## CHAPTER 4

# TYPES OF CHEMICAL REACTIONS AND SOLUTION STOICHIOMETRY

## **Aqueous Solutions: Strong and Weak Electrolytes**

- 10. Only statement b is true. A concentrated solution can also contain a nonelectrolyte dissolved in water, for example, concentrated sugar water. Acids are either strong or weak electrolytes. Some ionic compounds are not soluble in water, so they are not labeled as a specific type of electrolyte.
- a. Polarity is a term applied to covalent compounds. Polar covalent compounds have an unequal sharing of electrons in bonds that results in unequal charge distribution in the overall molecule. Polar molecules have a partial negative end and a partial positive end. These are not full charges as in ionic compounds but are charges much smaller in magnitude. Water is a polar molecule and dissolves other polar solutes readily. The oxygen end of water (the partial negative end of the polar water molecule) aligns with the partial positive end of the polar solute, whereas the hydrogens of water (the partial positive end of the polar water molecule) align with the partial negative end of the solute. These opposite charge attractions stabilize polar solutes in water. This process is called hydration. Nonpolar solutes do not have permanent partial negative and partial positive ends; nonpolar solutes are not stabilized in water and do not dissolve.
  - b. KF is a soluble ionic compound, so it is a strong electrolyte. KF(aq) actually exists as separate hydrated  $K^+$  ions and hydrated  $F^-$  ions in solution.  $C_6H_{12}O_6$  is a polar covalent molecule that is a nonelectrolyte.  $C_6H_{12}O_6$  is hydrated as described in part a.
  - c. RbCl is a soluble ionic compound, so it exists as separate hydrated Rb<sup>+</sup> ions and hydrated Cl<sup>-</sup> ions in solution. AgCl is an insoluble ionic compound so the ions stay together in solution and fall to the bottom of the container as a precipitate.
  - d. HNO<sub>3</sub> is a strong acid and exists as separate hydrated H<sup>+</sup> ions and hydrated NO<sub>3</sub><sup>-</sup> ions in solution. CO is a polar covalent molecule and is hydrated as explained in part a.
- 12. The electrolyte designation refers to how completely the dissolved solute breaks up into ions. Strong electrolytes completely break up into ions when in water, weak electrolytes only partially break up into ions (less than 5% usually), and nonelectrolytes do not break up into ions when they dissolve in water. The conductivity apparatus illustrated in Figure 4.4 of the text is one way to experimentally determine the type of electrolyte. As illustrated, a bright light indicates many charge carriers (ions) are present and the solute is a strong electrolyte. A dim light indicates few ions are present so the solute is a weak electrolyte, and no light indicates no ions are present so the solute is a nonelectrolyte.

- 13. a.  $Ba(NO_3)_2(aq) \rightarrow Ba^{2+}(aq) + 2 NO_3^-(aq)$ ; picture iv represents the  $Ba^{2+}$  and  $NO_3^-$  ions present in  $Ba(NO_3)_2(aq)$ .
  - b.  $NaCl(aq) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$ ; picture ii represents NaCl(aq).
  - c.  $K_2CO_3(aq) \rightarrow 2 K^+(aq) + CO_3^{2-}(aq)$ ; picture iii represents  $K_2CO_3(aq)$ .
  - d.  $MgSO_4(aq) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ ; picture i represents  $MgSO_4(aq)$ .
- 14.  $MgSO_4(s) \rightarrow Mg^{2+}(aq) + SO_4^{2-}(aq); NH_4NO_3(s) \rightarrow NH_4^{+}(aq) + NO_3^{-}(aq)$
- 15. Solution A:  $\frac{4 \text{ molecules}}{1.0 \text{ L}}$ ; solution B:  $\frac{6 \text{ molecules}}{4.0 \text{ L}} = \frac{1.5 \text{ molecules}}{1.0 \text{ L}}$

Solution C: 
$$\frac{4 \text{ molecules}}{2.0 \text{ L}} = \frac{2 \text{ molecules}}{1.0 \text{ L}}$$
; solution D:  $\frac{6 \text{ molecules}}{2.0 \text{ L}} = \frac{3 \text{ molecules}}{1.0 \text{ L}}$ 

Solution A has the most molecules per unit volume so solution A is most concentrated. This is followed by solution D, then solution C. Solution B has the fewest molecules per unit volume, so solution B is least concentrated.

## **Solution Concentration: Molarity**

16. a. 
$$1.00 \text{ L solution} \times \frac{0.50 \text{ mol H}_2 \text{SO}_4}{\text{L}} = 0.50 \text{ mol H}_2 \text{SO}_4$$

$$0.50~mol~H_2SO_4 \times \\ \frac{1~L}{18~mol~H_2SO_4}~= 2.8 \times 10^{-2}~L~concentrated~H_2SO_4~or~28~mL$$

Dilute 28 mL of concentrated  $H_2SO_4$  to a total volume of 1.00 L with water. The resulting 1.00 L of solution will be a 0.50 M  $H_2SO_4$  solution.

b. We will need 0.50 mol HCl.

$$0.50 \text{ mol HCl} \times \frac{1 \text{ L}}{12 \text{ mol HCl}} = 4.2 \times 10^{-2} \text{ L} = 42 \text{ mL}$$

Dilute 42 mL of concentrated HCl to a final volume of 1.00 L.

c. We need 0.50 mol NiCl<sub>2</sub>.

$$0.50 \text{ mol NiCl}_2 \times \frac{1 \text{ mol NiCl}_2 \bullet 6\text{H}_2\text{O}}{\text{mol NiCl}_2} \times \frac{237.69 \text{ g NiCl}_2 \bullet 6\text{H}_2\text{O}}{\text{mol NiCl}_2 \bullet 6\text{H}_2\text{O}} = 118.8 \text{ g NiCl}_2 \bullet 6\text{H}_2\text{O} \approx 120 \text{ g}$$

Dissolve  $120 \text{ g NiCl}_2 \cdot 6H_2O$  in water, and add water until the total volume of the solution is 1.00 L.

d. 
$$1.00 \text{ L} \times \frac{0.50 \text{ mol HNO}_3}{L} = 0.50 \text{ mol HNO}_3$$
  
 $0.50 \text{ mol HNO}_3 \times \frac{1 \text{ L}}{16 \text{ mol HNO}_3} = 0.031 \text{ L} = 31 \text{ mL}$ 

Dissolve 31 mL of concentrated reagent in water. Dilute to a total volume of 1.00 L.

e. We need 0.50 mol Na<sub>2</sub>CO<sub>3</sub>.

$$0.50 \text{ mol Na}_2\text{CO}_3 \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol}} = 53 \text{ g Na}_2\text{CO}_3$$

Dissolve 53 g Na<sub>2</sub>CO<sub>3</sub> in water, dilute to 1.00 L.

17. a. 
$$2.00 \text{ L} \times \frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{40.00 \text{ g NaOH}}{\text{mol}} = 20.0 \text{ g NaOH}$$

Place 20.0 g NaOH in a 2-L volumetric flask; add water to dissolve the NaOH, and fill to the mark with water, mixing several times along the way.

b. 
$$2.00 \text{ L} \times \frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ L stock}}{1.00 \text{ mol NaOH}} = 0.500 \text{ L}$$

Add 500. mL of  $1.00 \, M$  NaOH stock solution to a 2-L volumetric flask; fill to the mark with water, mixing several times along the way.

c. 
$$2.00 \text{ L} \times \frac{0.100 \text{ mol } \text{K}_2 \text{CrO}_4}{\text{L}} \times \frac{194.20 \text{ g K}_2 \text{CrO}_4}{\text{mol K}_2 \text{CrO}_4} = 38.8 \text{ g K}_2 \text{CrO}_4$$

Similar to the solution made in part a, instead using 38.8 g K<sub>2</sub>CrO<sub>4</sub>.

$$d. \quad 2.00 \text{ L} \times \frac{0.100 \, \text{mol} \, \text{K}_2 \text{CrO}_4}{\text{L}} \times \frac{1 \, \text{L stock}}{1.75 \, \text{mol} \, \text{K}_2 \text{CrO}_4} = 0.114 \, \text{L}$$

Similar to the solution made in part b, instead using 114 mL of the 1.75 M K<sub>2</sub>CrO<sub>4</sub> stock solution.

