SOLUTIONS TO BLACK EXERCISES

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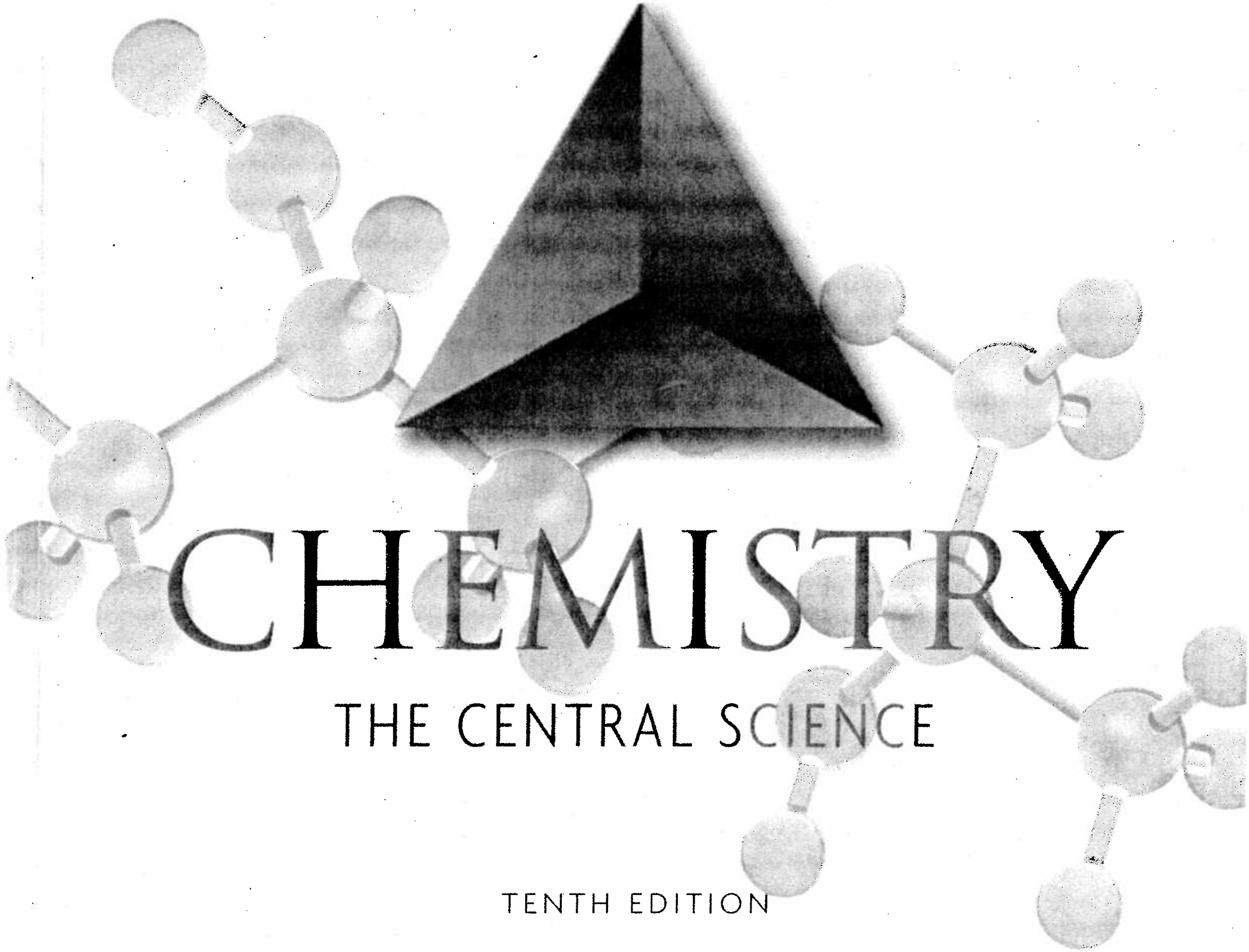

CHEMISTRY

THE CENTRAL SCIENCE

TENTH EDITION

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13

Properties of Solutions

Visualizing Concepts

13.2 ΔH_3 contains the interaction of a cation with the solvent. In the figure for Exercise 13.1, we see a single Na^+ cation separated from the bulk sample, and solvent molecules interacting with each other as well as the cation. The diagram shows attractive solvent-solvent and ion-solvent interactions, which contribute to an overall negative (-) ΔH. In Figure 13.4, only ΔH_3 is negative.

