

Chapter 11 – Textbook Assigned Problems

Exercises

Concentration of Solutions

25. Because the density of water is 1.00 g/mL, 100.0 mL of water has a mass of 100. g.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{10.0 \text{ g H}_3\text{PO}_4 + 100. \text{ g H}_2\text{O}}{104 \text{ mL}} = 1.06 \text{ g/mL} = 1.06 \text{ g/cm}^3$$

$$\text{mol H}_3\text{PO}_4 = 10.0 \text{ g} \times \frac{1 \text{ mol}}{97.99 \text{ g}} = 0.102 \text{ mol H}_3\text{PO}_4$$

$$\text{mol H}_2\text{O} = 100. \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 5.55 \text{ mol H}_2\text{O}$$

$$\text{mole fraction of H}_3\text{PO}_4 = \frac{0.102 \text{ mol H}_3\text{PO}_4}{(0.102 + 5.55) \text{ mol}} = 0.0180$$

$$\chi_{\text{H}_2\text{O}} = 1.000 - 0.0180 = 0.9820$$

$$\text{molarity} = \frac{0.102 \text{ mol H}_3\text{PO}_4}{0.104 \text{ L}} = 0.981 \text{ mol/L}$$

$$\text{molality} = \frac{0.102 \text{ mol H}_3\text{PO}_4}{0.100 \text{ kg}} = 1.02 \text{ mol/kg}$$

31. If we have 1.00 L of solution:

$$1.37 \text{ mol citric acid} \times \frac{192.12 \text{ g}}{\text{mol}} = 263 \text{ g citric acid (H}_3\text{C}_6\text{H}_5\text{O}_7)$$

$$1.00 \times 10^3 \text{ mL solution} \times \frac{1.10 \text{ g}}{\text{mL}} = 1.10 \times 10^3 \text{ g solution}$$

$$\text{mass \% of citric acid} = \frac{263 \text{ g}}{1.10 \times 10^3 \text{ g}} \times 100 = 23.9\%$$

In 1.00 L of solution, we have 263 g citric acid and $(1.10 \times 10^3 - 263) = 840 \text{ g}$ of H₂O.

$$\text{molality} = \frac{1.37 \text{ mol citric acid}}{0.84 \text{ kg H}_2\text{O}} = 1.6 \text{ mol/kg}$$

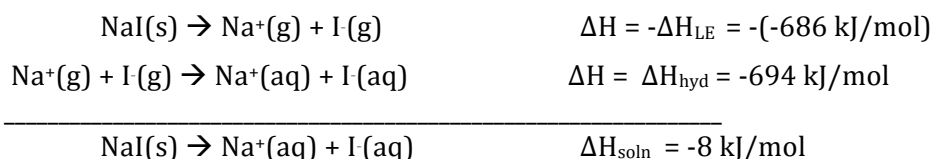
$$840 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 47 \text{ mol H}_2\text{O}; \quad \chi_{\text{citric acid}} = \frac{1.37}{47 + 1.37} = 0.028$$

Since citric acid is a triprotic acid, the number of protons citric acid can provide is three times the molarity. Therefore, normality = 3 × molarity:

$$\text{normality} = 3 \times 1.37 \text{ M} = 4.11 \text{ N}$$

Energetics of Solutions and Solubility

33. Using Hess's law:

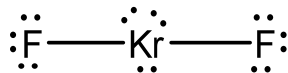


$\Delta\text{H}_{\text{soln}}$ refers to the heat released or gained when a solute dissolves in a solvent. Here, an ionic compound dissolves in water.

35. Both $\text{Al}(\text{OH})_3$ and NaOH are ionic compounds. Since the lattice energy is proportional to the charge of the ions, the lattice energy of aluminum hydroxide is greater than that of sodium hydroxide. The attraction of water molecules for Al^{3+} and OH^- cannot overcome the larger lattice energy and $\text{Al}(\text{OH})_3$ is insoluble. For NaOH , the favorable hydration energy is large enough to overcome the smaller lattice energy and NaOH is soluble.