18. 
$$75.0 \text{ mL} \times \frac{0.79 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{46.1 \text{ g}} = 1.3 \text{ mol } C_2H_5OH; \text{ molarity} = \frac{1.3 \text{ mol}}{0.250 \text{ L}} = 5.2 \text{ M } C_2H_5OH$$

19. Mol Na<sub>2</sub>CO<sub>3</sub> = 0.0700 L × 
$$\frac{3.0 \text{ mol Na}_2\text{CO}_3}{\text{L}}$$
 = 0.21 mol Na<sub>2</sub>CO<sub>3</sub>

$$Na_{2}CO_{3}(s) \rightarrow 2 \ Na^{+}(aq) + CO_{3}^{\ 2-}(aq); \ mol \ Na^{+} = 2(0.21 \ mol) = 0.42 \ mol$$

$$Mol NaHCO_3 = 0.0300 L \times \frac{1.0 \text{ mol NaHCO}_3}{L} = 0.030 \text{ mol NaHCO}_3$$

$$NaHCO_3(s) \rightarrow Na^+(aq) + HCO_3^-(aq); \text{ mol } Na^+ = 0.030 \text{ mol}$$

$$M_{\text{Na}^+} = \frac{\text{totalmol Na}^+}{\text{totalvolume}} = \frac{0.42 \,\text{mol} + 0.030 \,\text{mol}}{0.0700 \,\text{L} + 0.0300 \,\text{L}} = \frac{0.45 \,\text{mol}}{0.1000 \,\text{L}} = 4.5 \,M \,\text{Na}^+$$

$$20. \qquad 25.0 \; g \; (NH_4)_2 SO_4 \times \frac{1 \; mol}{132.15 \; g} = 1.89 \times 10^{-1} \; mol \; (NH_4)_2 SO_4$$

Molarity = 
$$\frac{1.89 \times 10^{-1} \text{ mol}}{100.0 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 1.89 \text{ M (NH4)}_2\text{SO}_4$$

Moles of 
$$(NH_4)_2SO_4$$
 in final solution =  $10.00 \times 10^{-3} L \times \frac{1.89 \text{ mol}}{L}$   
=  $1.89 \times 10^{-2} \text{ mol } (NH_4)_2SO_4$ 

Molarity of final solution = 
$$\frac{1.89 \times 10^{-2} \text{ mol}}{(10.00 + 50.00) \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 0.315 \text{ M (NH4)}_2\text{SO}_4$$

$$(NH_4)_2SO_4(s) \rightarrow 2 NH_4^+(aq) + SO_4^{2-}(aq); \quad M_{NH_4^+} = 2(0.315) = 0.630 M; \quad M_{SO_4^{2-}} = 0.315 M$$

21. Molar mass of NaOH = 22.99 + 16.00 + 1.008 = 40.00 g/mol

$$Mass\ NaOH = 0.2500\ L \times \frac{0.400\,mol\,NaOH}{L} \times \frac{40.00\,g\ NaOH}{mol\,NaOH} = 4.00\,g\ NaOH$$

22. Stock solution:

$$1.584 \text{ g Mn}^{2+} \times \frac{1 \text{ mol Mn}^{2+}}{54.94 \text{ g Mn}^{2+}} = 2.883 \times 10^{-2} \text{ mol Mn}^{2+}; M = \frac{2.883 \times 10^{-2} \text{ mol }}{1.000 \text{ L}}$$
$$= 2.883 \times 10^{-2} M \text{ Mn}^{2+}$$

Solution A contains:

$$50.00 \; mL \times \frac{1 \, L}{1000 mL} \times \frac{2.883 \times 10^{-2} \; mol}{L} = 1.442 \times 10^{-3} \; mol \; Mn^{2+}$$

Molarity = 
$$\frac{1.442 \times 10^{-3} \text{ mol}}{10000 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} = 1.442 \times 10^{-3} \text{ M Mn}^{2+}$$

Solution B contains:

$$10.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1.442 \times 10^{-3} \text{ mol}}{\text{L}} = 1.442 \times 10^{-5} \text{ mol Mn}^{2+}$$

$$\text{Molarity} = \frac{1.442 \times 10^{-5} \text{ mol}}{0.2500 \text{L}} = 5.768 \times 10^{-5} \textit{M} \, \text{Mn}^{2+}$$

Solution C contains:

$$10.00\times 10^{-3}~L\times \frac{5.768\times 10^{-5}~mol}{L} = 5.768\times 10^{-7}~mol~Mn^{2+}$$

Molarity = 
$$\frac{5.768 \times 10^{-7} \text{ mol}}{0.5000 \text{L}} = 1.154 \times 10^{-6} M \text{ Mn}^{2+}$$

23. Stock solution = 
$$\frac{10.0 \text{ mg}}{500.0 \text{ mL}} = \frac{10.0 \times 10^{-3} \text{ g}}{500.0 \text{ mL}} = \frac{2.00 \times 10^{-5} \text{ g steroid}}{\text{mL}}$$

$$100.0 \times 10^{\text{--}6} \, L \; stock \times \frac{1000 mL}{L} \times \frac{2.00 \times 10^{\text{--}5} \, g \; steroid}{mL} = 2.00 \times 10^{\text{--}6} \, g \; steroid$$

This is diluted to a final volume of 100.0 mL.

$$\frac{2.00 \times 10^{-6} \text{ g steroid}}{100.0 \text{ mL}} \times \frac{1000 \text{mL}}{\text{L}} \times \frac{1 \text{ mol steroid}}{336.4 \text{ g steroid}} = 5.95 \times 10^{-8} \text{ M steroid}$$

24. a. 
$$M_{\text{Ca(NO_3)}_2} = \frac{0.100 \,\text{mol}\,\text{Ca(NO_3)}_2}{0.100 \,\text{L}} = 1.00 \,M$$

$$Ca(NO_3)_2(s) \rightarrow Ca^{2+}(aq) + 2 NO_3^-(aq); M_{Ca^{2+}} = 1.00 M; M_{NO_3^-} = 2(1.00) = 2.00 M$$

b. 
$$M_{\text{Na}_2\text{SO}_4} = \frac{2.5 \text{ mol Na}_2\text{SO}_4}{1.25 \text{ L}} = 2.0 M$$

$$Na_2SO_4(s) \rightarrow 2 Na^+(aq) + SO_4^{2-}(aq); \quad M_{Na^+} = 2(2.0) = 4.0 M; \quad M_{SO_4^{2-}} = 2.0 M;$$

c. 
$$5.00 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} = 0.0935 \text{ mol NH}_4\text{Cl}$$

$$M_{\text{NH}_4\text{Cl}} = \frac{0.0935 \text{mol NH}_4\text{Cl}}{0.5000\text{L}} = 0.187 M$$

$$NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq); \ M_{NH_4^-} = M_{Cl^-} = 0.187 M$$

$$d. \quad 1.00 \; g \; K_3 PO_4 \times \frac{1 \, mol \, K_3 PO_4}{212.27 \, g} = 4.71 \times 10^{-3} \; mol \; K_3 PO_4$$

$$M_{\rm K_3PO_4} = \frac{4.71 \times 10^{-3} \text{ mol}}{0.2500 L} = 0.0188 M$$

$$K_3PO_4(s) \rightarrow 3 K^+(aq) + PO_4^{3-}(aq); \quad M_{K^+} = 3(0.0188) = 0.0564 M; \quad M_{PO_4^{3-}} = 0.0188 M$$

$$25. \qquad \text{Mol solute} = \text{volume (L)} \times \ \text{molarity} \bigg( \frac{\text{mol}}{\text{L}} \bigg); \ \ \text{AlCl}_3(s) \rightarrow \text{Al}^{3+}(\text{aq}) + 3 \ \text{Cl}^-(\text{aq})$$

$$Mol \ Cl^{-} = 0.1000 \ L \times \frac{0.30 \ mol \ AlCl_{3}}{L} \ \times \frac{3 \ mol \ Cl^{-}}{mol \ AlCl_{3}} = 9.0 \times 10^{-2} \ mol \ Cl^{-}$$

$$MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2 Cl^{-}(aq)$$

$$Mol \ Cl^- = 0.0500 \ L \times \frac{0.60 \ mol \ MgCl_2}{L} \ \times \frac{2 \ mol \ Cl^-}{mol \ MgCl_2} = 6.0 \times 10^{-2} \ mol \ Cl^-$$

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

$$Mol \; Cl^{-} = 0.2000 \; L \times \; \frac{0.40 \, mol \, NaCl}{L} \; \times \frac{1 \, mol \, Cl^{-}}{mol \, NaCl} \; = 8.0 \times \; 10^{-2} \, mol \; Cl^{-}$$

100.0 mL of 0.30 M AlCl<sub>3</sub> contains the most moles of Cl<sup>-</sup> ions.

26. 
$$10. \text{ g AgNO}_3 \times \frac{1 \text{ mol AgNO}_3}{169.9 \text{ g}} \times \frac{1 \text{ L}}{0.25 \text{ mol AgNO}_3} = 0.24 \text{ L} = 240 \text{ mL}$$

27. a. 5.0 ppb Hg in water = 
$$\frac{5.0 \text{ ng Hg}}{\text{mL H}_2\text{O}} = \frac{5.0 \times 10^{-9} \text{ g Hg}}{\text{mL H}_2\text{O}}$$

$$\frac{5.0 \times 10^{-9} \text{ g Hg}}{\text{mL}} \times \frac{1 \text{ mol Hg}}{200.6 \text{ g Hg}} \times \frac{1000 \text{mL}}{\text{L}} = 2.5 \times 10^{-8} M \text{ Hg}$$

b. 
$$\frac{1.0 \times 10^{-9} \text{ g CHCl}_3}{\text{mL}} \times \frac{1 \text{ mol CHCl}_3}{119.4 \text{ g CHCl}_3} \times \frac{1000 \text{mL}}{\text{L}} = 8.4 \times 10^{-9} \text{ M CHCl}_3$$

c. 
$$10.0 \text{ ppm As} = \frac{10.0 \,\mu\text{g As}}{\text{mL}} = \frac{10.0 \times 10^{-6} \text{ g As}}{\text{mL}}$$

$$\frac{10.0 \times 10^{-6} \text{ g As}}{\text{mL}} \times \frac{1 \text{ mol As}}{74.92 \text{ g As}} \times \frac{1000 \text{mL}}{\text{L}} = 1.33 \times 10^{-4} M \text{ As}$$

d. 
$$\frac{0.10 \times 10^{-6} \text{ g DDT}}{\text{mL}} \times \frac{1 \text{ molDDT}}{354.5 \text{ g DDT}} \times \frac{1000 \text{mL}}{\text{L}} = 2.8 \times 10^{-7} \text{ M DDT}$$

28. We want 100.0 mL of each standard. To make the 100. ppm standard:

$$\frac{100~\mu g~Cu}{mL} \times 100.0~mL~solution = 1.00 \times 10^4~\mu g~Cu~needed$$

$$1.00 \times 10^4 \,\mu\text{g Cu} \times \frac{1 \,\text{mL stock}}{10000 \,\mu\text{g Cu}} = 10.0 \,\text{mL of stock solution}$$

Therefore, to make 100.0 mL of 100. ppm solution, transfer 10.0 mL of the 1000.0 ppm stock solution to a 100-mL volumetric flask, and dilute to the mark.