13.3 The pink solid is hydrated $CoCl_2, CoCl_2 \bullet xH_2O$, where x is a specific integer. The waters of hydration are either associated with Co^{2+}, Cl^-, or sit in specific sites in the crystal lattice. When heated in an oven, the water molecules incorporated into the crystal lattice gradually gain kinetic energy and vaporize. The blue solid is anhydrous $CoCl_2$, absent the waters of hydration and with a different solid-state structure than the pink hydrate.

13.4 Diagram (b) is the best representation of a saturated solution. There is some undissolved solid with particles that are close together and ordered, in contact with a solution containing mobile, separated solute particles. As much solute has dissolved as can dissolve, leaving some undissolved solid in contact with the saturated solution.

13.5 Solubility increases in the order Ar, 1.50×10^{-3} *M* < Kr, 2.79×10^{-3} *M* < Xe, 5×10^{-5} *M*, the order of increasing polarizability. As the molar mass of the ideal gas increases, atomic size increases and the electron cloud is less tightly held by the nucleus, causing the cloud to be more polarizable. The greater the polarizability, the stronger the dispersion forces between the gas atoms and water, the more likely the gas atom is to stay dissolved rather than escape the solution, the greater the solubility of the gas.

13.7 (a) Yes, the *molarity* changes with a change in temperature. Molarity is defined as moles solute per unit volume of solution. If solution volume is different, molarity is different.

(b) No, *molality* does not change with change in temperature. Molality is defined as moles solute per kilogram of solvent. Even though the volume of solution has changed due to increased kinetic energy, the mass of solute and solvent have not changed, and the molality stays the same.

13.8 Ideally, 0.50 L. If the volume outside the balloon is very large compared to 0.25 L, solvent will flow across the semipermeable membrane until the molarities of the inner and outer solutions are equal, 0.10 *M*. This requires an "inner" solution volume twice as large as the initial volume, or 0.50 L. (In reality, osmosis across the balloon membrane is not perfect. The solution concentration inside the balloon will be slightly greater than 0.10 *M* and the volume of the balloon will be slightly less than 0.50 L.)

13.10 According to Figure 13.18, the solubility of CO at 25°C and 1 atm pressure is approximately 0.96 mM. By Henry's Law, $S_g = k P_g$. At the same temperature and pressure, k will be the same, so $S_1/P_1 = S_2/P_2$.

$$\frac{0.96\,\text{m}M}{1\,\text{atm}} = \frac{2.5\,\text{m}M}{\text{x atm}};\ \text{x} = \frac{2.5\,\text{m}M \times 1\,\text{atm}}{0.96\,\text{atm}} = 2.6\,\text{atm}$$

The Solution Process

13.12 (a) For the same solute, NaCl, in different solvents, solute-solute interactions (ΔH_1) are the same. Because water experiences hydrogen bonding while benzene has only dispersion forces, solvent-solvent interactions (ΔH_2) are greater for water. On the other hand, solute-solvent interactions (ΔH_3) are much weaker between ionic NaCl and nonpolar benzene than between ionic NaCl and polar water. It is the large difference in ΔH_3 that causes NaCl to be soluble in water but not in benzene.

(b) Lattice energy is the main component of ΔH_1, the enthalpy required to separate solute particles. If ΔH_1 is too large, the dissolving process is prohibitively endothermic, and the substance is not very soluble.

(c) Ion-dipole forces between cations and water molecules and relatively small lattice energies (ion-ion forces between cations and anions) lead to strongly hydrated cations.

13.14 From weakest to strongest solvent-solute interactions:

(b), dispersion forces < (c), hydrogen bonding < (a), ion-dipole

13.16 Separation of solvent molecules, ΔH_2, will be smallest in this case, because hydrogen bonding is the weakest of the intermolecular forces involved. ΔH_1 involves breaking ionic bonds, and ΔH_3 involves formation of ion-dipole interactions, both stronger forces than hydrogen bonding.

13.18 KBr is quite soluble in water because of the sizeable increase in disorder of the system (ordered KBr lattice → freely moving hydrated ions) associated with the dissolving process. An increase in disorder or randomness in a process tends to make that process spontaneous.

Saturated Solutions; Factors Affecting Solubility

13.20 (a)

$$\frac{1.22\,\text{mol MnSO}_4\bullet\text{H}_2\text{O}}{1\,\text{L soln}} \times \frac{169.0\,\text{g MnSO}_4\bullet\text{H}_2\text{O}}{1\,\text{mol}} \times 0.100\,\text{L} = 20.6\,\text{g MnSO}_4\bullet\text{H}_2\text{O}/100\,\text{mL}$$

The 1.22 *M* solution is unsaturated.