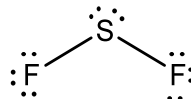
37. Water is a polar solvent and dissolves polar solutes and ionic solutes. Carbon tetrachloride (CCl_4) is a nonpolar solvent and dissolves nonpolar solutes (like dissolves like). To predict the polarity of the following molecules, draw the correct Lewis structure and then determine if the individual bond dipoles cancel or not. If the bond dipoles are arranged in such a manner that they cancel each other out, then the molecule is nonpolar. If the bond dipoles do not cancel each other out, then the molecule is polar.

a. KrF_2 , $8 + 2(7) = 22 \text{ e}^-$



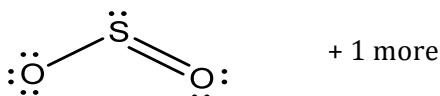
nonpolar; soluble in CCl_4

b. SF_2 , $6 + 2(7) = 20 \text{ e}^-$



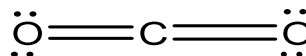
polar; soluble in H_2O

c. SO_2 , $6 + 2(6) = 18 \text{ e}^-$



polar; soluble in H_2O

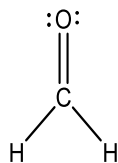
d. CO_2 , $4 + 2(6) = 16 \text{ e}^-$



nonpolar; soluble in CCl_4

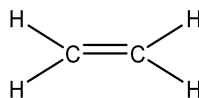
e. MgF_2 is an ionic compound so it is soluble in water.

f. CH_2O , $4 + 2(1) + 6 = 12 e^-$



polar; soluble in H_2O

g. C_2H_4 , $2(4) + 4(1) = 12 e^-$



nonpolar (like all compounds made up of only carbon and hydrogen); soluble in CCl_4

39. Water is a polar molecule capable of hydrogen bonding. Polar molecules, especially molecules capable of hydrogen bonding, and ions are all attracted to water. For covalent compounds, as polarity increases, the attraction to water increases. For ionic compounds, as the charge of the ions increases and/or the size of the ions decreases, the attraction to water increases.

a. $\text{CH}_3\text{CH}_2\text{OH}$; $\text{CH}_3\text{CH}_2\text{OH}$ is polar while $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar.

b. CHCl_3 ; CHCl_3 is polar while CCl_4 is nonpolar.

c. $\text{CH}_3\text{CH}_2\text{OH}$; $\text{CH}_3\text{CH}_2\text{OH}$ is much more polar than $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_2\text{OH}$.

40. For ionic compounds, as the charge of the ions increases and/or the size of the ions decreases, the attraction to water (hydration) increases.

a. Mg^{2+} ; smaller size, higher charge

b. Be^{2+} ; smaller

c. Fe^{3+} ; smaller size, higher charge

d. F^- ; smaller

e. Cl^- ; smaller

f. SO_4^{2-} ; higher charge

43. $C = kP$, $\frac{8.21 \times 10^{-4} \text{ mol}}{\text{L}} = k \times 0.790 \text{ atm}$, $k = 1.04 \times 10^{-3} \text{ mol/L} \cdot \text{atm}$

$$C = kP, C = \frac{1.04 \times 10^{-4} \text{ mol}}{\text{L atm}} \times 1.10 \text{ atm} = 1.14 \times 10^{-3} \text{ mol/L}$$

Vapor Pressures of Solutions

45. $\text{mol C}_3\text{H}_8\text{O}_3 = 164 \text{ g} \times \frac{1 \text{ mol}}{92.09 \text{ g}} = 1.78 \text{ mol C}_3\text{H}_8\text{O}_3$

$$\text{mol H}_2\text{O} = 338 \text{ mL} \times \frac{0.992 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 18.6 \text{ mol H}_2\text{O}$$

$$P_{\text{H}_2\text{O}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ = \frac{18.6 \text{ mol}}{(1.78 + 18.6) \text{ mol}} \times 54.74 \text{ torr} = 0.913 \times 54.74 \text{ torr} = 50.0 \text{ torr}$$