#### Similarly:

75.0 ppm standard, dilute 7.50 mL of the 1000.0 ppm stock to 100.0 mL.

50.0 ppm standard, dilute 5.00 mL of the 1000.0 ppm stock to 100.0 mL.

25.0 ppm standard, dilute 2.50 mL of the 1000.0 ppm stock to 100.0 mL.

10.0 ppm standard, dilute 1.00 mL of the 1000.0 ppm stock to 100.0 mL.

#### **Precipitation Reactions**

- 29. For the following answers, the balanced molecular equation is first, followed by the complete ionic equation, and then the net ionic equation.
  - a.  $(NH_4)_2SO_4(aq) + Ba(NO_3)_2(aq) \rightarrow 2 NH_4NO_3(aq) + BaSO_4(s)$

$$2\;N{H_4}^+(aq) + S{O_4}^{2-}(aq) + Ba^{2+}(aq) + 2\;N{O_3}^-(aq) \to 2\;N{H_4}^+(aq) + 2\;N{O_3}^-(aq) + BaS{O_4}(s)$$

 $Ba^{2+}(aq) + SO_4^{\ 2-}(aq) \to BaSO_4(s) \ is \ the \ net \ ionic \ equation \ (spectator \ ions \ omitted).$ 

b. 
$$Pb(NO_3)_2(aq) + 2 NaCl(aq) \rightarrow PbCl_2(s) + 2 NaNO_3(aq)$$

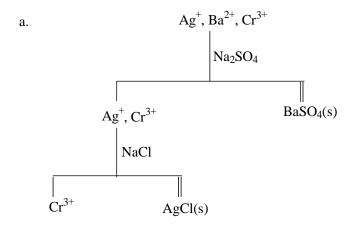
$$Pb^{2+}(aq) + 2 \; NO_3^-(aq) + 2 \; Na^+(aq) + 2 \; Cl^-(aq) \rightarrow PbCl_2(s) + 2 \; Na^+(aq) + 2 \; NO_3^-(aq)$$

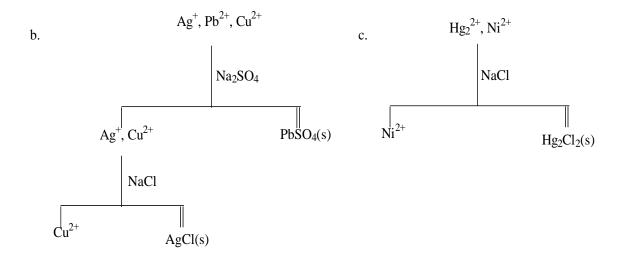
$$Pb^{2+}(aq) + 2 Cl^{-}(aq) \rightarrow PbCl_2(s)$$

- c. The possible products, potassium phosphate and sodium nitrate, are both soluble in water. Therefore, no reaction occurs.
- d. No reaction occurs because all possible products are soluble.

e. 
$$CuCl_2(aq) + 2 NaOH(aq) \rightarrow Cu(OH)_2(s) + 2 NaCl(aq)$$
  
 $Cu^{2+}(aq) + 2 Cl^{-}(aq) + 2 Na^{+}(aq) + 2 OH^{-}(aq) \rightarrow Cu(OH)_2(s) + 2 Na^{+}(aq) + 2 Cl^{-}(aq)$   
 $Cu^{2+}(aq) + 2 OH^{-}(aq) \rightarrow Cu(OH)_2(s)$ 

30. The following schemes show reagents to add in order to precipitate one ion at a time. In each scheme, NaOH can be added to precipitate the last remaining ion.





- 31. Use Table 4.1 to predict the solubility of the possible products.
  - a. Possible products =  $Hg_2SO_4$  and  $Cu(NO_3)_2$ ; precipitate =  $Hg_2SO_4$
  - b. Possible products =  $NiCl_2$  and  $Ca(NO_3)_2$ ; both salts are soluble so no precipitate forms.
  - c. Possible products = KI and MgCO<sub>3</sub>; precipitate = MgCO<sub>3</sub>
  - d. Possible products = NaBr and  $Al_2(CrO_4)_3$ ; precipitate =  $Al_2(CrO_4)_3$

32. a. 
$$Hg_2(NO_3)_2(aq) + CuSO_4(aq) \rightarrow Hg_2SO_4(s) + Cu(NO_3)_2(aq)$$
 
$$Hg_2^{2+}(aq) + 2 NO_3^{-}(aq) + Cu^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Hg_2SO_4(s) + Cu^{2+}(aq) + 2 NO_3^{-}(aq)$$
 
$$Hg_2^{2+}(aq) + SO_4^{2-}(aq) \rightarrow Hg_2SO_4(s)$$

- b. No reaction occurs since both possible products are soluble.
- c.  $K_2CO_3(aq) + MgI_2(aq) \rightarrow 2 KI(aq) + MgCO_3(s)$   $2 K^+(aq) + CO_3^{2-}(aq) + Mg^{2+}(aq) + 2I^-(aq) \rightarrow 2 K^+(aq) + 2 I^-(aq) + MgCO_3(s)$  $Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$
- d.  $3 \text{ Na}_2\text{CrO}_4(aq) + 2 \text{ Al}(\text{Br})_3(aq) \rightarrow 6 \text{ NaBr}(aq) + \text{Al}_2(\text{CrO}_4)_3(s)$   $6 \text{ Na}^+(aq) + 3 \text{ CrO}_4^{2-}(aq) + 2 \text{ Al}^{3+}(aq) + 6 \text{ Br}^-(aq) \rightarrow 6 \text{ Na}^+(aq) + 6 \text{ Br}^-(aq) + \text{Al}_2(\text{CrO}_4)_3(s)$  $2 \text{ Al}^{3+}(aq) + 3 \text{ CrO}_4^{2-}(aq) \rightarrow \text{Al}_2(\text{CrO}_4)_3(s)$
- 33. Use the solubility rules in Table 4.1. Some soluble bromides by Rule 2 would be NaBr, KBr, and NH<sub>4</sub>Br (there are others). The insoluble bromides by Rule 3 would be AgBr, PbBr<sub>2</sub>, and Hg<sub>2</sub>Br<sub>2</sub>. Similar reasoning is used for the other parts to this problem.

Sulfates:  $Na_2SO_4$ ,  $K_2SO_4$ , and  $(NH_4)_2SO_4$  (and others) would be soluble, and  $BaSO_4$ ,  $CaSO_4$ , and  $PbSO_4$  (or  $Hg_2SO_4$ ) would be insoluble.

Hydroxides: NaOH, KOH, Ca(OH)<sub>2</sub> (and others) would be soluble, and Al(OH)<sub>3</sub>, Fe(OH)<sub>3</sub>, and Cu(OH)<sub>2</sub> (and others) would be insoluble.

Phosphates:  $Na_3PO_4$ ,  $K_3PO_4$ ,  $(NH_4)_3PO_4$  (and others) would be soluble, and  $Ag_3PO_4$ ,  $Ca_3(PO_4)_2$ , and  $FePO_4$  (and others) would be insoluble.

Lead:  $PbCl_2$ ,  $PbBr_2$ ,  $PbI_2$ ,  $Pb(OH)_2$ ,  $PbSO_4$ , and PbS (and others) would be insoluble.  $Pb(NO_3)_2$  would be a soluble  $Pb^{2+}$  salt.

34.  $Pb(NO_3)_2(aq) + 2 KI(aq) \rightarrow PbI_2(s) + 2 KNO_3(aq)$  (molecular equation)

$$Pb^{2^{+}}(aq) + 2 \ NO_{3}^{-}(aq) + 2 \ K^{+}(aq) + 2 \ I^{-}(aq) \ \rightarrow \ PbI_{2}(s) + 2 \ K^{+}(aq) + 2 \ NO_{3}^{-}(aq) \ \ (complete)$$

The 1.0 mol of  $Pb^{2+}$  ions would react with the 2.0 mol of  $I^-$  ions to form 1.0 mol of the  $PbI_2$  precipitate. Even though the  $Pb^{2+}$  and  $I^-$  ions are removed, the spectator ions  $K^+$  and  $NO_3^-$  are still present. The solution above the precipitate will conduct electricity because there are plenty of charge carriers ( $K^+$  and  $NO_3^-$  ions) present in solution.