(b) Add a known mass, say 5.0 g, of $MnSO_4 \bullet H_2O$, to the unknown solution. If the solid dissolves, the solution is unsaturated. If there is undissolved $MnSO_4 \bullet H_2O$, filter the solution and weigh the solid. If there is less than 5.0 g of solid, some of the added $MnSO_4 \bullet H_2O$ dissolved and the unknown solution is unsaturated. If there is exactly 5.0 g, no additional solid dissolved and the unknown is saturated. If there is more than 5.0 g, excess solute has precipitated and the solution is supersaturated.

13.22 (a) at $30^\circ C, \dfrac{10\text{ g } KClO_3}{100\text{ g } H_2O} \times 250\text{ g } H_2O = 25\text{ g } KClO_3$

(b) $\dfrac{66\text{ g } Pb(NO_3)_2}{100\text{ g } H_2O} \times 250\text{ g } H_2O = 165 = 1.7 \times 10^2\text{ g } Pb(NO_3)_2$

(c) $\dfrac{3\text{ g } Ce_2(SO_4)_3}{100\text{ g } H_2O} \times 250\text{ g } H_2O = 7.5 = 8\text{ g } Ce_2(SO_4)_3$

13.24 Immiscible means that oil and water do not mix homogeneously; they do not dissolve. Many substances are called "oil," but they are typically nonpolar carbon-based molecules with fairly high molecular weights. As such, there are fairly strong dispersion forces among oil molecules. The properties of water are dominated by its strong hydrogen bonding. The dispersion-dipole interactions between water and oil are likely to be weak. Thus, ΔH_1 and ΔH_2 are large and positive, while ΔH_3 is small and negative. The net ΔH_{soln} is large and positive, and mixing does not occur.

13.26 For small *n* values, the dominant interactions among acid molecules will be hydrogen-bonding. As *n* increases, dispersion forces between carbon chains become more important and eventually dominate. Thus, as *n* increases, water solubility decreases and hexane solubility increases.

13.28 *Analyze/Plan.* Water, H_2O, is a polar solvent that forms hydrogen bonds with other H_2O molecules. The more soluble solute in each case will have intermolecular interactions that are most similar to the hydrogen bonding in H_2O. *Solve.*

(a) Glucose, $C_6H_{12}O_6$, is more soluble because it is capable of hydrogen bonding (Figure 13.12). Nonpolar C_6H_{12} is capable only of dispersion interactions and does not have strong intermolecular interactions with polar (hydrogen bonding) H_2O.

(b) Ionic sodium propionate, CH_3CH_2COONa, is more soluble. Sodium propionate is a crystalline solid, while propionic acid is a liquid. The increase in disorder or entropy when an ionic solid dissolves leads to significant water solubility, despite the strong ion-ion forces (large ΔH_1) present in the solute (see Solution 13.18).

(c) HCl is more soluble because it is a strong electrolyte and completely ionized in water. Ionization leads to ion-dipole solute-solvent interactions, and an increase in disorder. CH_3CH_2Cl is a molecular solute capable of relatively weak dipole-dipole solute-solvent interactions and is much less soluble in water.

13 Properties of Solutions

Solutions to Black Exercises

13.30 Pressure has an effect on O_2 solubility in water because, at constant temperature and volume, pressure is directly related to the amount of O_2 available to dissolve. The greater the partial pressure of Oabove water, the more O_2 molecules are available for dissolution, and the more molecules that strike the surface of the liquid.

Pressure does not affect the amount or physical properties of NaCl, or ionic solids in general, so it has little influence on the dissolving of NaCl in water.

13.32 $$665\text{ torr} \times \frac{1\text{ atm}}{760\text{ torr}} = 0.875\text{ atm};\ P_{O_2} = \chi_{O_2}(P_t) = 0.21(0.875\text{ atm}) = 0.1838 = 0.18\text{ atm}$$

$$S_{O_2} = kP_{O_2} = \frac{1.38 \times 10^{-3}\text{ mol}}{\text{L} \bullet \text{atm}} \times 0.1838\text{ atm} = 2.5 \times 10^{-4}\ M$$

Concentrations of Solutions

13.34 (a) $$\text{mass } \% = \frac{\text{mass solute}}{\text{total mass solution}} \times 100$$

$$\text{mass solute} = 0.045\text{ mol } I_2 \times \frac{253.8\text{ g } I_2}{1\text{ mol } I_2} = 11.421 = 11\text{ g } I_2$$

$$\text{mass } \% I_2 = \frac{11.421\text{ g } I_2}{11.421\text{ g } I_2 + 115\text{ g } CCl_4} \times 100 = 9.034 = 9.0\% I_2$$

