## Chapter 2

### Solutions

#### 1. How many grams of CuSO<sub>4</sub> are required to make 650. mL of a 0.115-M solution?

 $650. \text{ mL solution} \times \frac{1 \text{ L solution}}{1000 \text{ mL solution}} \times \frac{0.115 \text{ mol } \text{CuSO}_4}{\text{ L solution}} \times \frac{159.608 \text{ g } \text{CuSO}_4}{1 \text{ mol } \text{CuSO}_4} = 11.9 \text{ g } \text{CuSO}_4$ 

3. How many grams of Na<sub>2</sub>SO<sub>4</sub> are required to make 90.0 mL of a solution that is 0.200 M in Na<sup>1+</sup>?

90.0 mL solution  $\times \frac{1 \text{ L solution}}{1000 \text{ mL solution}} \times \frac{0.200 \text{ mol Na}^{1+}}{\text{ L solution}} \times \frac{1 \text{ mol Na}_2\text{SO}_4}{2 \text{ mol Na}^{1+}} \times \frac{142.042 \text{ g Na}_2\text{SO}_4}{1 \text{ mol Na}_2\text{SO}_4} = 1.28 \text{ g Na}_2\text{SO}_4$ 

5. How many mmoles of chloride ion are in 55.0 mL of 0.0688 M BaCl<sub>2</sub> solution?

55.0 mL solution  $\times \frac{0.0688 \text{ mmol BaCl}_2}{1 \text{ mL solution}} \times \frac{2 \text{ mmol Cl}^{1-}}{1 \text{ mmol BaCl}_2} = 7.57 \text{ mmol Cl}^{1-}$ 

7. How many mL of 0.124 M Ba(OH)<sub>2</sub> are required to deliver 38.6 mmol of hydroxide ion ?

38.6 mmol  $OH^{1-} \times \frac{1 \text{ mmol Ba}(OH)_2}{2 \text{ mmol OH}^{1-}} \times \frac{1 \text{ mL solution}}{0.124 \text{ mmol Ba}(OH)_2} = 156 \text{ mL solution}$ 

9. How many grams of sodium should be added to 15.0 g Hg to make a mixture in which the mole fraction of sodium is 0.800?

moles of mercury =15.0 g Hg  $\times \frac{1 \text{ mol Hg}}{200.59 \text{ g Hg}} = 0.0748 \text{ mol Hg}$ 

Use moles of Hg and the mole fraction equation:  $X_{Na} = 0.800 = \frac{n}{0.0748 + n}$ , rearrange to eliminate denominator:  $0.0598 + 0.800n = n \implies n = \frac{0.0598}{0.200} = 0.299$  mol Na Calculate the grams of Na: 0.299 mol Na $\times \frac{22.99 \text{ g Na}}{1 \text{ mol Na}} = 6.88 \text{ g Na}$ 

11. The density of a 1.140-M solution of NH<sub>4</sub>Cl at 20 °C is 1.0186 g/mL. What mass of water does 100. mL of this solution contain?

The total mass of this solution is 1.0186 g/mL x 100. mL = 102 (three significant figures)

The mass of NH<sub>4</sub>Cl in this solution is 0.100 L  $\times \frac{1.140 \text{ mol NH}_4\text{Cl}}{1 \text{ L NH}_4\text{Cl}} \times \frac{53.49 \text{ g}}{1 \text{ mol NH}_4\text{Cl}} = 6.10 \text{ NH}_4\text{Cl}$ 

The mass of water is then the difference between the total mass of the solution and the mass of the  $NH_4CI$ : 102 g solution - 6 g  $NH_4CI$  = 96 g water.

13. What mass of Fe(ClO<sub>4</sub>)<sub>3</sub> is required to make 275 mL of a solution that is 0.100 M in ClO<sub>4</sub><sup>1-</sup>?

$$0.0275 \text{ L} \times \frac{0.100 \text{ mol ClO}_4^{1-}}{1 \text{ L}} \times \frac{1 \text{ mol Fe}(\text{ClO}_4)_3}{3 \text{ mol ClO}_4^{1-}} \times \frac{354 \text{ g Fe}(\text{ClO}_4)_3}{1 \text{ mol}} = 3.25 \text{ g Fe}(\text{ClO}_4)_3$$

15. How many grams of CaCl<sub>2</sub> should be added to 50.0 g of water to make a solution in which the mole fraction of Cl<sup>1</sup>is 0.150?

First get the number of moles of water: 50.0 g H<sub>2</sub>O  $\times \frac{1 \text{ mol } \text{H}_2\text{O}}{18.0 \text{ g } \text{H}_2\text{O}}$  = 2.78 mol H<sub>2</sub>O

If n mol CaCl<sub>2</sub> are dissolved, n mol Ca<sup>2+</sup> and 2n mol Cl<sup>1-</sup> form in solution, or 3n mol ions.

The mole fraction of chloride ion is 0.150, so

 $\begin{array}{l} 0.150 \ = \ \displaystyle \frac{2n \ \text{mol} \ \text{Cl}^{-1}}{3n \ \text{mol} \ \text{ions} \ + \ 2.78 \ \text{mol} \ \text{of} \ \text{H}_2\text{O}} \\ \text{Rearrange and solve for n:} \ 0.450n + 0.417 \ = \ 2n \quad \Rightarrow \quad n = 0.269 \ \text{mol} \ \text{CaCl}_2 \\ 0.269 \ \text{mol} \ \text{CaCl}_2 \ \times \ \displaystyle \frac{111 \ \text{g} \ \text{CaCl}_2}{1 \ \text{mol}} \ = \ 29.9 \ \text{g} \ \text{CaCl}_2 \end{array}$ 

- 17. A concentrated solution of phosphoric acid is 75% H<sub>3</sub>PO<sub>4</sub> by mass and has a density of 1.57 g/mL.
  - a) What is the molarity of the concentrated phosphoric acid?