35. a. When  $CuSO_4(aq)$  is added to  $Na_2S(aq)$ , the precipitate that forms is CuS(s). Therefore,  $Na^+$  (the gray spheres) and  $SO_4^{2-}$  (the bluish green spheres) are the spectator ions.

$$CuSO_{4}(aq) + Na_{2}S(aq) \ \to CuS(s) + Na_{2}SO_{4}(aq); \ Cu^{2^{+}}(aq) + S^{2^{-}}(aq) \ \to CuS(s)$$

b. When CoCl<sub>2</sub>(aq) is added to NaOH(aq), the precipitate that forms is Co(OH)<sub>2</sub>(s). Therefore, Na<sup>+</sup> (the gray spheres) and Cl<sup>-</sup> (the green spheres) are the spectator ions.

$$CoCl_2(aq) + 2 NaOH(aq) \rightarrow Co(OH)_2(s) + 2 NaCl(aq)$$
  
 $Co^{2+}(aq) + 2 OH^{-}(aq) \rightarrow Co(OH)_2(s)$ 

c. When AgNO<sub>3</sub>(aq) is added to KI(aq), the precipitate that forms is AgI(s). Therefore, K<sup>+</sup> (the red spheres) and NO<sub>3</sub><sup>-</sup> (the blue spheres) are the spectator ions.

$$AgNO_3(aq) + KI(aq) \rightarrow AgI(s) + KNO_3(aq); Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$$

36. 
$$XCl_2(aq) + 2 AgNO_3(aq) \rightarrow 2 AgCl(s) + X(NO_3)_2(aq)$$

$$1.38 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.4 \text{ g}} \times \frac{1 \text{ mol XCl}_2}{2 \text{ mol AgCl}} = 4.81 \times 10^{-3} \text{ mol XCl}_2$$

$$\frac{1.00 \text{ g XCl}_2}{4.91 \times 10^{-3} \text{ mol XCl}_2} = 208 \text{ g/mol}; \quad x + 2(35.45) = 208, \quad x = 137 \text{ g/mol}$$

The metal X is barium (Ba).

37. 
$$M_2SO_4(aq) + CaCl_2(aq) \rightarrow CaSO_4(s) + 2 MCl(aq)$$

$$1.36 \text{ g CaSO}_4 \times \frac{1 \text{ molCaSO}_4}{136.15 \text{ g CaSO}_4} \times \frac{1 \text{ molM}_2 \text{SO}_4}{\text{molCaSO}_4} = 9.99 \times 10^{-3} \text{ mol M}_2 \text{SO}_4$$

From the problem, 1.42 g M<sub>2</sub>SO<sub>4</sub> was reacted, so:

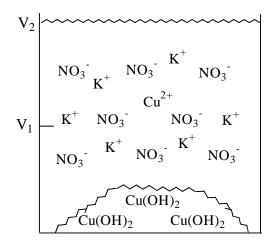
molar mass = 
$$\frac{1.42 \text{ g M}_2\text{SO}_4}{9.99 \times 10^{-3} \text{ molM}_2\text{SO}_4} = 142 \text{ g/mol}$$

142 amu = 2(atomic mass M) + 32.07 + 4(16.00), atomic mass M = 23 amu

From periodic table, M is Na (sodium).

38. a. 
$$Cu(NO_3)_2(aq) + 2 KOH(aq) \rightarrow Cu(OH)_2(s) + 2 KNO_3(aq)$$

Solution A contains  $2.00 \text{ L} \times 2.00 \text{ mol/L} = 4.00 \text{ mol Cu(NO}_3)_2$ , and solution B contains  $2.00 \text{ L} \times 3.00 \text{ mol/L} = 6.00 \text{ mol KOH}$ . Let's assume in our picture that we have 4 formula units of Cu(NO<sub>3</sub>)<sub>2</sub> (4 Cu<sup>2+</sup> ions and 8 NO<sub>3</sub><sup>-</sup> ions) and 6 formula units of KOH (6 K<sup>+</sup> ions and 6 OH<sup>-</sup> ions). With 4 Cu<sup>2+</sup> ions and 6 OH<sup>-</sup> ions present, then OH<sup>-</sup> is limiting. One Cu<sup>2+</sup> ion remains as 3 Cu(OH)<sub>2</sub>(s) formula units form as precipitate. The following illustration summarizes the ions that remain in solution and the relative amount of precipitate that forms. Note that K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions are spectator ions. In the illustration, V<sub>1</sub> is the volume of solution A or B and V<sub>2</sub> is the volume of the combined solutions with V<sub>2</sub> = 2V<sub>1</sub>. The illustration exaggerates the amount of precipitate that would actually form.



b. The spectator ion concentrations will be one-half the original spectator ion concentrations in the individual beakers because the volume was doubled. Or using moles,  $M_{\kappa^+}$  =

$$\frac{6.00 \,\mathrm{mol}\,\mathrm{K}^{+}}{4.00 \,\mathrm{L}} = 1.50 \,M \,\mathrm{and} \,M_{\mathrm{NO_{3}}^{-}} = \frac{8.00 \,\mathrm{mol}\,\mathrm{NO_{3}}^{-}}{4.00 \,\mathrm{L}} = 2.00 \,M.$$
 The concentration of

OH ions will be zero because OH is the limiting reagent. From the drawing, the number of Cu<sup>2+</sup> ions will decrease by a factor of four as the precipitate forms. Because the volume of solution doubled, the concentration of Cu<sup>2+</sup> ions will decrease by a factor of eight after the two beakers are mixed:

$$M_{\text{Cu}^+} = 2.00 \ M \left(\frac{1}{8}\right) = 0.250 \ M$$

Alternately, one could certainly use moles to solve for  $M_{Cu^{2+}}$ :

$$Mol~Cu^{2+}~reacted = 2.00~L~\times~\frac{3.00\,mol\,OH^{-}}{L}~\times~\frac{1\,mol\,Cu^{2+}}{2\,mol\,OH^{-}} = 3.00~mol~Cu^{2+}~reacted$$

$$Mol\ Cu^{2+}\ present\ initially = 2.00\ L\times\ \frac{2.00\ mol\ Cu^{2+}}{L} = 4.00\ mol\ Cu^{2+}\ present\ initially$$

Excess  $Cu^{2+}$  present after reaction =  $4.00 \text{ mol} - 3.00 \text{ mol} = 1.00 \text{ mol} Cu^{2+}$  excess

$$M_{\text{Cu}^{2+}} = \frac{1.00 \,\text{mol Cu}^{2+}}{2.00 \,\text{L} + 2.00 \,\text{L}} = 0.250 \,M$$

$$Mass \ of \ precipitate = 6.00 \ mol \ KOH \times \frac{1 \, mol \, Cu(OH)_2}{2 \, mol \, KOH} \times \frac{97.57 \, g \, Cu(OH)_2}{mol \, Cu(OH)_2}$$

Mass of precipitate =  $293 \text{ g Cu}(OH)_2$ 

39. 
$$2 \text{ AgNO}_3(\text{aq}) + \text{Na}_2\text{CrO}_4(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{s}) + 2 \text{ NaNO}_3(\text{aq})$$

$$0.0750 \text{ L} \times \frac{0.100 \text{ mol AgNO}_3}{\text{L}} \times \frac{1 \text{ mol Na}_2 \text{CrO}_4}{2 \text{ mol AgNO}_3} \times \frac{161.98 \text{ g Na}_2 \text{CrO}_4}{\text{mol Na}_2 \text{CrO}_4} = 0.607 \text{ g Na}_2 \text{CrO}_4$$

40.  $2 \text{ Na}_3\text{PO}_4(\text{aq}) + 3 \text{ Pb}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{Pb}_3(\text{PO}_4)_2(\text{s}) + 6 \text{ Na}_3(\text{NO}_3(\text{aq}))$ 

$$0.1500 \text{ L} \times \frac{0.250 \text{ mol Pb}(\text{NO}_3)_2}{\text{L}} \times \frac{2 \text{ mol Na}_3 \text{PO}_4}{3 \text{ mol Pb}(\text{NO}_3)_2} \times \frac{1 \text{ L Na}_3 \text{PO}_4}{0.100 \text{ mol Na}_3 \text{PO}_4} = 0.250 \text{ L}$$

$$= 250. \text{ mL Na}_3 \text{PO}_4$$

41.  $2 \text{ AgNO}_3(\text{aq}) + \text{CaCl}_2(\text{aq}) \rightarrow 2 \text{ AgCl}(\text{s}) + \text{Ca}(\text{NO}_3)_2(\text{aq})$ 

$$Mol \ AgNO_3 = 0.1000 \ L \times \frac{0.20 \ mol \ AgNO_3}{L} = 0.020 \ mol \ AgNO_3$$

$$Mol\ CaCl_2 = 0.1000\ L \times \frac{0.15\,mol\,CaCl_2}{L} = 0.015\ mol\ CaCl_2$$

The required mol  $AgNO_3$  to mol  $CaCl_2$  ratio is 2 : 1 (from the balanced equation). The actual mole ratio present is 0.020/0.015 = 1.3 (1.3 : 1). Therefore,  $AgNO_3$  is the limiting reagent.

$$Mass\ AgCl = 0.020\ mol\ AgNO_3 \times \frac{1\ mol\ AgCl}{1\ mol\ AgNO_3} \times \frac{143.4\ g\ AgCl}{mol\ AgCl} = 2.9\ g\ AgCl$$

The net ionic equation is  $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ . The ions remaining in solution are the unreacted  $Cl^-$  ions and the spectator ions,  $NO_3^-$  and  $Ca^{2+}$  (all  $Ag^+$  is used up in forming AgCl). The moles of each ion present initially (before reaction) can be easily determined from the moles of each reactant. 0.020 mol  $AgNO_3$  dissolves to form 0.020 mol  $Ag^+$  and 0.020 mol  $NO_3^-$ . 0.015 mol  $CaCl_2$  dissolves to form 0.015 mol  $Ca^{2+}$  and  $Ca^{2+}$  an

