 \text{ m}$$

Using the "delta T' equation:

$\Delta t = m \bullet K_{fp} \bullet i$, we can solve for i: $\frac{\Delta t}{m \bullet K_{fp}} = i$

$$\frac{-0.237^\circ\text{C}}{0.075\text{m} \bullet -1.86^\circ\text{C/m}} = 1.7$$

So approximately **2 moles of ions are present per mole of compound**.

77. (a) We can calculate the freezing point of sea water if we calculate the molality of the solution. Let's imagine that we have 1,000,000 (or 10^6) g of sea water. The amounts of the ions are then equal to the concentration (in ppm).

Cl^-: $1.95 \times 10^4 \text{ g Cl}^- \bullet \frac{1 \text{ mol Cl}^-}{35.45 \text{ g Cl}^-} = 550. \text{ mol Cl}^-$

Na^+: $1.08 \times 10^4 \text{ g Cl}^- \bullet \frac{1 \text{mol Na}^+}{22.99 \text{ g Na}^+} = 470. \text{ mol Na}^+$

Mg^{+2}: $1.29 \times 10^3 \text{ g Mg}^{+2} \bullet \frac{1 \text{mol Mg}^{+2}}{24.31 \text{ g Mg}^{+2}} = 53.1 \text{ mol Mg}^{+2}$

SO_4^{-2}: $9.05 \times 10^2 \text{ g SO}_4^{-2} \bullet \frac{1 \text{mol SO}_4^{-2}}{96.06 \text{ g SO}_4^{-2}} = 9.42 \text{ mol SO}_4^{-2}$

Ca^{+2}: $4.12 \times 10^2 \text{ g Ca}^{+2} \bullet \frac{1 \text{mol Ca}^{+2}}{40.08 \text{ g Ca}^{+2}} = 10.3 \text{ mol Ca}^{+2}$

K^+: $3.80 \times 10^2 \text{ g K}^+ \bullet \frac{1 \text{mol K}^+}{39.10 \text{ g K}^+} = 9.72 \text{ mol K}^+$

Br^-: $67 \text{ g Br}^- \bullet \frac{1 \text{mol Br}^-}{79.90 \text{ g Br}^-} \underline{= 0.84 \text{ mol Br}^-}$

For a total of: 1103 mol ions

The concentration per gram is: $\frac{1103 \text{ mol ions}}{10^6 \text{ g H}_2\text{O}}$

The *change* in the freezing point of the sea water is:

$$\Delta t = m \bullet K_{fp} = \frac{1103 \text{ mol ions}}{10^6 \text{ g } H_2O} \bullet \frac{1000 \text{ g } H_2O}{1 \text{ kg } H_2O} \bullet -1.86 \text{ ˚C/molal} = -2.05 \text{ ˚C}$$

So we expect this sea water to begin freezing at -2.05 ˚C.

(b) The osmotic pressure (in atmospheres) can be calculated if *we assume the density of sea water is 1.00 g/mL.*

$$\Pi = MRT = \frac{1.103 \text{ mol}}{1 \text{ L}} \bullet 0.082057 \frac{\text{L} \bullet \text{atm}}{\text{K} \bullet \text{mol}} \bullet 298 \text{ K} = 27.0 \text{ atm}$$

The pressure needed to purify sea water by reverse osmosis would then be a pressure greater than 27.0 atm.

79. A 2.00 % aqueous solution of sulfuric acid is also 98.00 % in water.

Assume that we begin with 100 g of solution.

(a) We can calculate the van't Hoff factor by first calculating the molality of the solution:

$$\frac{2.00\text{g} \bullet \frac{1 \text{ mol } H_2SO_4}{98.06 \text{ g } H_2SO_4}}{0.09800 \text{ kg water}} = 0.208 \text{ m}$$

Using the "delta T' equation:

$$\Delta t = m \bullet K_{fp} \bullet i \text{ , we can solve for i: } \frac{\Delta t}{m \bullet K_{fp}} = i$$

$$\frac{-0.796 ˚C}{0.208 m \bullet -1.86 ˚C/m} = 2.06 = i$$

(b) Given the van't Hoff factor of 2 (above), the best representation of a dilute solution of sulfuric acid in water has to be: $H^+ + HSO_4^-$.