Assume 100. g of concentrated phosphoric acid then 75% translates to 75 g of  $H_3PO_4$ . Calculate the moles of  $H_3PO_4$ .

75 g  $H_3PO_4 \times \frac{1 \text{ mol } H_3PO_4}{97.994 \text{ g}}$ =0.77 mol  $H_3PO_4$ 

Use the density to calculate the volume of 100 g of concentrated phosphoric acid.

100. g conc  $H_3PO_4 \times \frac{1 \text{ mL}}{1.57 \text{ g}}$ =63.7 mL conc  $H_3PO_4$ 

The molarity of the solution can then be calculated,  $\frac{0.77 \text{ mol } \text{H}_3\text{PO}_4}{0.0637 \text{ L solution}}$ =12. M H<sub>3</sub>PO<sub>4</sub>

b) How many mL of the concentrated acid would be required to prepare 1.5 L of a 0.20-M solution?

Use dilution equation,  $C_i V_i = C_f V_f$ : (0.20 M H<sub>3</sub>PO<sub>4</sub>)(1.5 L) = (12 M H<sub>3</sub>PO<sub>4</sub>)(V<sub>f</sub>)  $V_c = \frac{(1.5 L)(0.20 M H_3 PO_4)}{0.25 L} = 25 mL$ 

$$V_{\rm f} = \frac{(10 - 1)(10 - 1)(10 - 1)}{12 \text{ M H}_3\text{PO}_4} = 0.025 \text{ L} = 25$$

19. A 60/40 solder is a solution which is 60% Pb and 40% Sn. What are the two mole fractions in the solder?

Work with 100. g of solder, which contains 60. g of Pb and 40. g of Sn.

Calculate the moles of Pb and the moles of Sn

60. g Pb×
$$\frac{1 \text{ mol Pb}}{207.19 \text{ g}}$$
=0.290 mol Pb and 40. g Sn× $\frac{1 \text{ mol Sn}}{118.71 \text{ g}}$ =0.3370 mol Sn

Use Equation 2.2 to determine the mole fraction of Pb. The mole fraction of Sn can be determined by difference because the sum of the two mole fractions must be one.

$$X_{Pb} = \frac{0.290}{0.290 + 0.3370} = 0.46$$
 and  $X_{Sn} = 1 - X_{Pb} = 1 - 0.46 = 0.54$ 

#### 21. What is the molality of a sucrose solution if its mole fraction is 0.025?

A mole fraction of 0.025 means that there are 0.025 mol of sucrose in 1 mole of particles (sucrose +  $H_2O$ ). Thus, the number of moles of water present must be 1.000 mol total – 0.025 mol sucrose = 0.975 mol  $H_2O$ . Thus, the solution has 0.025 mol sucrose for each 0.975 mol  $H_2O$ . Starting here, we can more easily convert between concentrations.

$$\frac{0.025 \text{ mol sucrose}}{0.975 \text{ mol H}_2\text{O}} = \frac{0.025 \text{ mol sucrose}}{(0.975 \text{ mol H}_2\text{O}) \left(\frac{18.0 \text{ g H}_2\text{O}}{\text{mol H}_2\text{O}}\right) \left(\frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}}\right)} = \frac{0.025 \text{ mol sucrose}}{0.01755 \text{ kg H}_2\text{O}} = 1.4 \text{ m}$$

23. Pure, crystalline Si is a poor conductor, but it can be converted into a p-type semiconductor by dissolving 1.0 ppm Ga in the Si crystal. This is a process called "doping" in the semiconductor industry. Given that the molar mass of Si is 28.086 and of Ga is 69.72, what is the mole fraction of Ga in the crystal? The density of the p-type Si semiconductor is 2.33 g/cm<sup>3</sup>.

Use the definition of ppm and assume a 1.0 g sample of semiconductor to obtain the mass of gallium.

ppm Ga = 
$$\frac{g Ga}{g \text{ semiconductor}} \times 10^6 \Rightarrow g Ga = \frac{1.0 \text{ ppm} \times 1.0 \text{ g semiconductor}}{10^6} \text{ g} = 1.0 \times 10^{-6} \text{ g Ga}$$
  
Then calculate the moles of each component: Moles Ga =  $\frac{1.0 \times 10^{-6} \text{ g}}{10^{-6} \text{ g}} = 1.4 \times 10^{-8} \text{ mol Ga}$ 

Then calculate the moles of each component: Moles Ga =  $\frac{1000000}{69.72}$  = 1.4×10<sup>-6</sup> mol Ga

The mass of the Si would then be calculated as the difference between the total mass, 1.0 g, and the mass of Ga. However, the mass of Ga is negligibly small, so it can be ignored. Thus, the mass of silicon is 1.0 g. Next, determine the males of silicon is 1.0 g. Si up 1 mol Si and Si and

determine the moles of silicon: moles Si = 1.0 g Si 
$$\times \frac{1.000}{28.086}$$
 g Si = 0.0356 mol Si

$$X_{Ga} = \frac{\text{mole Ga}}{\text{mole Ga + mole Si}} = \frac{1.4 \times 10^{-8} \text{ mol Ga}}{1.4 \times 10^{-8} \text{ mol Ga + 0.0356 mol Si}} = 4.02 \times 10^{-7}$$

#### 25. What is the molality of a 2.06-M solution of H<sub>2</sub>SO<sub>4</sub> that has a density of 1.124 g/mL?

Assume a total volume of 1 L, which has a total mass of (1000 mL)(1.124 g/mL) = 1124 g = 1.124 kg.