Mol unreacted  $Cl^- = 0.030 \text{ mol } Cl^- \text{ initially } -0.020 \text{ mol } Cl^- \text{ reacted}$ 

Mol unreacted  $Cl^- = 0.010 \text{ mol } Cl^-$ 

$$M_{\rm Cl^-} = \frac{0.010\,{
m mol\,Cl^-}}{{
m total volume}} = \frac{0.010\,{
m mol\,Cl^-}}{0.1000{
m L} + 0.1000{
m L}} = 0.050\,M\,{
m Cl^-}$$

The molarity of the spectator ions are:

$$M_{\text{NO}_3^-} = \frac{0.020 \,\text{mol NO}_3^-}{0.2000 \,\text{L}} = 0.10 \,M \,\text{NO}_3^-; \ M_{\text{Ca}_2^+} = \frac{0.015 \,\text{mol Ca}^{2+}}{0.2000 \,\text{L}} = 0.075 \,M \,\text{Ca}^{2+}$$

42. Use the silver nitrate data to calculate the mol Cl<sup>-</sup> present, then use the formula of douglasite to convert from Cl<sup>-</sup> to douglasite. The net ionic reaction is  $Ag^+ + Cl^- \rightarrow AgCl(s)$ .

$$0.03720 \text{ L} \times \frac{0.1000 \text{mol Ag}^+}{\text{L}} \times \frac{1 \text{ mol Cl}^-}{\text{mol Ag}^+} \times \frac{1 \text{ mol douglasite}}{4 \text{ mol Cl}^-} \times \frac{311.88 \text{ g douglasite}}{\text{mol}} \\ = 0.2900 \text{ g douglasite}$$

Mass % douglasite = 
$$\frac{0.2900g}{0.4550g} \times 100 = 63.74\%$$

43. All the sulfur in BaSO<sub>4</sub> came from the saccharin. The conversion from BaSO<sub>4</sub> to saccharin uses the molar masses and formulas of each compound.

$$0.5032~g~BaSO_{4} \times \frac{32.07 g~S}{233.4 g~BaSO_{4}} \times \frac{183.9 g~saccharin}{32.07 g~S} = 0.3949~g~saccharin$$

$$\frac{\text{Average mass}}{\text{Tablet}} = \frac{0.3949 \,\text{g}}{10 \,\text{tablets}} = \frac{3.949 \times 10^{-2} \,\text{g}}{\text{tablet}} = \frac{39.49 \,\text{mg}}{\text{tablet}}$$

Average mass % = 
$$\frac{0.3949g \ saccharin}{0.5894g} \times 100 = 67.00\%$$
 saccharin by mass

44. All the Tl in TlI came from Tl in Tl<sub>2</sub>SO<sub>4</sub>. The conversion from TlI to Tl<sub>2</sub>SO<sub>4</sub> uses the molar masses and formulas of each compound.

$$0.1824 \text{ g TII} \times \frac{204.4 \text{ g TI}}{331.3 \text{ g TII}} \times \frac{504.9 \text{ g Tl}_2\text{SO}_4}{408.8 \text{ g TI}} = 0.1390 \text{ g Tl}_2\text{SO}_4$$

Mass % 
$$Tl_2SO_4 = \frac{0.1390g\ Tl_2SO_4}{9.486g\ pesticide} \times 100 = 1.465\%\ Tl_2SO_4$$

45. Use aluminum in the formulas to convert from mass of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> in the mixture.

$$0.107 \text{ g Al(OH)}_{3} \times \frac{1 \, \text{mol Al(OH)}_{3}}{78.00 \, \text{g}} \times \frac{1 \, \text{mol Al}^{3^{+}}}{\text{mol Al(OH)}_{3}} \times \frac{1 \, \text{mol Al}_{2}(\text{SO}_{4})_{3}}{2 \, \text{mol Al}^{3^{+}}} \times \frac{1 \, \text{mol Al}^{3^{+}}}{2 \, \text{mol Al}^{3^{+}}} \times \frac{1 \, \text{mol Al}^{3^{+$$

$$\frac{342.17g \text{ Al}_2(\text{SO}_4)_3}{\text{mol Al}_2(\text{SO}_4)_3} = 0.235 \text{ g Al}_2(\text{SO}_4)_3$$

Mass % 
$$Al_2(SO_4)_3 = \frac{0.235 g}{1.45 g} \times 100 = 16.2\%$$

- 46. There are many acceptable choices for spectator ions. We will generally choose Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> as the spectator ions because sodium salts and nitrate salts are usually soluble in water.
  - a.  $Fe(NO_3)_3(aq) + 3 NaOH(aq) \rightarrow Fe(OH)_3(s) + 3 NaNO_3(aq)$
  - b.  $Hg_2(NO_3)_2(aq) + 2 NaCl(aq) \rightarrow Hg_2Cl_2(s) + 2 NaNO_3(aq)$
  - c.  $Pb(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow PbSO_4(s) + 2 NaNO_3(aq)$
  - d.  $BaCl_2(aq) + Na_2CrO_4(aq) \rightarrow BaCrO_4(s) + 2 NaCl(aq)$

47. Because a precipitate formed with Na<sub>2</sub>SO<sub>4</sub>, the possible cations are Ba<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sub>2</sub><sup>2+</sup>, and Ca<sup>2+</sup> (from the solubility rules). Because no precipitate formed with KCl, Pb<sup>2+</sup>, and Hg<sub>2</sub><sup>2+</sup> cannot be present. Because both Ba<sup>2+</sup> and Ca<sup>2+</sup> form soluble chlorides and soluble hydroxides, both these cations could be present. Therefore, the cations could be Ba<sup>2+</sup> and Ca<sup>2+</sup> (by the solubility rules in Table 4.1). For students who do a more rigorous study of solubility, Sr<sup>2+</sup> could also be a possible cation (it forms an insoluble sulfate salt, whereas the chloride and hydroxide salts of strontium are soluble).

### **Acid-Base Reactions**

48. Strong bases contain the hydroxide ion,  $OH^-$ . The reaction that occurs is  $H^+ + OH^- \rightarrow H_2O$ .

$$0.0120 \text{ L} \times \frac{0.150 \text{ mol H}^+}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol H}^+} = 1.80 \times 10^{-3} \text{ mol OH}^-$$

The 30.0 mL of the unknown strong base contains  $1.80 \times 10^{-3} \,$  mol  $OH^-$  .

$$\frac{1.8 \times 10^{-3} \text{ molOH}^{-}}{0.0300 \text{L}} = 0.0600 \, M \, \text{OH}^{-}$$

The unknown base concentration is one-half the concentration of OH<sup>-</sup> ions produced from the base, so the base must contain 2 OH<sup>-</sup> in each formula unit. The three soluble strong bases that have 2 OH<sup>-</sup> ions in the formula are Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>. These are all possible identities for the strong base.

49. If we begin with 50.00 mL of 0.100 *M* NaOH, then:

$$50.00 \times 10^{-3} \text{ L} \times \frac{0.100 \text{ mol}}{\text{L}} = 5.00 \times 10^{-3} \text{ mol NaOH to be neutralized.}$$

a.  $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$ 

$$5.00 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol HCl}}{\text{mol NaOH}} \times \frac{1 \text{ L soln}}{0.100 \text{mol}} = 5.00 \times 10^{-2} \text{ L or } 50.0 \text{ mL}$$

b.  $2 \text{ NaOH(aq)} + \text{H}_2\text{SO}_3(\text{aq}) \rightarrow 2 \text{ H}_2\text{O}(1) + \text{Na}_2\text{SO}_3(\text{aq})$ 

$$5.00 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol H}_2 \text{SO}_3}{2 \text{ mol NaOH}} \times \frac{1 \text{ L soln}}{0.100 \text{ mol H}_2 \text{SO}_3} = 2.50 \times 10^{-2} \text{ L or } 25.0 \text{ mL}$$

c.  $3 \text{ NaOH(aq)} + \text{H}_3\text{PO}_4(\text{aq}) \rightarrow \text{Na}_3\text{PO}_4(\text{aq}) + 3 \text{ H}_2\text{O}(1)$ 

$$5.00 \times 10^{-3} \ mol \ NaOH \times \ \frac{1 \ mol \ H_3 PO_4}{3 \ mol \ NaOH} \ \times \ \frac{1 \ L \ soln}{0.200 mol \ H_3 PO_4} = 8.33 \times 10^{-3} \ L \ or \ 8.33 \ mL$$

d.  $HNO_3(aq) + NaOH(aq) \rightarrow H_2O(1) + NaNO_3(aq)$ 

$$5.00 \times 10^{-3} \ mol \ NaOH \times \ \frac{1 \ mol \ HNO_3}{mol \ NaOH} \ \times \ \frac{1 \ L \ soln}{0.150 mol \ HNO_3} = 3.33 \times 10^{-2} \ L \ or \ 33.3 \ mL$$

e. 
$$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow H_2O(1) + NaC_2H_3O_2(aq)$$

$$5.00 \times 10^{-3} \text{ mol NaOH} \times \frac{1 \text{ mol HC}_2 \text{H}_3 \text{O}_2}{\text{mol NaOH}} \times \frac{1 \text{ L soln}}{0.200 \text{mol HC}_2 \text{H}_3 \text{O}_2} = 2.50 \times 10^{-2} \text{ L}$$
 or 25.0 mL

f. 
$$H_2SO_4(aq) + 2 NaOH(aq) \rightarrow 2 H_2O(1) + Na_2SO_4(aq)$$

$$5.00 \times 10^{-3} \ mol \ NaOH \times \ \frac{1 \ mol \ H_2SO_4}{2 \ mol \ NaOH} \ \times \ \frac{1 \ L \ soln}{0.300 mol \ H_2SO_4} = 8.33 \times 10^{-3} \ L \ or \ 8.33 \ mL$$