(b) $$\text{ppm} = \frac{\text{mass solute}}{\text{total mass solution}} \times 10^6 = \frac{0.0079\text{ g } Sr^{2+}}{1 \times 10^3\text{ g } H_2O} \times 10^6 = 7.9\text{ ppm } Sr^{2+}$$

13.36 (a) $$\frac{25.5\text{ g } C_6H_5OH}{94.11\text{ g/mol}} = 0.2710 = 0.271\text{ mol } C_6H_5OH$$

$$\frac{495\text{ g } CH_3CH_2OH}{46.07\text{ g/mol}} = 10.7445 = 10.7\text{ mol } CH_3CH_2OH$$

$$\chi_{C_6H_5OH} = \frac{0.2710}{0.2710 + 10.7445} = 0.02460 = 0.0246$$

(b) $$\text{mass } \% = \frac{25.5\text{ g } C_6H_5OH}{25.5\text{ g } C_6H_5OH + 495\text{ g } CH_3CH_2OH} \times 100 = 4.90\%\ C_6H_5OH$$

(c) $$m = \frac{0.2710\text{ mol } C_6H_5OH}{0.495\text{ kg } CH_3CH_2OH} = 0.54747 = 0.547\text{ m } C_6H_5OH$$

13.38 (a) $$M = \frac{\text{mol solute}}{\text{L soln}};\ \frac{25.0\text{ g } Al_2(SO_4)_3}{0.350\text{ L soln}} \times \frac{1\text{ mol } Al_2(SO_4)_3}{342.2\text{ g } Al_2(SO_4)_3} = 0.209\ M\ AL_2(SO_4)_3$$

(b) $$\frac{5.25\text{ g } Mn(NO_3)_2 \bullet 2H_2O}{0.175\text{ L soln}} \times \frac{1\text{ mol } Mn(NO_3)_2 \bullet 2H_2O}{215.0\text{ g } Mn(NO_3)_2 \bullet 2H_2O} = 0.140\ M\ Mn(NO_3)_2$$

(c) $M_c \times L_c = M_d \times L_d$; $9.00\ M\ H_2SO_4 \times 0.0350\text{ L} = ?M\ H_2SO_4 \times 0.500\text{ L}$
500 mL of $0.630\ M\ H_2SO_4$

13.40 (a) $$16.0\text{ mol } H_2O \times \frac{18.02\text{ g } H_2O}{1\text{ mol } H_2O} = 288.3\text{ g } H_2O = 0.288\text{ kg } H_2O$$

$$m = \frac{1.50\text{ mol KCl}}{0.2883\text{ kg } H_2O} = 5.2026 = 5.20\ m\text{ KCl}$$

(b) $m = \frac{\text{mol solute}}{\text{kg solute}}$; $\text{mol } S_8 = m \times \text{kg } C_{10}H_8 = 0.12\,m \times 0.1000 \text{ kg } C_{10}H_8 = 0.012 \text{ mol}$

$$0.012 \text{ mol } S_8 \times \frac{256.5 \text{ g } S_8}{1 \text{ mol } S_8} = 3.078 = 3.1 \text{ g } S_8$$

13.42 (a) $\text{mass \%} = \frac{\text{mass } C_6H_8O_6}{\text{total mass solution}} \times 100$;

$$\frac{80.5 \text{ g } C_6H_8O_6}{80.5 \text{ g } C_6H_8O_6 + 210 \text{ g } H_2O} \times 100 = 27.71 = 27.7\% \; C_6H_8O_6$$

(b) $\text{mol } C_6H_8O_6 = \frac{80.5 \text{ g } C_6H_8O_6}{176.1 \text{ g/mol}} = 0.4571 = 0.457 \text{ mol } C_6H_8O_6$

$$\text{mol } H_2O = \frac{210 \text{ g } H_2O}{18.02 \text{ g/mol}} = 11.654 = 11.7 \text{ mol } H_2O$$

$$\chi_{C_6H_8O_6} = \frac{0.4571 \text{ mol } C_6H_8O_6}{0.4571 \text{ mol } C_6H_8O_6 + 11.654 \text{ mol } H_2O} = 0.0377$$

(c) $m = \frac{0.4571 \text{ mol } C_6H_8O_6}{0.210 \text{ kg } H_2O} = 2.18\,m\; C_6H_8O_6$

(d) $M = \frac{\text{mol } C_6H_8O_6}{\text{L solution}}$; $290.5 \text{ g soln} \times \frac{1 \text{ mL}}{1.22 \text{ g}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.2381 = 0.238 \text{ L}$

$$M = \frac{0.4571 \text{ mol } C_6H_8O_6}{0.2381 \text{ L soln}} = 1.92\,M\; C_6H_8O_6$$