The mass of H<sub>2</sub>SO<sub>4</sub> in 1 L of solution is (1 L)(2.06 mol/L)(98.1 g/mol) = 202 g = 0.202 kg H<sub>2</sub>SO<sub>4</sub>

The mass of water is obtained by difference: 1.124 kg solution - 0.202 kg H<sub>2</sub>SO<sub>4</sub> = 0.922 kg H<sub>2</sub>O

the molality is: m =  $\frac{2.06 \text{ mol } \text{H}_2\text{SO}_4}{0.922 \text{ kg } \text{H}_2\text{O}}$  = 2.23 m

27. What is the molarity of a solution prepared by adding 30.0 mL of water to 57.0 mL of a 0.114 M CuSO<sub>4</sub> solution? Assume additive volumes.

Calculate the moles of CuSO<sub>4</sub> and divide by the total volume.

 $\frac{0.114 \text{ mol } \text{CuSO}_4}{\text{L } \text{H}_2 \text{O}} \times 0.057 \text{ L } \text{H}_2 \text{O} = 6.50 \times 10^{-3} \text{ mol } \text{CuSO}_4; \quad \text{V} = \frac{6.50 \times 10^{-3} \text{ mol } \text{CuSO}_4}{0.030 \text{ L } \text{H}_2 \text{O} + 0.057 \text{ L } \text{H}_2 \text{O}} = 0.0747 \text{ M}_2 \text$ 

Thus, 10 mL of 12 M HCl should be diluted to 240 mL to prepare a 0.50 M solution.

29. What volume of an 18.0 M "stock solution" of H<sub>2</sub>SO<sub>4</sub> is needed in order to make 100. mL of a 3.0 M H<sub>2</sub>SO<sub>4</sub> solution?

Using Equation 2.5,  $C_iV_i = C_fV_f$ , to solve for the volume of the  $H_2SO_4$  needed to make 100 mL of the 3.0 M solution:

 $V \times 18.0 \text{ M H}_2\text{SO}_4 = 100 \text{ mL} \times 3.0 \text{ M H}_2\text{SO}_4$ 

Rearranging the equation and solving for V yields: V =  $\frac{100 \text{ mL} \times 3.0 \text{ MH}_2\text{SO}_4}{18.0 \text{ MH}_2\text{SO}_4} = 17 \text{ mLH}_2\text{SO}_4$ 

17 mL of the stock solution should be diluted to a total volume of 100 mL.

#### 31. What is the [H<sup>1+</sup>] in a solution prepared by diluting 20.0 mL of 12.0 M HCl to 350. mL?

Use the dilution equation:  $C_iV_i = C_fV_f$ 

(12.0 M)(20.0 mL) = C<sub>f</sub>(350 mL), so C<sub>f</sub> =  $\frac{(12.0)(20.0) \text{ mmol } \text{H}^{1+}}{350 \text{ mL}}$  = 0.69 M

33. What is the molarity of the chloride ion in a solution prepared by mixing 75 mL of 0.20 M NaCl and 55 mL of 0.15 M MgCl<sub>2</sub>?

$$[Cl^{1-}] = \frac{\text{mmol Cl}^{1-}}{\text{total milliliters}} = \frac{(75 \text{ mL})(0.20 \text{ mmol Cl}^{1-}/\text{mL}) + (55 \text{ mL})(0.15 \text{ mmol MgCl}_2/\text{mL})(2 \text{ mmol Cl}^{1-}/\text{mmol MgCl}_2)}{75 \text{ mL} + 55 \text{ mL}}$$
$$[Cl^{1-}] = \frac{31.5 \text{ mmol Cl}^{1-}}{130 \text{ mL}} = 0.24 \text{ M}$$

35. 100.0 mL of a stock solution of hydrochloric acid was diluted to 250.0 mL. A 10.0 mL of the resulting solution was then diluted 250.0 mL. The final solution was prepared by diluting 30.0 mL of this solution to 100.0 mL. A 40.0-mL sample of the final solution was titrated with 0.0887 M NaOH. If the titration required 32.6 mL of the base, what is the concentration of the original stock solution.

The reaction is  $H^{1+} + OH^{1-} \rightarrow H_2O$ , so the acid:base stoichiometry is 1:1, and we can use  $M_AV_A = M_BV_B$  to determine the concentration of the acid in the diluted solution.

$$M_{A} = \frac{(0.0887)(32.6) \text{ mmol}}{40.0 \text{ mL}} = 0.0723 \text{ M}$$

This is the concentration of the 40.0 mL sample, which is the same concentration as the 100.0 mL solution it came from.

Next, use the dilution equation to take 100 mL of 0.0723 M solution to the original solution.

$$C_f = C_i \times \frac{V_i}{V_f}$$
. Each successive concentration is multiplied by the ratio of volumes to yield the following:

C = 
$$(0.0723 \text{ M}) \times \frac{100.0 \text{ mL}}{30.0 \text{ mL}} \times \frac{250.0 \text{ mL}}{10.0 \text{ mL}} \times \frac{250.0 \text{ mL}}{100.0 \text{ mL}} = 15.1 \text{ M}$$

37. A stock solution that is 0.4762 M undergoes the following successive dilutions: 1:3, 2:5, 1:10, and 2:15. What is the concentration of the final solution?

c = 0.4762 M
$$\left(\frac{1}{3}\right)\left(\frac{2}{5}\right)\left(\frac{1}{10}\right)\left(\frac{2}{15}\right)$$
 = 8.466×10<sup>-4</sup> M = 0.8466 mM

39. Formaldehyde can be measured in aqueous solutions by reaction with 1,3,5-trihydroxybenzene to produce a redorange dye. The absorbance is measured with a spectrophotometer at a 470 nm wavelength. A standard solution was prepared by dissolving 1.50 mL of formaldehyde gas (at 1.00 atm pressure and 25 °C) in 1.00 L of water. This solution was treated with an excess of 1,3,5-trihydroxybenzene. A couple of milliliters of the resulting solution was placed in a spectrophoto-metric cell with a thickness of 1.00 cm, and the absorbance was measured to be 0.967. A 1.00-L sample of rainwater was similarly treated with 1,3,5-trihydroxybenzene and the absorbance was found to be 0.426 in the same spectrophotometric cell. What is the concentration of formaldehyde in the rain water?