$$47. \quad P_B = \chi_B P_B^{\circ}, \quad \chi_B = P_B / P_B^{\circ} = 0.900 \text{ atm} / 0.930 \text{ atm} = 0.968$$

$$0.968 = \frac{\text{mol benzene}}{\text{total mol}}; \quad \text{mol benzene} = 78.11 \text{ g C}_6\text{H}_6 \times \frac{1 \text{ mol}}{78.11 \text{ g}} = 1.000 \text{ mol}$$

$$\text{Let } x = \text{mol solute, then: } \chi_B = 0.968 = \frac{1.000 \text{ mol}}{1.000 + x}, \quad 0.968 + 0.968x = 1.000, \quad x = 0.033 \text{ mol}$$

$$\text{molar mass} = \frac{10.0 \text{ g}}{0.033 \text{ mol}} = 303 \text{ g/mol} \approx 3.0 \times 10^2 \text{ g/mol}$$

53. Compared to H₂O, solution d (methanol/water) will have the highest vapor pressure because methanol is more volatile than water. Both solution b (glucose/water) and solution c (NaCl/water) will have a lower vapor pressure than water by Raoult's law. NaCl dissolves to give Na⁺ ions and Cl⁻ ions; glucose is a nonelectrolyte. Since there are more solute particles in solution c, the vapor pressure of solution c will be the lowest.

Colligative Properties

$$57. \quad \text{molality} = m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{27.0 \text{ g N}_2\text{H}_4\text{CO}}{150.0 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol N}_2\text{H}_4\text{CO}}{60.06 \text{ g N}_2\text{H}_4\text{CO}} = 3.00 \text{ molal}$$

$$\Delta T_b = K_b m = \frac{0.51 \text{ }^\circ\text{C}}{\text{molal}} \times 3.00 \text{ molal} = 1.5 \text{ }^\circ\text{C}$$

The boiling point is raised from 100.0°C to 101.5°C (assuming P = 1 atm).

$$58. \quad \Delta T_b = 77.85 \text{ }^\circ\text{C} - 76.50 \text{ }^\circ\text{C} = 1.35 \text{ }^\circ\text{C}; \quad m = \frac{\Delta T_b}{K_b} = \frac{1.35 \text{ }^\circ\text{C}}{5.03 \text{ }^\circ\text{C kg/mol}} = 0.268 \text{ mol/kg}$$

$$\text{mol biomolecule} = 0.0150 \text{ kg solvent} \times \frac{0.268 \text{ mol hydrocarbon}}{\text{kg solvent}} = 4.02 \times 10^{-3} \text{ mol}$$

From the problem, 2.00 g biomolecule was used that must contain 4.02×10^{-3} mol biomolecule. The molar mass of the biomolecule is:

$$\frac{2.00 \text{ g}}{4.02 \times 10^{-3} \text{ mol}} = 498 \text{ g/mol}$$

$$59. \quad \Delta T_f = K_f m, \quad \Delta T_f = 1.50 \text{ }^\circ\text{C} = \frac{1.86 \text{ }^\circ\text{C}}{\text{molal}} \times m, \quad m = 0.806 \text{ mol/kg}$$

$$0.200 \text{ kg H}_2\text{O} \times \frac{0.806 \text{ mol C}_3\text{H}_8\text{O}_3}{\text{kg H}_2\text{O}} \times \frac{92.09 \text{ g C}_3\text{H}_8\text{O}_3}{\text{mol C}_3\text{H}_8\text{O}_3} = 14.8 \text{ g C}_3\text{H}_8\text{O}_3$$

$$63. \quad \Delta T_f = K_f m, \quad m = \frac{\Delta T_f}{K_f} = \frac{0.300 \text{ }^\circ\text{C}}{5.12 \text{ }^\circ\text{C kg/mol}} = \frac{5.86 \times 10^{-2} \text{ mol thyroxine}}{\text{kg benzene}}$$

The mol of thyroxine present is:

$$0.0100 \text{ kg benzene} \times \frac{5.86 \times 10^{-2} \text{ mol thyroxine}}{\text{kg benzene}} = 5.86 \times 10^{-4} \text{ mol thyroxine}$$