50. a. 
$$NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$$
 (molecular equation) 
$$NH_3(aq) + H^+(aq) + NO_3^-(aq) \rightarrow NH_4^+(aq) + NO_3^-(aq)$$
 (complete ionic equation) 
$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$
 (net ionic equation)

b. 
$$Ba(OH)_2(aq) + 2 \ HCl(aq) \rightarrow 2 \ H_2O(l) + BaCl_2(aq)$$
 
$$Ba^{2+}(aq) + 2 \ OH^-(aq) + 2 \ H^+(aq) + 2 \ Cl^-(aq) \rightarrow Ba^{2+}(aq) + 2 \ Cl^-(aq) + 2 \ H_2O(l)$$
 
$$OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$$

c. 
$$3 \text{ HClO}_4(aq) + \text{Fe}(OH)_3(s) \rightarrow 3 \text{ H}_2O(1) + \text{Fe}(ClO_4)_3(aq)$$
  
 $3 \text{ H}^+(aq) + 3 \text{ ClO}_4^-(aq) + \text{Fe}(OH)_3(s) \rightarrow 3 \text{ H}_2O(1) + \text{Fe}^{3+}(aq) + 3 \text{ ClO}_4^-(aq)$   
 $3 \text{ H}^+(aq) + \text{Fe}(OH)_3(s) \rightarrow 3 \text{ H}_2O(1) + \text{Fe}^{3+}(aq)$ 

d. 
$$AgOH(s) + HBr(aq) \rightarrow AgBr(s) + H_2O(l)$$
 
$$AgOH(s) + H^{+}(aq) + Br^{-}(aq) \rightarrow AgBr(s) + H_2O(l)$$
 
$$AgOH(s) + H^{+}(aq) + Br^{-}(aq) \rightarrow AgBr(s) + H_2O(l)$$

51. a. Perchloric acid reacted with potassium hydroxide is a possibility.

$$HClO_4(aq) + KOH(aq) \rightarrow H_2O(1) + KClO_4(aq)$$

b. Nitric acid reacted with cesium hydroxide is a possibility.

$$HNO_3(aq) + CsOH(aq) \rightarrow H_2O(1) + CsNO_3(aq)$$

c. Hydroiodic acid reacted with calcium hydroxide is a possibility.

$$2 \text{ HI}(aq) + \text{Ca}(OH)_2(aq) \rightarrow 2 \text{ H}_2O(1) + \text{CaI}_2(aq)$$

52. We get the empirical formula from the elemental analysis. Out of 100.00 g carminic acid there are:

$$53.66 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 4.468 \text{ mol C}; \ 4.09 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 4.06 \text{ mol H}$$

$$42.25 \text{ g O} \times \frac{1 \text{ mol O}}{15.999 \text{ g O}} = 2.641 \text{ mol O}$$

Dividing the moles by the smallest number gives:

$$\frac{4.468}{2.641} = 1.692;$$
  $\frac{4.06}{2.641} = 1.54$ 

These numbers don't give obvious mole ratios. Let's determine the mol C to mol H ratio:

$$\frac{4.468}{4.06} = 1.10 = \frac{11}{10}$$

So let's try 
$$\frac{4.06}{10} = 0.406$$
 as a common factor:  $\frac{4.468}{0.406} = 11.0$ ;  $\frac{4.06}{0.406} = 10.0$ ;  $\frac{2.641}{0.406} = 6.50$ 

Therefore,  $C_{22}H_{20}O_{13}$  is the empirical formula.

We can get molar mass from the titration data. The balanced reaction is  $HA(aq) + OH^{-}(aq) \rightarrow H_2O(l) + A^{-}(aq)$  where HA is an abbreviation for carminic acid, an acid with one acidic proton  $(H^+)$ .

$$18.02\times10^{-3}\,L\,soln\times\,\frac{0.0406mol\,NaOH}{L\,soln}\times\frac{1\,mol\,carminicacid}{mol\,NaOH}$$

 $= 7.32 \times 10^{-4}$  mol carminic acid

Molar mass = 
$$\frac{0.3602g}{7.32 \times 10^{-4} \text{ mol}} = \frac{492g}{\text{mol}}$$

The empirical formula mass of  $C_{22}H_{20}O_{13} \approx 22(12) + 20(1) + 13(16) = 492$  g.

Therefore, the molecular formula of carminic acid is also C<sub>22</sub>H<sub>20</sub>O<sub>13</sub>.

53. HCl and HNO<sub>3</sub> are strong acids; Ca(OH)<sub>2</sub> and RbOH are strong bases. The net ionic equation that occurs is  $H^+(aq) + OH^-(aq) \rightarrow H_2O(1)$ .

$$Mol~H^{^{+}} = 0.0500~L \times \frac{0.100\,mol\,HCl}{L} \times \frac{1\,mol\,H^{^{+}}}{mol\,HCl}~+$$

$$0.1000~L \times \frac{0.200\,mol\,HNO_3}{L} \times \frac{1\,mol\,H^+}{mol\,HNO_3} = 0.00500 + 0.0200 = 0.0250~mol~H^+$$

$$Mol\ OH^- = 0.5000\ L \times \frac{0.0100 mol\ Ca(OH)_2}{L} \times \frac{2\ mol\ OH^-}{mol\ Ca(OH)_2} \ +$$

$$0.2000 \text{ L} \times \frac{0.100 \text{ mol RbOH}}{\text{L}} \times \frac{1 \text{ mol OH}^{-}}{\text{mol RbOH}} = 0.0100 + 0.0200 = 0.0300 \text{ mol OH}^{-}$$

We have an excess of OH<sup>-</sup>, so the solution is basic (not neutral). The moles of excess OH<sup>-</sup> =  $0.0300 \text{ mol OH}^-$  initially  $-0.0250 \text{ mol OH}^-$  reacted (with H<sup>+</sup>) =  $0.0050 \text{ mol OH}^-$  excess.

$$M_{\rm OH^-} = \frac{0.0050 \, \rm mol\, OH^-}{(0.05000 + 0.1000 + 0.5000 + 0.2000) \, L} = \frac{0.0050 \, \rm mol}{0.8500 \, L} = 5.9 \times 10^{-3} \, M$$

54. Because KHP is a monoprotic acid, the reaction is (KHP is an abbreviation for potassium hydrogen phthalate):

$$NaOH(aq) + KHP(aq) \rightarrow NaKP(aq) + H_2O(l)$$

$$0.1082 \text{ g KHP} \times \frac{1 \text{ mol KHP}}{204.22 \text{ g KHP}} \times \frac{1 \text{ mol NaOH}}{\text{mol KHP}} = 5.298 \times 10^{-4} \text{ mol NaOH}$$

There is  $5.298 \times 10^{-4}$  mol of sodium hydroxide in 34.67 mL of solution. Therefore, the concentration of sodium hydroxide is:

$$\frac{5.298 \times 10^{-4} \text{ mol}}{34.67 \times 10^{-3} \text{ L}} = 1.528 \times 10^{-2} M \text{ NaOH}$$

- 55.  $HC_2H_3O_2(aq) + NaOH(aq) \rightarrow H_2O(1) + NaC_2H_3O_2(aq)$ 
  - a.  $16.58 \times 10^{-3} \text{ L soln H } \frac{0.5062 \text{mol NaOH}}{\text{L soln}} \times \frac{1 \text{ mol acetic acid}}{\text{mol NaOH}}$

 $= 8.393 \times 10^{-3}$  mol acetic acid

Concentration of acetic acid = 
$$\frac{8.393 \times 10^{-3} \text{ mol}}{0.01000 \text{L}} = 0.8393 \text{ M HC}_2\text{H}_3\text{O}_2$$

b. If we have 1.000 L of solution: total mass = 1000. mL  $\times \frac{1.006 \text{ g}}{\text{mL}} = 1006 \text{ g}$  solution

Mass of 
$$HC_2H_3O_2 = 0.8393 \text{ mol} \times \frac{60.052 \text{ g}}{\text{mol}} = 50.40 \text{ g } HC_2H_3O_2$$

Mass % acetic acid = 
$$\frac{50.40 \,\text{g}}{1006 \,\text{g}} \times 100 = 5.010\%$$

$$56. \qquad 39.47 \times 10^{-3} \; L \; HCl \; \times \; \frac{0.0984 \, mol \, HCl}{L} \times \\ \frac{1 \, mol \, NH_3}{mol \, HCl} \; = 3.88 \times 10^{-3} \; mol \; NH_3$$

Molarity of NH<sub>3</sub> = 
$$\frac{3.88 \times 10^{-3} \text{ mol}}{50.00 \times 10^{-3} \text{ L}} = 0.0776 \text{ M NH}_3$$

57. 
$$Ba(OH)_2(aq) + 2 HCl(aq) \rightarrow BaCl_2(aq) + 2 H_2O(1); H^+(aq) + OH^-(aq) \rightarrow H_2O(1)$$

$$75.0\times10^{-3}~L\times\frac{0.250\,mol\,HCl}{L}=1.88\times10^{-2}~mol~HCl=1.88\times10^{-2}~mol~H^{+}~+~1.88\times10^{-2}~mol~Cl^{-}$$

$$225.0\times10^{-3}~L\times~\frac{0.0550mol\,Ba(OH)_2}{L}=1.24\times10^{-2}~mol~Ba(OH)_2=1.24\times10^{-2}~mol~Ba^{2+}+\\2.48\times10^{-2}~mol~OH^{-}$$