First the concentration of the formaldehyde must be found for the standard solution in units of mols per liter. To do this, use the ideal gas law, PV = nRT, to calculate mols formaldehyde, then divide by the total volume of 1.0 L to get the concentration:

$$n = \frac{PV}{RT} = \frac{1.00 \text{ atm} \times 0.0015 \text{ L}}{298 \text{ K} \times 0.082057 \text{ L} \cdot \text{atm/mol} \cdot \text{K}} = 6.13 \times 10^{-5} \text{ mols formalydehyde}$$
$$Molarity = \frac{\text{moles formaldehyde}}{\text{L solution}} = \frac{6.13 \times 10^{-5} \text{ mols formalydehyde}}{1.00 \text{ L}} = 6.13 \times 10^{-5} \text{ M}$$

The absorbances can be determined from Beer's law (Eq. 2.6) as:  $A_{std} = \epsilon lc_{std}$   $A_{stample} = \epsilon lc_{sample}$ where  $A_{std}$  is the absorbance of the standard and  $A_{sample}$  is the absorbance of the sample. However, the absorbance of the same complex is being measured and the two measurements use the same path length, so the values of  $\epsilon$  and I are the same in both the standard and the sample solutions. Divide the  $A_{std}$  expression by the  $A_{sample}$  expression to eliminate  $\epsilon$  and I.

$$\frac{A_{std}}{A_{sample}} = \frac{c_{std}}{c_{sample}} \implies c_{sample} = c_{std} \times \frac{A_{sample}}{A_{std}} = 6.13 \times 10^{-5} \text{ M} \times \frac{0.426}{0.967} = 2.70 \times 10^{-5} \text{ M}$$

Recall that ppm =  $\frac{g \text{ solute}}{g \text{ solution}} \times 10^6$  and that 1000. mL water has a mass of 1000. g. Therefore:

$$\frac{2.70 \times 10^{-5} \text{ mols CH}_2\text{O}}{1 \text{ L}} \times \frac{30.03 \text{ g CH}_2\text{O}}{1 \text{ mol CH}_2\text{O}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1000 \text{ mL}}{1000 \text{ g}} \times 10^6 = 0.811 \text{ ppm}$$

- 41. Ru(bpy)<sub>3</sub><sup>2+</sup> (bpy = 2,2'-bipyridine) is being investigated for use in solar energy conversion because it is deeply colored and has interesting redox capabilities in the excited state. A solution was prepared by dissolving 58.2 mg Ru(bpy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub> (M<sub>m</sub> = 612 g/mol) in enough water to make 100.0 mL of solution. However, the resulting solution absorbed too strongly at 450 nm to be measured, so 5.0 mL of the solution was diluted to 100.0 mL. The absorbance of the final solution at 450 nm in a 1.00-cm cell was determined to be 0.571.
  - a) What is the molar absorptivity of  $Ru(bpy)_3^{2+}$  at 450 nm?

52.8 mg Ru(bpy)<sub>3</sub><sup>2+</sup> × 
$$\frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol}}{612 \text{ g}} = 9.51 \times 10^{-5} \text{ mol Ru(bpy)}_3^{2+}$$
  
[Ru(bpy)<sub>3</sub><sup>2+</sup>] =  $\frac{9.51 \times 10^{-5} \text{ mol Ru(bpy)}_3^{2+}}{0.100 \text{ L}} = 9.51 \times 10^{-4} \text{ M}$   
Use M<sub>1</sub>V<sub>1</sub> = M<sub>2</sub>V<sub>2</sub> to account for dilution.  
(9.51 × 10<sup>-4</sup> M)(0.005 L) = (M<sub>2</sub>)(0.100 L)  $\Rightarrow$  M<sub>2</sub> = 4.75×10<sup>-5</sup> M  
Use A =  $\varepsilon$ /c to solve for  $\varepsilon$   
0.571 =  $\varepsilon$  (1.00)(4.75×10<sup>-5</sup> M)  $\Rightarrow$   $\varepsilon$  = 1.20×10<sup>4</sup> M<sup>-1</sup>·cm<sup>-1</sup>

b) What is the concentration of  $\operatorname{Ru}(\operatorname{bpy})_3^{2^+}$  in a solution with an absorbance of 0.885 at 450 nm?  $A = \varepsilon lc \Rightarrow 0.885 = (1.20 \times 10^4)(1.00)(c) \Rightarrow c = 7.37 \times 10^{-5} \text{ M} = [\operatorname{Ru}(\operatorname{bpy})_3^{2^+}]$ 

#### 43. What is the colligative molality of a solution prepared by dissolving 15.2 g of AlCl<sub>3</sub> in 155 mL of water?

Determine the molality:

Mass of water = (155 mL)(1.00 g/mL)(1 kg/1000 g) = 0.155 kg water

Moles of AlCl<sub>3</sub>: 15.2 g AlCl<sub>3</sub> 
$$\times \frac{1 \text{ mol AlCl}_3}{133.3 \text{ g AlCl}_3} = 0.114 \text{ mol AlCl}_3$$

Molality of AlCl<sub>3</sub> in solution = 
$$\frac{0.114 \text{ mol AlCl}_3}{0.155 \text{ kg H}_2\text{O}} = 0.736 \text{ m}$$

 $AICI_3 \rightarrow AI^{3+} + 3CI^{1-}$ , so the van't Hoff factor is i = 4;  $m_c = im = 4(0.736) = 2.94 \text{ m}$ 

#### 45. What is the freezing point of a 0.11 m aqueous CaCl<sub>2</sub> solution?

The solution can be started by calculating the freezing point depression:

 $CaCl_{2}(s) \rightarrow Ca^{2+}(aq) + 2 Cl^{1-}(aq)$  so i = 3.  $k_{f} = 1.86 \ ^{o}C \cdot m^{-1}$  (from Table 2.2) and m = 0.11 m  $\Delta T_{f} = ik_{f}m = (3)(1.86 \ ^{o}C \cdot m^{-1})(0.11 \ m) \implies \Delta T_{f} = 0.61 \ ^{o}C \implies fp = 0.00 \ ^{o}C - 0.61 \ ^{o}C = -0.61 \ ^{o}C$ 

#### 47. What is the osmotic pressure of a 0.20 M CaCl<sub>2</sub> solution at 298 K?

The osmotic pressure can be calculated as follows:

 $CaCl_2 \rightarrow Ca^{2+}(aq) + 2 Cl^{1-}(aq)$  i = 3. M = 0.20 M. R = 0.0821 atm · K<sup>-1</sup> · M<sup>-1</sup>. T = 298 K  $\Pi$  = iMRT = (3)(0.20 M)(0.0821 atm · K<sup>-1</sup> · M<sup>-1</sup>)(298 K) =15 atm

#### 49. 1.0 g of CaCl<sub>2</sub> is dissolved in 100 mL of water to produce a solution with a density 1.1 g/mL.

a) What is the vapor pressure of the solution at 20 °C? The vapor pressure of water at 20 °C is 17.5 mm Hg. Use equation 2.10b to calculate the vapor pressure of the solution, but first the mole fraction of solvent must be determined. Any amount of solvent can be used to the numbers of moles, so we assume 100 mL. In 100 mL of solution, there are

100. mL water  $\times \frac{1 \text{ g water}}{1 \text{ mL water}} \times \frac{1 \text{ mol water}}{18.02 \text{ g water}} = 5.549 \text{ mol water}$  and

 $CaCl_2$  is ionic, so it disolves as ions:  $CaCl_2 \rightarrow Ca^{2+} + 2Cl^{1-}$ . Thus, the van't Hoff factor is i = 3.

1.0 g CaCl<sub>2</sub> × 
$$\frac{1 \text{ mol CaCl}_2}{110.98 \text{ g CaCl}_2}$$
 ×  $\frac{3 \text{ mol particles}}{1 \text{ mol CaCl}_2}$  = 0.027 mol particles

The mole fraction of water is  $X_{solvent} = \frac{5.549 \text{ mol water}}{(5.549 \text{ mol water} + 0.027 \text{ mol solute particles})} = 0.995$ 

so the vapor pressure of the solution is  $P_{solution} = X_{solvent} \times P_{solvent}^{o} = 0.995 \times 17.5 \text{ mm Hg} = 17.4 \text{ mm Hg}$ 

#### b) What is the boiling point of the solution?

To calculate the boiling point of the solution, we must first find the colligative molality of the  $CaCl_2$  solution. From part (a), we already know that there is 0.027 moles of particles (ions) are in 100 mL of solution, so we must now determine the kilograms of solvent.

100. mL water  $\times \frac{1 \text{ g water}}{1 \text{ mL water}} \times \frac{1 \text{ kg water}}{1000 \text{ g water}} = 0.10 \text{ kg water}$ 

Therefore, the colligative molality is found to be  $m_c = (0.027 \text{ mol particles})/(0.10 \text{ kg water}) = 0.27 \text{ m}$ . Now, using Table 2.3 to find  $k_b$  for water and using Eq. 2.9 (Note: in this case the solute dissociates into 3 components; one Ca<sup>2+</sup> and two Cl<sup>1-</sup> ions, therefore, i = 3):

 $\Delta T_{b} = ik_{b}m = k_{b}m_{c} = (0.512 \text{ °C/m})(0.27 \text{ m}) = 0.14 \text{ °C}; T_{b} = 100 + \Delta T_{b} = 100.14 \text{ °C}$ 

#### c) What is the freezing point of the solution?

The procedure for this problem is very similar to that in part (b).

 $\Delta T_{f} = i x k_{f} x m = k_{f}m_{c} = (1.86 \text{ }^{\circ}\text{C/m})(0.27 \text{ }m) = 0.50 \text{ }^{\circ}\text{C}; T_{f} = 0.0 - \Delta T_{f} = -0.50 \text{ }^{\circ}\text{C}$ 

d) What osmotic pressure would develop at 25 °C when the solution is placed in contact with pure water at a semipermeable membrane?

For this problem we need to calculate the molarity of the CaCl<sub>2</sub>. From part (a), we know that there is 0.027 moles of particles in solution, so the colligative molarity of particles in the solution is.

 $M_c = (0.027 \text{ mol particles})/(0.100 \text{L water}) = 0.27 \text{ M}$ 

Using Equation 2.13, we obtain  $\Pi = M_c RT = (0.27 \text{ M})(0.0821 \text{ atm} \text{K}^{-1} \text{M}^{-1})(298 \text{ K}) = 6.6 \text{ atm}$ 

51. The colligative molarity of living cells is typically 0.3 M. What osmotic pressure would develop when the cells are placed in pure water at 37 °C? What effect would this have on the cell?

 $\Pi = M_c RT = (0.3 \text{ mol} \cdot L)(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(310 \text{ K}) = 8 \text{ atm}$ 

Water moves from higher concentration to lower concentration, so the 8 atm is the pressure pushing water into the cell. Consequently, water will flow into the cell, and since the cell membrane cannot withstand such pressures, it would most likely rupture.

53. 15.8 mg of a protein is dissolved in enough water to make a 5.00-mL solution. What is the molar mass of the protein if the osmotic pressure of the solution at 15 °C is 4.65 torr?