From the problem, 0.455 g thyroxine were used; this must contain 5.86×10^{-4} mol thyroxine. The molar mass of the thyroxine is:

$$\text{molar mass} = \frac{0.455 \text{ g}}{5.86 \times 10^{-4} \text{ mol}} = 776 \text{ g/mol}$$

65. a. $M = \frac{1.0 \text{ g protein}}{\text{L}} \times \frac{1 \text{ mol}}{9.0 \times 10^{-4} \text{ g}} = 1.1 \times 10^{-5} \text{ mol/L}; \pi = MRT$

At 298 K: $\pi = \frac{1.1 \times 10^{-5} \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 298 \text{ K} \times \frac{760 \text{ torr}}{\text{atm}}, \pi = 0.20 \text{ torr}$

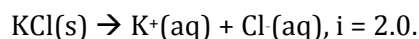
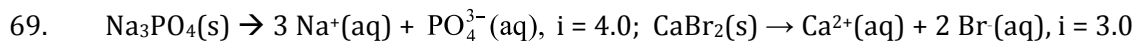
Because $d = 1.0 \text{ g/cm}^3$, 1.0 L solution has a mass of 1.0 kg. Because only 1.0 g of protein is present per liter of solution, 1.0 kg of H_2O is present and molality equals molarity.

$$\Delta T_f = K_f m = \frac{1.86^\circ\text{C}}{\text{molal}} \times 1.1 \times 10^{-5} \text{ molal} = 2.0 \times 10^{-5} \text{ }^\circ\text{C}$$

b. Osmotic pressure is better for determining the molar mass of large molecules. A temperature change of $10^{-5} \text{ }^\circ\text{C}$ is very difficult to measure. A change in height of a column of mercury by 0.2 mm (0.2 torr) is not as hard to measure precisely.

67. $\pi = MRT, M = \frac{\pi}{RT} = \frac{8.00 \text{ atm}}{\frac{0.08206 \text{ L atm}}{\text{mol K}} \times 298 \text{ K}} = 0.327 \text{ mol/L}$

Properties of Electrolyte Solutions

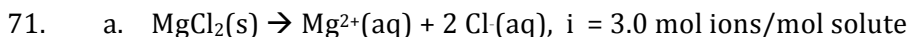


The effective particle concentrations of the solutions are:

$4.0(0.010 \text{ molal}) = 0.040 \text{ molal}$ for Na_3PO_4 solution; $3.0(0.020 \text{ molal}) = 0.060 \text{ molal}$ for CaBr_2 solution; $2.0(0.020 \text{ molal}) = 0.040 \text{ molal}$ for KCl solution; slightly greater than 0.020 molal for HF solution since HF only partially dissociates in water (it is a weak acid).

a. The 0.010 *m* Na_3PO_4 solution and the 0.020 *m* KCl solution both have effective particle concentrations of 0.040 *m* (assuming complete dissociation), so both of these solutions should have the same boiling point as the 0.040 *m* $\text{C}_6\text{H}_{12}\text{O}_6$ solution (a nonelectrolyte).

- b. $P = \chi P^\circ$; As the solute concentration decreases, the solvent's vapor pressure increases since χ increases. Therefore, the 0.020 *m* HF solution will have the highest vapor pressure since it has the smallest effective particle concentration.
- c. $\Delta T = K_f m$; The 0.020 *m* CaBr₂ solution has the largest effective particle concentration so it will have the largest freezing point depression (largest ΔT).