13.44 Given: 10.0 g C_4H_4S, 1.065 g/mL; 250.0 mL C_7H_8, 0.867 g/mL

(a) $\text{mol } C_4H_4S = 10.0 \text{ g } C_4H_4S \times \frac{1 \text{ mol } C_4H_4S}{84.15 \text{ g } C_4H_4S} = 0.1188 = 0.119 \text{ mol } C_4H_4S$

$$\text{mol } C_7H_8 = \frac{0.867 \text{ g}}{1 \text{ mL}} \times 250.0 \text{ mL} \times \frac{1 \text{ mol } C_7H_8}{92.14 \text{ g } C_7H_8} = 2.352 = 2.35 \text{ mol}$$

$$\chi_{C_4H_4S} = \frac{0.1188 \text{ mol } C_4H_4S}{0.1188 \text{ mol } C_4H_4S + 2.352 \text{ mol } C_7H_8} = 0.04809 = 0.0481$$

(b) $m_{C_4H_4S} = \frac{\text{mol } C_4H_4S}{\text{kg } C_7H_8}$; $250.0 \text{ mL} \times \frac{0.867 \text{ g}}{1 \text{ mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.2168 = 0.217 \text{ kg } C_7H_8$

$$m_{C_4H_4S} = \frac{0.1188 \text{ mol } C_4H_4S}{0.2168 \text{ kg } C_7H_8} = 0.548\,m\; C_4H_4S$$

(c) $10.0 \text{ g } C_4H_4S \times \frac{1 \text{ mL}}{1.065 \text{ g}} = 9.390 = 9.39 \text{ mL } C_4H_4S$;

$V_{soln} = 9.39 \text{ mL } C_4H_4S + 250.0 \text{ mL } C_7H_8 = 259.4 \text{ mL}$

$$M_{C_4H_4S} = \frac{0.1188 \text{ mol } C_4H_4S}{0.2594 \text{ L soln}} = 0.458\,M\; C_4H_4S$$

13.46 (a) $\frac{1.50 \text{ mol } HNO_3}{1 \text{ L soln}} \times 0.245 \text{ L} = 0.3675 = 0.368 \text{ mol } HNO_3$

(b) Assume that for dilute aqueous solutions, the mass of the solvent is the mass of solution.

$$\frac{1.25\text{ mol NaCl}}{1\text{ kg H}_2\text{O}} \times \frac{x\text{ mol}}{50.0 \times 10^{-6}\text{ kg}};\ x = 6.25 \times 10^{-5}\text{ mol NaCl}$$

(c) $$\frac{1.50\text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{100\text{ g soln}} = \frac{x\text{ g C}_{12}\text{H}_{22}\text{O}_{11}}{124.0\text{ g soln}};\ x = 1.125 = 1.13\text{ g C}_{12}\text{H}_{22}\text{O}_{11}$$

$$1.125\text{ g C}_{12}\text{H}_{22}\text{O}_{11} \times \frac{1\text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{342.3\text{ g C}_{12}\text{H}_{22}\text{O}_{11}} = 3.287 \times 10^{-3} = 3.29 \times 10^{-3}\text{ mol C}_{12}\text{H}_{22}\text{O}_{11}$$

13.48 (a) $$\frac{0.110\text{ mol (NH}_4)_2\text{SO}_4}{1\text{ L soln}} \times 1.50\text{ L} \times \frac{132.2\text{ g (NH}_4)_2\text{SO}_4}{1\text{ mol (NH}_4)_2\text{SO}_4} = 21.81 = 21.8\text{ g (NH}_4)_2\text{SO}_4$$

Weigh 21.8 g $(NH_4)_2SO_4$, dissolve in a small amount of water, continue adding water with thorough mixing up to a total solution volume of 1.50 L.

(b) Determine the mass fraction of Na_2CO_3 in the solution:

$$\frac{0.65\text{ mol Na}_2\text{CO}_3}{1000\text{ g H}_2\text{O}} \times \frac{106.0\text{ g Na}_2\text{CO}_3}{1\text{ mol Na}_2\text{CO}_3} = 68.9\text{ g} = \frac{69\text{ g Na}_2\text{CO}_3}{1000\text{ g H}_2\text{O}}$$

$$\text{mass fraction} = \frac{68.9\text{ g Na}_2\text{CO}_3}{1000\text{ g H}_2\text{O} + 68.9\text{ g Na}_2\text{CO}_3} = 0.06446 = 0.064$$

In 120 g of solution, there are 0.06446(120) = 7.735 = 7.7 g Na_2CO_3.

Weigh out 7.7 g Na_2CO_3 and dissolve it in 120 - 7.7 = 112.3 g H_2O to make exactly 120 g of solution.