IN THE LABORATORY

81. Using the freezing point depression and boiling point elevation equations, calculate the term (m•i). Since we have no quantitative information about the quantity of benzoic acid dissolved in the benzene, the term (m•i) will be the best metric by which we can judge the degree of dissociation of benzoic acid at the freezing point and boiling point of benzene.

At the freezing point: $\Delta t = m \bullet i \bullet K_{fp}$; (3.1 ˚C - 5.50 ˚C) = m•i(-5.12 ˚C/molal) i

$$\text{and } \frac{-2.4 \text{ ˚C}}{-5.12 \text{ ˚C/molal}} = m \bullet i \text{ so } 0.47 \text{ molal} = m \bullet i$$

At the boiling point: $\Delta t = m \bullet i \bullet K_{bp}$; (82.6 ˚C – 80.1 ˚C) = m•i(+2.53 ˚C/molal) i

$$\text{and } \frac{+2.5 \text{ ˚C}}{+2.53 \text{ ˚C/molal}} = m \bullet i \text{ so } 0.97 \text{ molal} = m \bullet i$$

If we assume the amount of benzoic acid dissolved in benzene is constant over the temperature range described, the conclusion one reaches is that *i* has a greater value at higher temperatures than at lower ones. Another way of expressing this is that *at higher temperatures*, the *degree of association* between benzoic acid molecules *decreases*,

83. The apparent molecular weight of acetic acid in benzene, determined by the depression of benzene's freezing point.

$$\Delta t = m \bullet K_{fp} \bullet i;\ (3.37\ ^\circ C - 5.50\ ^\circ C) = m(-5.12\ ^\circ C/\text{molal})\ i$$

$$\text{and } \frac{-2.13^\circ C}{-5.12^\circ C/\text{molal}} = m \bullet i \text{ so } 0.416 \text{ molal} = m \bullet i \text{ (assume i =1)}$$

and the apparent molecular weight is:

$$0.416 \text{ molal} = \frac{\dfrac{5.00 \text{ g acetic acid}}{\text{MM}}}{0.100 \text{ kg}} \text{ and solving for MM; } 120 \text{ g/mol} = \text{MM}$$

The apparent molecular weight of acetic acid in water

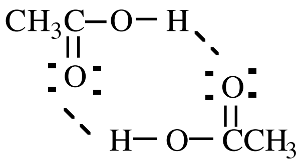
$$\Delta t = m \bullet K_{fp} \bullet i;\ (-1.49\ ^\circ C - 0.00\ ^\circ C) = m(-1.86\ ^\circ C/\text{molal})\ i$$

$$\text{and } \frac{-1.49^\circ C}{-1.86^\circ C/\text{molal}} = m \bullet i \text{ so } 0.801 \text{ molal} = m \bullet i$$

(once again, i = 1) and the apparent molecular weight is:

$$0.801 \text{ molal} = \frac{\dfrac{5.00 \text{ g acetic acid}}{\text{MM}}}{0.100 \text{ kg}} \text{ and solving for MM; } 62.4 \text{ g/mol} = \text{MM}$$

The accepted value for acetic acid's molecular weight is approximately 60.1 g/mol. Hence the value for i isn't much larger than 1, indicating that the degree of dissociation of acetic acid molecules in water is not great—a finding consistent with the designation of acetic acid as a weak acid. The apparently doubled molecular weight of acetic acid in benzene indicates that the acid must exist primarily as a dimer.



85. The vapor pressure data should permit us to calculate the molar mass of the boron compound.

$$P_{\text{benzene}} = X_{\text{benzene}} \bullet P^\circ_{\text{benzene}}$$

$$94.16 \text{ mm Hg} = X_{\text{benzene}} \bullet 95.26 \text{ mm Hg, and rearranging: } X_{\text{benzene}} = \frac{94.16 \text{ mm Hg}}{95.26 \text{ mm Hg}}$$

$$X_{\text{benzene}} = 0.9885$$

Now we need to know the # of moles of the boron compound, so let's use the mf of benzene to find that: $10.0 \text{ g benzene} \bullet \frac{1 \text{ mol benzene}}{78.11 \text{ g benzene}} = 0.128 \text{ mol benzene}$

$$0.9885 = \frac{0.128 \text{ mol benzene}}{0.128 \text{ mol benzene} + x \text{ mol BxFy}}$$

$0.9885(0.128 + x) = 0.128\ x$ and solving for $x = 0.001489$ mol B_xF_y

Knowing that this # of moles of compound has a mass of 0.146 g, we can calculate the molar mass:

$$\frac{0.146}{0.001489} = 98.0 \text{ g/mol}$$

We can calculate the empirical formula, since we know that the compound is 22.1% boron and 77.9% fluorine.