Proteins do not dissociate in water (i = 1). T = 
$$15 + 273 = 288$$
 K. R = 0.0821 atm K<sup>-1</sup>·M<sup>-1</sup>.

$$\Pi = iMRT = 4.65 \text{ torr} \implies M = \frac{\Pi}{iRT} = \frac{4.65 \text{ torr} (1 \text{ atm}/760 \text{ torr})}{(1)(0.0821 \text{ atm} \cdot \text{K}^{1-} \cdot \text{M}^{1-})(288 \text{ K})} = 2.59 \cdot 10^{-4} \text{ M}$$

Notice that the pressure was converted from torr to atm.

The number of moles of protein can be calculated from the relationship  $n = M \times V$ .

n = 
$$(2.59 \cdot 10^{-4} \text{ M})(5.00 \cdot 10^{-3} \text{ L}) = 1.29 \cdot 10^{-6} \text{ mol}$$
  

$$M_{m} = \frac{15.8 \cdot 10^{-3} \text{ g protein}}{1.29 \cdot 10^{-6} \text{ mol protein}} = 12,200 \text{ g/mol}$$

55. Vitamin K is involved in normal blood clotting. When 1.00 g of vitamin K is dissolved in 20.0 g of camphor, (k<sub>f</sub> = 40.0 °C/m) the freezing point of the solution is lowered by 4.43 °C. What is the molar mass of vitamin K?

Use Eq 2.12 to find the molality of vitamin K (vitamin K does not dissociate in solution, so i = 1)

$$\Delta T_{f} = i x k_{f} x m = 1 x 40.0 \ ^{\circ}C/m x m = 4.43 \ ^{\circ}C$$

Solving for m yields m = m = 
$$\frac{\Delta T_f}{k} = \frac{4.43 \ ^{\circ}C}{40.0 \ ^{\circ}C \cdot m^{-1}} = 0.111 \ m$$

Determine the number of moles of pepsin dissolved in the 20.0 g (0.0200 kg) of solvent

0.0200 kg camphor 
$$\times \frac{0.111 \text{ mol vitamin K}}{\text{kg camphor}} = 0.00222 \text{ mol vitamin K}$$

The molar mass is obtained as the ratio of the mass of vitamin K to the number of moles that the mass represents.

 $M_{m} = \frac{\text{mass of vitamin K}}{\text{moles of vitamin K}} = \frac{1.00 \text{ g vitamin K}}{0.00222 \text{ mol vitamin K}} = 451 \text{ g/mol}$ 

57. What is the concentration of the excess reactant in a solution prepared by mixing 25.0 mL of 0.242 M HCl with 36.3 mL of 0.167 M Ba(OH)<sub>2</sub>? Is this solution acidic, basic or neutral?

$25.0 \text{ mL} \times \frac{0.242 \text{ mm}}{2}$	$\frac{100 \text{ H}_3 \text{O}^{1+}}{100 \text{ H}_3 \text{O}^{1+}} = 6$	.05 mmo	I H₂O <sup>1+</sup> &	$36.3 \text{ mL} \times \frac{0.1}{2}$	I67 mmol Ba(O⊦	$\frac{1}{2} \times \frac{2 \text{ mmol OH}^{1-}}{12.1 \text{ mmol OH}^{1-}} = 12.1 \text{ mmol OH}^{1-}$	nmol OH <sup>1-</sup>
m	L		5 -		1 mL	1 mmol Ba(OH) <sub>2</sub>	
The reaction table:	H <sub>3</sub> O <sup>1+</sup>	+ 0H <sup>1-</sup>	$\rightarrow 2H_2O$				
initial	6.05	12.1	mmol				
$\Delta$	-6.05	-6.05	mmol				
final	~	6.05	mmol				
Note that the 5 is wri	tten as a subs	script in th	ne final mn	nol of OH <sup>1-</sup> to i	indicate that it is	not significant but that it will be	

Note that the 5 is written as a subscript in the final mmol of OH<sup>+\*</sup> to indicate that it is not significant but that it will be used in future calculations. Therefore, the solution is basic because there is an excess amount of Ba(OH)<sub>2.</sub> The

concentration of hydroxide in the final solution can be calculated as follows:  $[OH^{1-}] = \frac{6.0_5 \text{ mmol OH}^{1-}}{(36.3 + 25.0) \text{ mL}} = 0.099 \text{ M}$ 

# 59. Determine the amount of precipitate that will form if 50.0 mL of 0.100 M Na<sub>2</sub>SO<sub>4</sub>(aq) and 100. mL of 0.300 M BaCl<sub>2</sub> are mixed.

The reaction is  $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ . (50.0 mL)(0.100 mmol/mL) = 5.00 mmol  $SO_4^{2-}$  and (100. ML)(0.300 mmol/mL) = 30.0 mmol  $Ba^{2+}$  are mixed, so  $SO_4^{2-}$  ion is the limiting reagent. 5.00 mmol  $SO_4^{2-} \times \frac{1 \text{ mmol } BaSO_4}{1 \text{ mmol } SO_4^{2-}} \times \frac{233.4 \text{ mg } BaSO_4}{1 \text{ mmol } BaSO_4} = 1.17 \times 10^3 \text{ mg } BaSO_4$  so 1.17 g of BaSO\_4 precipitate.

#### 61. Construct the reaction table for the net reaction of 36.6 mL of 0.0668 M FeCl<sub>3</sub> and 24.2 mL of 0.100 K<sub>2</sub>S.

The solubility rules indicate that KCl is soluble, but that  $Fe_2S_3$  should be insoluble. Thus, the reaction is between  $Fe^{3^+}$  and  $S^{2^-}$ . Next, determine he number of millimoles of each reactant

 $36.6 \text{ mL soln} \times \frac{0.0668 \text{ mmol FeCl}_3}{\text{mL soln}} \times \frac{1 \text{ mmol Fe}^{3+}}{1 \text{ mmol FeCl}_3} = 2.44 \text{ mmol Fe}^{3+}$   $24.2 \text{ mL soln} \times \frac{0.100 \text{ mmol K}_2\text{S}}{\text{mL soln}} \times \frac{1 \text{ mmol S}^{2-}}{1 \text{ mmol K}_2\text{S}} = 2.42 \text{ mmol S}^{2-}$ 

Sulfide is the limiting reactant as it can produce only  $\frac{1}{3}(2.42) = 0.807$  mmol Fe<sub>2</sub>S<sub>3</sub> while Fe<sup>3+</sup> can produce  $\frac{1}{2}(2.44) = 1.22$  mmol Fe<sub>2</sub>S<sub>3</sub>.