(112.3 g H_2O/0.997 g H_2O/mL @ 25° = 112.6 mL H_2O)

(c) $$1.20\text{ L} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1.16\text{ g}}{1\text{ mL}} = 1392\text{ g solution};\ 0.150(1392\text{ g soln}) = 209\text{ g Pb(NO}_3)_2$$

Weigh 209 g $Pb(NO_3)$ and add (1392 - 209) = 1183 g H_2O to make exactly (1392 = 1.39×10^3) g or 1.20 L of solution.

(1183 g H_2O/0.997 g/mL @ 25°C = 1187 mL H_2O)

(d) Calculate the mol HCl necessary to neutralize 5.5 g $Ba(OH)_2$.

$Ba(OH)_2(s) + 2HCl(aq) \rightarrow BaCl_2(aq) + 2H_2O(l)$

$$5.5\text{ g Ba(OH)}_2 + \frac{1\text{ mol Ba(OH)}_2}{171\text{ g Ba(OH)}_2} \times \frac{2\text{ mol HCl}}{1\text{ mol Ba(OH)}_2} = 0.0643 = 0.064\text{ mol HCl}$$

$$M = \frac{\text{mol}}{\text{L}};\ \text{L} = \frac{\text{mol}}{M} = \frac{0.0643\text{ mol HCl}}{0.50\ M\text{ HCl}} = 0.1287 = 0.13\text{ L} = 130\text{ mL}$$

130 mL of 0.50 M HCl are needed.

$M_c \times L_c = M_d \times L_d$; $6.0\ M \times L_c = 0.50\ M \times 0.1287$ L; $L_c = 0.01072$ L = 11 mL

Using a pipette, measure exactly 11 mL of 6.0 M HCl and dilute with water to a total volume of 130 mL.

13.50 *Analyze/Plan.* Assume 1.00 L of solution. Calculate mass of 1 L of solution using density. Calculate mass of NH_3 using mass %, then mol NH_3 in 1.00 L. *Solve.*

$$1.00\text{ L soln} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{0.90\text{ g soln}}{1\text{ mL soln}} = 9.0 \times 10^2\text{ g soln/L}$$

$$\frac{900\text{ g soln}}{1.00\text{ L soln}} \times \frac{28\text{ g NH}_3}{100\text{ g soln}} \times \frac{1\text{ mol NH}_3}{17.03\text{ g NH}_3} = 14.80 = 15\text{ mol NH}_3\text{/L soln} = 15\ M\text{ NH}_3$$

13.52 (a) $$\frac{0.0750\text{ mol C}_8\text{H}_{10}\text{N}_4\text{O}_2}{1\text{ kg CHCl}_3} \times \frac{194.2\text{ g C}_8\text{H}_{10}\text{N}_4\text{O}_2}{1\text{ mol C}_8\text{H}_{10}\text{N}_4\text{O}_2} = 14.565$$

$$= 14.6\text{ g C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{/kg CHCl}_3$$

$$\frac{14.565\text{ g C}_8\text{H}_{10}\text{N}_4\text{O}_2}{14.565\text{ g C}_8\text{H}_{10}\text{N}_4\text{O}_2 + 1000.00\text{ g CHCl}_3} \times 100 = 1.436 = 1.44\%\text{ C}_8\text{H}_{10}\text{N}_4\text{O}_2\text{ by mass}$$

(b) $$1000\text{ g CHCl}_3 \times \frac{1\text{ mol CHCl}_3}{119.4\text{ CHCl}_3} = 8.375 = 8.38\text{ mol CHCl}_3$$

$$\chi_{C_8H_{10}N_4O_2} = \frac{0.0750}{0.0750 + 8.375} = 0.00888$$

13.54 (a) For gases at the same temperature and pressure, volume % = mol %. The volume and mol % of CO_2 in this breathing air is 4.0%.

(b) $$P_{CO_2} = \chi_{CO_2} \times P_t = 0.040\,(1\text{ atm}) = 0.040\text{ atm}$$

$$M_{CO_2} = \frac{P_{CO_2}}{RT} = \frac{0.040\text{ atm}}{310\text{ K}} \times \frac{\text{K}\bullet\text{mol}}{0.08206\text{ L}\bullet\text{atm}} = 1.6 \times 10^{-3}\ M$$

Colligative Properties

13.56 (a) decrease (b) decrease

(c) increase (d) increase

13.58 (a) An *ideal solution* is a solution that obeys Raoult's Law.