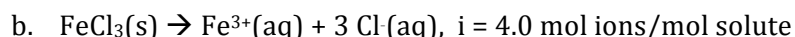


$$\Delta T_f = iK_f m = 3.0 \times 1.86^\circ\text{C/molal} \times 0.050 \text{ molal} = 0.28^\circ\text{C}; T_f = -0.28^\circ\text{C}$$

(Assuming water freezes at 0.00°C.)

$$\Delta T_b = iK_b m = 3.0 \times 0.51^\circ\text{C/molal} \times 0.050 \text{ molal} = 0.077^\circ\text{C}; T_b = 100.077^\circ\text{C}$$

(Assuming water boils at 100.000°C.)



$$\Delta T_f = iK_f m = 4.0 \times 1.86^\circ\text{C/molal} \times 0.050 \text{ molal} = 0.37^\circ\text{C}; T_f = -0.37^\circ\text{C}$$

$$\Delta T_b = iK_b m = 4.0 \times 0.51^\circ\text{C/molal} \times 0.050 \text{ molal} = 0.10^\circ\text{C}; T_b = 100.10^\circ\text{C}$$

73. $\Delta T_f = iK_f m$, $i = \frac{\Delta T_f}{K_f m} = \frac{0.110^\circ\text{C}}{1.86^\circ\text{C/molal} \times 0.0225 \text{ molal}} = 2.63$ for 0.0225 *m* CaCl₂

$$i = \frac{0.440}{1.86 \times 0.0910} = 2.60 \text{ for } 0.0910 \text{ } m \text{ CaCl}_2; i = \frac{1.330}{1.86 \times 0.278} = 2.57 \text{ for } 0.278 \text{ } m \text{ CaCl}_2$$

$$i_{\text{ave}} = (2.63 + 2.60 + 2.57)/3 = 2.60$$

Note that i is less than the ideal value of 3.0 for CaCl₂. This is due to ion pairing in solution. Also note that as molality increases, i decreases. More ion pairing occurs as the solute concentration increases.

75. a. $T_c = 5(T_f - 32)/9 = 5(-29 - 32)/9 = -34^\circ\text{C}$; Assuming the solubility of CaCl₂ is temperature independent, the molality of a saturated CaCl₂ solution is:

$$\frac{74.5 \text{ g CaCl}_2}{100.0 \text{ g}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol CaCl}_2}{110.98 \text{ g CaCl}_2} = \frac{6.71 \text{ mol CaCl}_2}{\text{kg H}_2\text{O}}$$

$$\Delta T_f = iK_f m = 3.00 \times 1.86^\circ\text{C kg/mol} \times 6.71 \text{ mol/kg} = 37.4^\circ\text{C}$$

Assuming $i = 3.00$, a saturated solution of CaCl₂ can lower the freezing point of water to -37.4°C . Assuming these conditions, a saturated CaCl₂ solution should melt ice at -34°C (-29°F).

- b. From Exercise 11.73, $i_{\text{ave}} = 2.60$; $\Delta T_f = iK_f m = 2.60 \times 1.86 \times 6.71 = 32.4^\circ\text{C}$

$$T_f = -32.4^\circ\text{C}$$

Assuming $i = 2.60$, a saturated CaCl_2 solution will not melt ice at $-34^\circ\text{C}(-29^\circ\text{F})$.

Additional Exercises

94. a. $m = \frac{\Delta T_f}{K_f} = \frac{1.32^\circ\text{C}}{5.12^\circ\text{C kg/mol}} = 0.258 \text{ mol/kg}$

$$\text{mol unknown} = 0.01560 \text{ kg} \times \frac{0.258 \text{ mol unknown}}{\text{kg}} = 4.02 \times 10^{-3} \text{ mol}$$

$$\text{molar mass of unknown} = \frac{1.22 \text{ g}}{4.02 \times 10^{-3} \text{ mol}} = 303 \text{ g/mol}$$

$$\text{Uncertainty in temperature} = \frac{0.04}{1.32} \times 100 = 3\%; \text{ A } 3\% \text{ uncertainty in } 303 \text{ g/mol} \\ = 9 \text{ g/mol.}$$

So, molar mass = $303 \pm 9 \text{ g/mol}$.

- b. No, codeine could not be eliminated since its molar mass is in the possible range including the uncertainty.
- c. We would really like the uncertainty to be $\pm 1 \text{ g/mol}$. We need the freezing point depression to be about 10 times what it was in this problem. Two possibilities are:
1. make the solution ten times more concentrated (may be a solubility problem) or
 2. use a solvent with a larger K_f value, e.g., camphor