The reaction table:	2Fe <sup>3+</sup> +	3S <sup>2-</sup>	$\rightarrow \ Fe_2S_3$		
initial	2.44	2.42	0	mmol	
$\Delta$	-1.62	-2.42	+0.81	mmol	
final	0.82	0	0.81	mmol	
What mass of Fe <sub>2</sub> S	» nrecinitates?	0 807	mmol Fe <sub>o</sub> So	$207.9 \text{ mg Fe}_2\text{S}_3$	=168 ma Fe

a) What mass of Fe<sub>2</sub>S<sub>3</sub> precipitates? 0.807 mmol Fe<sub>2</sub>S<sub>3</sub>  $\times \frac{207.9 \text{ mg Fe}_2S_3}{\text{mmol Fe}_2S_3} = 168 \text{ mg Fe}_2S_3$ 

b) What is the concentration of the excess reactant after complete reaction? Assume additive volumes.

Total volume of the reaction solution is 60.8 mL, so  $[Fe^{3+}] = \frac{0.82 \text{ mmol Fe}^{3+}}{60.8 \text{ mL solution}} = 0.014 \text{ M}$ 

63. Given the unbalanced chemical equation:  $Zn(s) + HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq)$ 

What is the molarity of an HCl solution if 130. mL of the solution reacts with an excess of Zn to produce 7.00 L of H<sub>2</sub>(g) at 273 K and 1.00 atm?  $Zn(s) + 2HCl(aq) \rightarrow 2H_2(g) + ZnCl_2(aq)$ 

Use the ideal gas law to determine the number of moles of  $H_2(g)$  and the balanced equation to get mol HCl.

$$n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(7.00 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})} \text{ mol } \text{H}_2 \times \frac{2 \text{ mol } \text{HCI}}{1 \text{ mol } \text{H}_2} = 0.624 \text{ mol } \text{HCI reacted}$$
$$[\text{HCI}] = \frac{0.624 \text{ mol } \text{HCI}}{0.130 \text{ L} \text{ soln}} = 4.81 \text{ M } \text{HCI}$$

65. A solution is prepared by dissolving 5.863 g of impure NaOH in sufficient water to make 1.000 L of solution. The solution is added to a buret and used to titrate 25.00 mL of a 0.1173 M solution of HCl.

The balanced chemical equation for the titration is  $H^{1+} + OH^{1-} \rightarrow H_2O$ .

#### a) What is the molarity of the NaOH solution if the titration requires 28.04 mL of base?

mmol NaOH required:  $25.00 \text{ mL} \times \frac{0.1173 \text{ mmol H}^{1+}}{1 \text{ mL}} \times \frac{1 \text{ mmol OH}^{1-}}{1 \text{ mmol OH}^{1-}} \times \frac{1 \text{ mmol NaOH}}{1 \text{ mmol OH}^{1-}} = 2.932 \text{ mmol NaOH}$ molarity of the NaOH solution.  $\frac{2.932 \text{ mmol NaOH}}{28.04 \text{ mL}} = 0.1046 \text{ M}$  NaOH

#### b) What is the percent purity of the original NaOH sample?

Determine the amount of analytically pure NaOH in the base solution in milligrams/mL. The molar mass of NaOH is  $39.995 \text{ g mol}^{-1}$ .

 $2.932 \text{ mmol NaOH} \times \frac{39.995 \text{ mg NaOH}}{1 \text{ mmol}} = 117.3 \text{ mg NaOH in 28.04 mL}$ Therefore there were 117.3 mg NaOH ×  $\frac{1000 \text{ mL}}{28.04 \text{ mL}}$  = 4183 mg NaOH in 1 L of solution

Percent purity =  $\frac{\text{mass pure NaOH}}{\text{mass of sample}} \times 100\% = \frac{4183 \text{ mg}}{5863 \text{ mg}} \times 100\% = 71.35\%$ 

67. A 10.00-mL blood sample was diluted to 100.00 mL. 10.00 mL of the resulting solution was analyzed for calcium by precipitating all of the calcium as calcium oxalate, CaC<sub>2</sub>O<sub>4</sub>. The solid CaC<sub>2</sub>O<sub>4</sub> was then redissolved in H<sub>2</sub>SO<sub>4</sub> and titrated with 0.00886 M KMnO<sub>4</sub>. What is the concentration of Ca<sup>2+</sup> in the blood sample expressed as milligrams Ca<sup>2+</sup>/mL blood if the endpoint was reached with the addition of 1.14 mL of the KMnO<sub>4</sub> solution?