(b) *Analyze/Plan.* Calculate the vapor pressure predicted by Raoult's law and compare it to the experimental vapor pressure. Assume ethylene glycol (eg) is the solute. *Solve.*

$$\chi_{H_2O} = \chi_{eg} = 0.500;\ P_A = \chi_A P_A{}^\circ = 0.500(149)\text{ mm Hg} = 74.5\text{ mm Hg}$$

The experimental vapor pressure (P_A), 67 mm Hg, is less than the value predicted by Raoult's law for an ideal solution. The solution is not ideal.

Check. An ethylene glycol-water solution has extensive hydrogen bonding, which causes deviation from ideal behavior. We expect the experimental vapor pressure to be less than the ideal value and it is.

13.60 (a) H_2O vapor pressure will be determined by the mole fraction of H_2O in the solution. The vapor pressure of pure H_2O at 343 K (70°C) = 233.7 torr.

$$\frac{35.0\text{ g } C_3H_8O_3}{92.10\text{ g/mol}} = 0.3800 = 0.380\text{ mol}; \quad \frac{125\text{ g } H_2O}{18.02\text{ g/mol}} = 6.937 = 6.94\text{ mol}$$

$$P_{H_2O} = \frac{6.937\text{ mol } H_2O}{6.937 + 0.380} \times 233.7\text{ torr} = 221.6 = 222\text{ torr}$$

(b) Calculate χ_B by vapor pressure lowering; $\chi_B = \Delta P_A / P_A{}^{\circ}$ (see Solution 13.59(b)). Given moles solvent, calculate moles solute from the definition of mole fraction.

$$\chi_{C_2H_6O_2} = \frac{10.0\text{ torr}}{100\text{ torr}} = 0.100$$

$$\frac{1.00 \times 10^3\text{ g } C_2H_5OH}{46.07\text{ g/mol}} = 21.71 = 21.7\text{ mol } C_2H_5OH;\text{ let y} = \text{mol } C_2H_6O_2$$

$$\chi_{C_2H_6O_2} = \frac{\text{y mol } C_2H_6O_2}{\text{y mol } C_2H_6O_2 + 21.71\text{ mol } C_2H_5OH} = 0.100 = \frac{y}{y + 21.71}$$

$0.100\text{ y} + 2.171 = \text{y};\ 0.900\text{ y} = 2.171;\ \text{y} = 2.412 = 2.41\text{ mol } C_2H_6O_2$

$$2.412\text{ mol } C_2H_6O_2 \times \frac{62.07\text{ g}}{1\text{ mol}} = 150\text{ g } C_2H_6O_2$$

13.62 (a) Since C_6H_6 and C_7H_8 form an ideal solution, we can use Raoult's Law. Since both components are volatile, both contribute to the total vapor pressure of 35 torr.

$$P_t = P_{C_6H_6} + P_{C_7H_8};\ P_{C_6H_6} = \chi_{C_6H_6} P^{\circ}_{C_6H_6};\ P_{C_7H_8} = \chi_{C_7H_8} P^{\circ}_{C_7H_8}$$

$$\chi_{C_7H_8} = 1 - \chi_{C_6H_6};\ P_T = \chi_{C_6H_6} P^{\circ}_{C_6H_6} + (1 - \chi_{C_6H_6}) P^{\circ}_{C_7H_8}$$

$$35\text{ torr} = \chi_{C_6H_6}(75\text{ torr}) + (1 - \chi_{C_6H_6})22\text{ torr}$$

$$13\text{ torr} = 53\text{ torr}(\chi_{C_6H_6});\ \chi_{C_6H_6} = \frac{13\text{ torr}}{53\text{ torr}} = 0.2453 = 0.25;\quad \chi_{C_7H_8} = 0.7547 = 0.75$$

(b) $P_{C_6H_6} = 0.2453(75\text{ torr}) = 18.4\text{ torr};\ P_{C_7H_8} = 0.7547(22\text{ torr}) = 16.6\text{ torr}$

In the vapor, $\chi_{C_6H_6} = \frac{P_{C_6H_6}}{P_t} = \frac{18.4\text{ torr}}{35\text{ torr}} = 0.53;\ \chi_{C_7H_8} = 0.47$

13.64 *Analyze/Plan.* ΔT_b depends on mol dissolved particles. Assume 100 g of each solution, calculate mol solute and mol dissolved particles. Glucose and sucrose are molecular solutes, but $NaNO_3$ dissociates into 2 mol particles per mol solute. *Solve.*

10% by mass means 10 g solute in 100 g solution. If we have 10 g of each solute, the one with the smallest molar mass will have the largest mol solute. The molar masses are: glucose, 180.2 g/mol; sucrose, 342.3 g/mol; $NaNO_3$, 85.0 g/mol. $NaNO_3$ has most mol solute, and twice as many dissolved particles, so it will have the highest boiling point. Sucrose has least mol solute and lowest boiling point. Glucose is intermediate.