The net ionic equation requires a 1:1 mol ratio between OH<sup>-</sup> and H<sup>+</sup>. The actual mol OH<sup>-</sup> to mol H<sup>+</sup> ratio is greater than 1:1, so OH<sup>-</sup> is in excess. Because  $1.88 \times 10^{-2}$  mol OH<sup>-</sup> will be neutralized by the H<sup>+</sup>, we have  $(2.48-1.88) \times 10^{-2} = 0.60 \times 10^{-2}$  mol OH<sup>-</sup> in excess.

$$M_{\rm OH^-} = {{
m mol\,OH^-\,excess} \over {
m totalvolume}} = {{6.0 \times 10^{-3} \; {
m mol\,OH^-}} \over {0.0750 {
m L} + 0.2250 {
m L}}} = 2.0 \times 10^{-2} \, {\it M\,OH^-}$$

58. Because KHP is a monoprotic acid, the reaction is:  $NaOH(aq) + KHP(aq) \rightarrow H_2O(l) + NaKP(aq)$ 

$$Mass~KHP = 0.02046~L~NaOH \times \\ \\ \frac{0.1000 mol\,NaOH}{L~NaOH} \times \\ \\ \frac{1\,mol\,KHP}{mol\,NaOH} \times \\ \\ \frac{204.22\,g~KHP}{mol\,KHP}$$

= 0.4178 g KHP

59. The acid is a diprotic acid  $(H_2A)$  meaning that it has two  $H^+$  ions in the formula to donate to a base. The reaction is  $H_2A(aq) + 2 \text{ NaOH}(aq) \rightarrow 2 H_2O(1) + \text{Na}_2A(aq)$ , where  $A^{2^-}$  is what is left over from the acid formula when the two protons  $(H^+$  ions) are reacted.

For the HCl reaction, the base has the ability to accept two protons. The most common examples are  $Ca(OH)_2$ ,  $Sr(OH)_2$ , and  $Ba(OH)_2$ . A possible reaction would be 2 HCl(aq) +  $Ca(OH)_2(aq) \rightarrow 2 H_2O(1) + CaCl_2(aq)$ .

60. Let HA = unknown acid;  $HA(aq) + NaOH(aq) \rightarrow NaA(aq) + H_2O(l)$ 

$$Mol~HA~present = 0.0250~L \times \\ \\ \frac{0.500\,mol~NaOH}{L} \times \\ \\ \\ \frac{1\,mol\,HA}{1\,mol\,NaOH} \\ \\ = 0.0125~mol~HA$$

$$\frac{x \text{ g HA}}{\text{mol HA}} = \frac{2.20 \text{ g HA}}{0.0125 \text{mol HA}}$$
,  $x = \text{molar mass of HA} = 176 \text{ g/mol}$ 

Empirical formula mass  $\approx 3(12) + 4(1) + 3(16) = 88$  g/mol.

Because 176/88 = 2.0, the molecular formula is  $(C_3H_4O_3)_2 = C_6H_8O_6$ .

61. The pertinent reactions are:

$$2 \text{ NaOH(aq)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2 \text{ H}_2\text{O}(1)$$

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

Amount of NaOH added = 
$$0.0500~L \times \frac{0.213\,mol}{L} = 1.07 \times 10^{-2}~mol~NaOH$$

Amount of NaOH neutralized by HCl:

$$0.01321~L~HCl~\times \frac{0.103\,mol\,HCl}{L~HCl} \times \frac{1\,mol\,NaOH}{mol\,HCl} = 1.36 \times 10^{-3}\,mol~NaOH$$

The difference,  $9.3 \times 10^{-3}$  mol, is the amount of NaOH neutralized by the sulfuric acid.

$$9.3 \times 10^{-3} \; mol \; NaOH \times \; \frac{1 \, mol \, H_2 SO_4}{2 \, mol \, NaOH} \; = 4.7 \times 10^{-3} \; mol \; H_2 SO_4$$

Concentration of 
$$H_2SO_4 = \frac{4.7 \times 10^{-3} \text{ mol}}{0.1000 \text{L}} = 4.7 \times 10^{-2} M H_2SO_4$$

62. 
$$2 H_3PO_4(aq) + 3 Ba(OH)_2(aq) \rightarrow 6 H_2O(1) + Ba_3(PO_4)_2(s)$$

$$0.01420~L \times \frac{0.141 mol H_3 PO_4}{L} \times \frac{3~mol Ba(OH)_2}{2~mol H_3 PO_4} \times \frac{1~L~Ba(OH)_2}{0.0521 mol Ba(OH)_2} = 0.0576~L$$

 $= 57.6 \text{ mL Ba}(OH)_2$ 

## **Oxidation-Reduction Reactions**

- 63. a.  $SrCr_2O_7$ : Composed of  $Sr^{2+}$  and  $Cr_2O_7^{2-}$  ions. Sr, +2; O, -2; Cr, 2x + 7(-2) = -2, x = +6
  - b. Cu, +2; Cl, -1;
- c. O, 0;
- d. H, +1; O, -1
- e.  $Mg^{2+}$  and  $CO_3^{2-}$  ions present. Mg, +2; O, -2; C, +4; f. Ag, 0
- 8 4 4 5 5 7 7 7 7 7 7 7 7 7 8 7
- g.  $Pb^{2+}$  and  $SO_3^{2-}$  ions present. Pb, +2; O, -2; S, +4; h. O, -2; Pb, +4
- i. Na<sup>+</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions present. Na, +1; O, -2; C, 2x + 4(-2) = -2, x = +3
- j. O, -2; C, +4
- k. Ammonium ion has a 1+ charge ( $NH_4^+$ ), and sulfate ion has a 2- charge ( $SO_4^{2-}$ ). Therefore, the oxidation state of cerium must be +4 ( $Ce^{4+}$ ). H, +1; N, -3; O, -2; S, +6
- 1. O, -2; Cr, +3
- 64. a.  $UO_2^{2+}$ : O, -2; for U: x + 2(-2) = +2, x = +6
  - b. As<sub>2</sub>O<sub>3</sub>: O, -2; for As: 2(x) + 3(-2) = 0, x = +3
  - c. NaBiO<sub>3</sub>: Na, +1; O, -2; for Bi: +1 + x + 3(-2) = 0, x = +5
  - d. As<sub>4</sub>: As, 0
  - e. HAsO<sub>2</sub>: Assign H = +1 and O = -2; for As: +1 + x + 2(-2) = 0, x = +3
  - f.  $Mg_2P_2O_7$ : Composed of  $Mg^{2+}$  ions and  $P_2O_7^{4-}$  ions.  $Mg_1+2$ ;  $O_1-2$ ;  $P_1+5$

- g.  $Na_2S_2O_3$ : Composed of  $Na^+$  ions and  $S_2O_3^{2-}$  ions.  $Na_1+1$ ;  $O_1-2$ ;  $S_1+2$
- h.  $Hg_2Cl_2$ : Hg, +1; Cl, -1
- i.  $Ca(NO_3)_2$ : Composed of  $Ca^{2+}$  ions and  $NO_3^-$  ions. Ca, +2; O, -2; N, +5
- 65. Apply rules in Table 4.3.
  - a. KMnO₄ is composed of K<sup>+</sup> and MnO₄<sup>−</sup> ions. Assign oxygen an oxidation state value of −2, which gives manganese a +7 oxidation state because the sum of oxidation states for all atoms in MnO₄<sup>−</sup> must equal the 1− charge on MnO₄<sup>−</sup>. K, +1; O, −2; Mn, +7.
  - b. Assign O a -2 oxidation state, which gives nickel a +4 oxidation state. Ni, +4; O, -2.
  - c.  $K_4Fe(CN)_6$  is composed of  $K^+$  cations and  $Fe(CN)_6^{4-}$  anions.  $Fe(CN)_6^{4-}$  is composed of iron and  $CN^-$  anions. For an overall anion charge of 4–, iron must have a +2 oxidation state.
  - d.  $(NH_4)_2HPO_4$  is made of  $NH_4^+$  cations and  $HPO_4^{2-}$  anions. Assign +1 as oxidation state of H and -2 as the oxidation state of O. For N in  $NH_4^+$ : x + 4(+1) = +1, x = -3 = oxidation state of N. For P in  $HPO_4^{2-}$ : +1 + y + 4(-2) = -2, y = +5 = oxidation state of P.
  - e. O, -2; P, +3

f. O, -2; Fe, +8/3

g. O, -2; F, -1; Xe, +6

h. F, -1; S, +4

i. O, -2; C, +2

- i.  $H_1 + 1$ ;  $O_2 2$ ;  $C_3 = 0$
- 66. The key to the oxidation states method is to balance the electrons gained by the species reduced with the number of electrons lost from the species oxidized. This is done by assigning oxidation states and, from the change in oxidation states, determining the coefficients necessary to balance electrons gained with electrons lost. After the loss and gain of electrons is balanced, the remainder of the equation is balanced by inspection.
- a. The species reduced is the element that gains electrons. The reducing agent causes reduction to occur by itself being oxidized. The reducing agent generally refers to the entire formula of the compound/ion that contains the element oxidized.
  - b. The species oxidized is the element that loses electrons. The oxidizing agent causes oxidation to occur by itself being reduced. The oxidizing agent generally refers to the entire formula of the compound/ion that contains the element reduced.
  - c. For simple binary ionic compounds, the actual charge on the ions are the same as the oxidation states. For covalent compounds and ions, nonzero oxidation states are imaginary charges the elements would have if they were held together by ionic bonds (assuming the bond is between two different nonmetals). Nonzero oxidation states for elements in covalent compounds are not actual charges. Oxidation states for covalent compounds are a bookkeeping method to keep track of electrons in a reaction.