In 100 g of the compound there are $22.1 \text{ g B} \bullet \frac{1 \text{ mol B}}{10.81 \text{ g B}} = 2.11 \text{ mol B}$ and

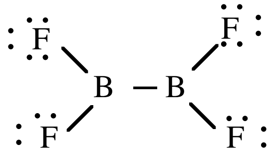
$$77.9 \text{ g F} \bullet \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 4.10 \text{ mol F}$$

The empirical formula is BF_2, which would have a formula weight of 48.8.

Dividing the molar mass (found from the vapor pressure experiment) by the mass of the empirical formula, we get: $\frac{98.0}{48.8} = 2.00$.

(a) The molecular formula is then B_2F_4.

(b) A Lewis structure for the molecule:



We know that the molecule is nonpolar (does not have a dipole moment), The F-B-F bond angles are 120°, as are the F-B-B bond angles, hence the molecule is planar (flat). The hybridization of the boron atoms is sp^2.

SUMMARY AND CONCEPTUAL QUESTIONS

87. More likely to have a more negative heat of hydration:

(a) **LiF** or RbF—See SQ14.15 for similar data. The aquation of the larger Rb ion requires more energy ($\Delta_f H$ is less negative) and the resulting $\Delta_{hyd}H$ is less negative than for the smaller lithium cation.

(b) KNO_3 or **$Ca(NO_3)_2$**: The greater charge of the Ca^{2+} compared to the K^+ ion will have a stronger attraction to water, and a *more negative* heat of hydration.

(c) CsBr or **$CuBr_2$**: The smaller dipositive Cu ion will cause $CuBr_2$ to have the more negative heat of hydration. Here two factors are in play: (1)the smaller size of the metal cation, and (2) the greater charge of the copper cation over that of the cesium cation.

89. Li_2SO_4 is expected to have the more exothermic (negative) heat of solution. See SQ14.87 for additional information on this concept.

91. Equimolar amounts of $CaCl_2$ and NaCl lower freezing points differently. The formulas tell us that $CaCl_2$ provides 3 particles per formula unit while NaCl provides only two. Hence we expect—given van't Hoff factors of 3 and 2 respectively that $CaCl_2$ should have a freezing point depression that is about 50% greater than that of NaCl.

93. Solutes likely to dissolve in water; and solutes likely to dissolve in benzene:
Substances likely to dissolve in water are polar (ionic compounds) and those polar substances capable of hydrogen-bonding. Substances likely to dissolve in benzene are non-polar substances.
Likely to dissolve in water: (a) $NaNO_3$-ionic; (d) NH_4Cl
Likely to dissolve in benzene: (b) $CH_3CH_2OCH_2CH_3$- only slightly polar, with large fraction of the molecule being non-polar (C-C, and C-H bonds); (c) $C_{10}H_8$--nonpolar

95. Since hydrophilic colloids are those that “love water”, we would expect starch to form a hydrophilic colloid since it contains the OH bonds that can hydrogen bond to water. Hydrocarbons on the other hand have non-polar bonds that should have little-to-no attraction to water molecules, and form a hydrophobic colloid.

97. Semipermeable membrane dividing container into two parts; one side containing 5.85 g NaCl in 100 mL solution, and the other side containing 8.88 g KNO_3 in 100 mL solution.

Calculate the osmotic pressure of both solutions: $\Pi = MRT$

Note that we don't actually have to calculate the osmotic pressures, only to note that the solution with the **greater molarity** will have the greater osmotic pressure.

M for NaCl: $\frac{5.85 \text{ g NaCl}}{1} \bullet \frac{1 \text{ mol NaCl}}{58.5 \text{ g NaCl}} \bullet \frac{1}{0.100\text{L}} = 1.00 \text{ M}$

M for KNO_3: $\frac{8.88 \text{ g } KNO_3}{1} \bullet \frac{1 \text{ mol } KNO_3}{101.1 \text{ g } KNO_3} \bullet \frac{1}{0.100\text{L}} = 0.878 \text{ M}$

So the osmotic pressure for NaCl will be greater than that for KNO_3, and the *solvent should flow from the KNO_3 to the NaCl*, reducing the osmotic pressure for NaCl.