The balanced chemical reaction for the titration is

5 
$$\text{C}_2\text{O}_4^{2\text{-}}$$
 + 2  $\text{MnO}_4^{1\text{-}}$  + 16  $\text{H}^{1\text{+}}$   $ightarrow$  2  $\text{Mn}^{2\text{+}}$  + 10  $\text{CO}_2$  + 8  $\text{H}_2\text{O}_2$ 

Use the factor-label method, determine the moles of Ca<sup>2+</sup> ion required to reach the equivalence point.

$$1.14 \text{ mL} \times \frac{0.00886 \text{ mmol MnO}_{4}^{-1}}{1 \text{ mL}} \times \frac{5 \text{ mmol C}_{2}\text{O}_{4}^{2^{-}}}{2 \text{ mmol MnO}_{4}^{-1}} \times \frac{1 \text{ mmol CaC}_{2}\text{O}_{4}}{1 \text{ mmol C}_{2}\text{O}_{4}^{2^{-}}} \times \frac{1 \text{ mmol CaC}_{2}\text{O}_{4}}{1 \text{ mmol CaC}_{2}\text{O}_{4}} = 0.0253 \text{ mmol Ca}^{2+}$$

$$0.0253 \text{ mmol Ca}^{2+} \times \frac{40.08 \text{ mg Ca}^{2+}}{1 \text{ mmol Ca}^{2+}} = 1.01 \text{ mg Ca}^{2+} \text{ . However, this is the calcium in only 1/10 of the}$$
sample. Therefore, there are  $10.00 \times 1.01 \text{ mg Ca}^{2+} = 10.1 \text{ mg Ca}^{2+}$  in  $10.00 \text{ mL of blood}$ , so the calcium concentration is  $\frac{10.1 \text{ mg Ca}^{2+}}{10.00 \text{ mL blood}} = 1.01 \text{ mg mL}^{-1} \text{ Ca}^{2+}$ 

69. All of the iron in 1.314 g of an ore sample was converted to an aqueous solution of Fe<sup>2+</sup>, which was analyzed by titration with dichromate. What is the mass percent of iron in the ore if 38.64 mL of 0.02063 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was required to reach the equivalence point?

The balanced chemical equation for the titration is 14 H<sup>1+</sup> +  $Cr_2O_7^{2-}$  + 6 Fe<sup>2+</sup>  $\rightarrow$  6 Fe<sup>3+</sup> + 2 Cr<sup>3+</sup> + 7 H<sub>2</sub>O Using the factor-label method, determine the mass of Fe<sup>2+</sup> present in the iron ore sample.

$$38.64 \text{ mL} \times \frac{0.02063 \text{ mmol } \text{Cr}_2 \text{O}_7^{2^-}}{1 \text{ mL}} \times \frac{6 \text{ mmol } \text{Fe}^{2^+}}{1 \text{ mmol } \text{Cr}_2 \text{O}_7^{2^-}} \times \frac{55.847 \text{mg } \text{Fe}^{2^+}}{1 \text{ mmol } \text{Fe}^{2^+}} = 267.1 \text{ mg } \text{Fe}^{2^+}$$
Calculate the mass percent of iron in the iron ore sample. 
$$\frac{0.2671 \text{ g } \text{Fe}^{2^+}}{1.314 \text{ g iron ore}} \times 100\% = 20.33\%$$

71. The concentration of a stock solution of Rhodamine B, a commercial dye (ε = 1.060x10<sup>5</sup> M<sup>-1</sup>.cm<sup>-1</sup> at 543 nm) is determined spectrophotometrically, but the absorbance of the stock solution was too great to read on a spectrometer, so 15.00 mL of the solution was diluted to 250.00 mL. The resulting solution was still too concentrated, so 10.00 mL of that solution was diluted to 500.00 mL, but the solution was still too concentrated. However, a dilution of 25.00 mL of the resulting solution to a final volume of 500.00 mL provided an acceptable solution with an absorbance of 0.1814 in a 1.000 cm cell. What is the concentration of the stock solution?

Concentration of the final solution: 
$$c = \frac{A}{\varepsilon l} = \frac{0.1814}{(1.060 \times 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1})(1.000 \text{ cm})} = 1.711 \times 10^{-6} \text{ M}$$
  
Dilutions:  $1.711 \times 10^{-6} \text{ M} = c_{\text{stock}} \left(\frac{15.00}{250.00}\right) \left(\frac{10.00}{500.00}\right) \left(\frac{25.00}{500.00}\right) = c_{\text{stock}} (6.000 \times 10^{-5})$   
Condentration of stock:  $c_{\text{stock}} = \frac{1.711 \times 10^{-6} \text{ M}}{6.000 \times 10^{-5}} = 0.02852 \text{ M}$ 

What volume of stock solution would be required to make 2.000 L of a solution A = 1.000 in a 1.000 cm cell?

Use Beer's law to determine the concentration of the final solution,

c = 
$$\frac{A}{\varepsilon l}$$
 =  $\frac{1.000}{(1.060 \times 10^5 \text{ M}^{-1} \cdot \text{cm}^{-1})(1.000 \text{ cm})}$  = 9.434×10<sup>-6</sup> M

Then use the dilution to determine the initial volume.

$$V_{i} = \frac{C_{f}V_{f}}{C_{i}} = \frac{(9.434 \times 10^{-6} \text{ M})(2000 \text{ mL})}{0.02852 \text{ M}} = 0.6617 \text{ mL} = 661.7 \ \mu\text{L}$$

73. How many grams of NaCl must be added to 120 mL of water at 25 °C to prepare a solution with a vapor pressure of 22.0 torr?

The vapor pressure of pure water at 25 °C from Table 2.1 is 23.8 torr. Use that vapor pressure and the given vapor pressure to determine the required mole fraction of water.

$$X_{\text{water}} = \frac{P}{P^{\circ}} = \frac{22.0}{23.8} = 0.924$$
. The mole fraction of particles is 1.000 – 0.924 = 0.076

Determine the number of moles of water in 126 mL: 120 mL  $\times \frac{1.0 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.0 \text{ g}}$  = 6.7 mol

Let y = moles of NaCl required. The van't Hoff factor for NaCl is 2, so 2y moles of particles are in solution. Use the mole fraction and moles of water above to determine y.

$$X = 0.076 = \frac{\text{moles particles}}{\text{moles water + moles particles}} = \frac{2y}{6.7 + 2y}$$
  
0.076(6.7 + 2y) = 2y  
0.51 = (2 - 0.15)y  
$$y = \frac{0.51}{1.85} = 0.28 \text{ mol NaCl}$$
  
(0.28 mol)(58.5 g/mol) = 16 g NaCl