In order of increasing boiling point: 10% sucrose < 10% glucose < 10% $NaNO_3$.

13.66 0.030 *m* phenol > 0.040 *m* glycerin = 0.020 *m* KBr. Phenol is very slightly ionized in water, but not enough to match the number of particles in a 0.040 *m* glycerin solution. The KBr solution is 0.040 *m* in particles, so it has the same freezing point as 0.040 *m* glycerin, which is a nonelectrolyte.

13.68 $\Delta T = K(m)$; first calculate the **molality** of the solute particles.

(a) $0.40\ m$

(b) $$\frac{20.0\text{ g C}_{10}\text{H}_{22}}{0.455\text{ kg CHCl}_3} \times \frac{1\text{ mol C}_{10}\text{H}_{22}}{142.3\text{ g C}_{10}\text{H}_{22}} = 0.3089 = 0.309\ m$$

(c) $$m = \frac{0.45\text{ mol eg} + 2(0.15)\text{ mol KBr}}{0.150\text{ kg H}_2\text{O}} = \frac{0.75\text{ mol particles}}{0.150\text{ kg H}_2\text{O}} = 5.0\ m$$

Then, f.p. = $T_f - K_f(m)$; b.p. = $T_b + K_b(m)$; T in °C

	m	T_f	$-K_f(m)$	f.p.	T_b	$+K_b(m)$	b.p.
(a)	0.40	−114.6	−1.99(0.40) = −0.80	−115.4	78.4	1.22(0.40) = 0.49	78.9
(b)	3.09	−63.5	−4.68(3.09) = −14.5	−78.0	61.2	3.63(3.09) = 11.2	72.4
(c)	5.0	0.0	−1.86(5.0) = −9.3	−9.3	100.0	0.51(5.0) = 2.6	102.6

13.70 $\pi = MRT$; T = 20°C + 273 = 293 K

$$M\text{ (of ions)} = \frac{\text{mol NaCl} \times 2}{\text{L soln}} = \frac{3.4\text{ g NaCl}}{1\text{ L soln}} \times \frac{1\text{ mol NaCl}}{58.4\text{ g NaCl}} \times \frac{2\text{ mol ions}}{1\text{ mol NaCl}} = 0.116 = 0.12\ M$$

$$\pi = \frac{0.116\text{ mol}}{\text{L}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times 293\text{ K} = 2.8\text{ atm}$$

13.72 $\Delta T_f = 5.5 - 4.1 = 1.4;\quad m = \dfrac{\Delta T_f}{K_f} = \dfrac{1.4}{5.12} = 0.273 = 0.27\ m$

$$\text{MM lauryl alcohol} = \frac{\text{g lauryl alcohol}}{m \times \text{kg C}_6\text{H}_6} = \frac{5.00\text{ g lauryl alcohol}}{0.273 \times 0.100\text{ kg C}_6\text{H}_6}$$
$$= 1.8 \times 10^2\text{ g/mol lauryl alcohol}$$

13.74 $$M = \pi/RT = \frac{0.605\text{ atm}}{298\text{ K}} \times \frac{\text{mol}\bullet\text{K}}{0.08206\text{ L}\bullet\text{atm}} = 0.02474 = 0.0247\ M$$

$$\text{MM} = \frac{\text{g}}{M \times \text{L}} = \frac{2.35\text{ g}}{0.02474\ M \times 0.250\text{ L}} = 380\text{ g/mol}$$

13.76 If these were ideal solutions, they would have equal ion concentrations and equal ΔT_f values. Data in Table 13.5 indicates that the van't Hoff factors (*i*) for both salts are less than the ideal values. For 0.030 *m* NaCl, *i* is between 1.87 and 1.94, about 1.92. For 0.020 *m* K_2SO_4, *i* is between 2.32 and 2.70, about 2.62. From Equation 13.14,

ΔT_f (measured) = $i \times \Delta T_f$ (calculated for nonelectrolyte)

NaCl: ΔT_f (measured) = $1.92 \times 0.030\ m \times 1.86\ °\text{C}/m = 0.11\ °\text{C}$

K_2SO_4: ΔT_f (measured) = $2.62 \times 0.020\ m \times 1.86°\text{C}/m = 0.097\ °\text{C}$

0.030 *m* NaCl would have the larger ΔT_f.

The deviations from ideal behavior are due to ion-pairing in the two electrolyte solutions. K_2SO_4 has more extensive ion-pairing and a larger deviation from ideality because of the higher charge on SO_4^{2-} relative to Cl^-.