68. a. The first step is to assign oxidation states to all atoms (see numbers above the atoms).

Each carbon atom changes from -3 to +4, an increase of seven. Each oxygen atom changes from 0 to -2, a decrease of 2. We need 7/2 O atoms for every C atom.

$$C_2H_6 + 7/2 O_2 \rightarrow CO_2 + H_2O$$

Balancing the remainder of the equation by inspection:

b. The oxidation state of magnesium changes from 0 to +2, an increase of 2. The oxidation state of hydrogen changes from +1 to 0, a decrease of 1. We need 2 H atoms for every Mg atom. The balanced equation is:

$$Mg(s) + 2 HCl(aq) \rightarrow Mg^{2+}(aq) + 2 Cl^{-}(aq) + H_2(g)$$

c. The oxidation state of copper increases by 2 (0 to +2) and the oxidation state of silver decreases by 1 (+1 to 0). We need 2 Ag atoms for every Cu atom. The balanced equation is:

$$Cu(s) + 2 Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2 Ag(s)$$

d. The equation is balanced. Each hydrogen atom gains one electron  $(+1 \rightarrow 0)$ , and each zinc atom loses two electrons  $(0 \rightarrow +2)$ . We need 2 H atoms for every Zn atom. This is the ratio in the given equation:

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

69. a. 
$$Al(s) + 3 HCl(aq) \rightarrow AlCl_3(aq) + 3/2 H_2(g) \text{ or } 2 Al(s) + 6 HCl(aq) \rightarrow 2 AlCl_3(aq) + 3 H_2(g)$$

Hydrogen is reduced (goes from the +1 oxidation state to the 0 oxidation state), and aluminum Al is oxidized  $(0 \rightarrow +3)$ .

b. Balancing S is most complicated because sulfur is in both products. Balance C and H first; then worry about S.

$$CH_4(g) + 4 S(s) \rightarrow CS_2(1) + 2 H_2S(g)$$

Sulfur is reduced  $(0 \rightarrow -2)$ , and carbon is oxidized  $(-4 \rightarrow +4)$ .

c. Balance C and H first; then balance O.

$$C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(1)$$

Oxygen is reduced  $(0 \rightarrow -2)$ , and carbon is oxidized  $(-8/3 \rightarrow +4)$ .

d. Although this reaction is mass balanced, it is not charge balanced. We need 2 mol of silver on each side to balance the charge.

$$Cu(s) + 2 Ag^{+}(aq) \rightarrow 2 Ag(s) + Cu^{2+}(aq)$$

Silver is reduced  $(+1 \rightarrow 0)$ , and copper is oxidized  $(0 \rightarrow +2)$ .

70. To determine if the reaction is an oxidation-reduction reaction, assign oxidation states. If the oxidation states change for some elements, then the reaction is a redox reaction. If the oxidation states do not change, then the reaction is not a redox reaction. In redox reactions, the species oxidized (called the reducing agent) shows an increase in the oxidation states, and the species reduced (called the oxidizing agent) shows a decrease in oxidation states.

	Redox?	Oxidizing	Reducing	Substance	Substance
		Agent	Agent	Oxidized	Reduced
a.	Yes	$O_2$	$\mathrm{CH}_4$	$\mathrm{CH_{4}}\left( \mathrm{C}\right)$	$O_2$ (O)
b.	Yes	HCl	Zn	Zn	HCl (H)
c.	No	_	_	_	_
d.	Yes	$O_3$	NO	NO(N)	$O_3(O)$
e.	Yes	$H_2O_2$	$H_2O_2$	$H_2O_2(O)$	$H_2O_2(O)$
f.	Yes	CuCl	CuCl	CuCl (Cu)	CuCl (Cu)
g.	No	_	_	_	_
h.	No	_	_	_	_
i.	Yes	$SiCl_4$	Mg	Mg	SiCl <sub>4</sub> (Si)

In c, g, and h, no oxidation states change from reactants to products.

71. a. HCl(aq) dissociates to  $H^+(aq) + Cl^-(aq)$ . For simplicity, let's use  $H^+$  and  $Cl^-$  separately.

$$\begin{array}{c} H^{+} \rightarrow H_{2} & \text{Fe} \rightarrow \text{HFeCl}_{4} \\ (2 \, H^{+} + 2 \, e^{-} \rightarrow H_{2}) \times 3 & (H^{+} + 4 \, \text{Cl}^{-} + \text{Fe} \rightarrow \text{HFeCl}_{4} + 3 \, e^{-}) \times 2 \\ \\ 6 \, H^{+} + 6 \, e^{-} \rightarrow 3 \, H_{2} \\ 2 \, H^{+} + 8 \, \text{Cl}^{-} + 2 \, \text{Fe} \rightarrow 2 \, \text{HFeCl}_{4} + 6 \, e^{-} \\ \hline \\ 8 \, H^{+} + 8 \, \text{Cl}^{-} + 2 \, \text{Fe} \rightarrow 2 \, \text{HFeCl}_{4} + 3 \, H_{2} \\ \text{or} & 8 \, \text{HCl}(\text{aq}) + 2 \, \text{Fe}(\text{s}) \rightarrow 2 \, \text{HFeCl}_{4}(\text{aq}) + 3 \, H_{2}(\text{g}) \\ \text{b.} & IO_{3}^{-} \rightarrow I_{3}^{-} \\ & 3 \, IO_{3}^{-} \rightarrow I_{3}^{-} \\ & 3 \, IO_{3}^{-} \rightarrow I_{3}^{-} + 9 \, H_{2}O \\ & 16 \, e^{-} + 18 \, H^{+} + 3 \, IO_{3}^{-} \rightarrow I_{3}^{-} + 9 \, H_{2}O \\ & 24 \, \Gamma \rightarrow 8 \, I_{3}^{-} + 16 \, e^{-} \\ \hline & 18 \, H^{+} + 24 \, \Gamma + 3 \, IO_{3}^{-} \rightarrow 9 \, I_{3}^{-} + 9 \, H_{2}O \\ \hline \end{array}$$

Reducing:  $6 \text{ H}^+(\text{aq}) + 8 \text{ I}^-(\text{aq}) + \text{IO}_3^-(\text{aq}) \rightarrow 3 \text{ I}_3^-(\text{aq}) + 3 \text{ H}_2\text{O}(1)$ 

c. 
$$(Ce^{4+} + e^{-} \rightarrow Ce^{3+}) \times 97$$
  
 $Cr(NCS)_{6}^{4-} \rightarrow Cr^{3+} + NO_{3}^{-} + CO_{2} + SO_{4}^{2-}$   
 $54 \text{ H}_{2}O + Cr(NCS)_{6}^{4-} \rightarrow Cr^{3+} + 6 \text{ N}O_{3}^{-} + 6 \text{ C}O_{2} + 6 \text{ S}O_{4}^{2-} + 108 \text{ H}^{+}$ 

Charge on left = -4. Charge on right = +3 + 6(-1) + 6(-2) + 108(+1) = +93. Add 97 e<sup>-</sup> to the product side, and then add the two balanced half-reactions with a common factor of 97 e<sup>-</sup> transferred.

54 
$$\text{H}_2\text{O} + \text{Cr}(\text{NCS})_6^{4-} \rightarrow \text{Cr}^{3+} + 6 \text{ NO}_3^{-} + 6 \text{ CO}_2 + 6 \text{ SO}_4^{2-} + 108 \text{ H}^+ + 97 \text{ e}^-$$
  
97  $\text{e}^- + 97 \text{ Ce}^{4+} \rightarrow 97 \text{ Ce}^{3+}$ 

$$97 \text{ Ce}^{4+}(\text{aq}) + 54 \text{ H}_2\text{O}(\text{l}) + \text{Cr}(\text{NCS})_6^{4-}(\text{aq}) \rightarrow 97 \text{ Ce}^{3+}(\text{aq}) + \text{Cr}^{3+}(\text{aq}) + 6 \text{ NO}_3^{-}(\text{aq}) + 6 \text{ CO}_2(\text{g}) + 6 \text{ SO}_4^{2-}(\text{aq}) + 108 \text{ H}^+(\text{aq})$$

This is very complicated. A check of the net charge is a good check to see if the equation is balanced. Left: charge = 97(+4) - 4 = +384. Right: charge = 97(+3) + 3 + 6(-1) + 6(-2) + 108(+1) = +384.

d. 
$$CrI_3 \rightarrow CrO_4^{\ 2^-} + IO_4^{\ -}$$
  $Cl_2 \rightarrow Cl^ (16 \text{ H}_2\text{O} + \text{CrI}_3 \rightarrow \text{CrO}_4^{\ 2^-} + 3 \text{ IO}_4^{\ -} + 32 \text{ H}^+ + 27 \text{ e}^-) \times 2$   $(2 \text{ e}^- + \text{Cl}_2 \rightarrow 2 \text{ Cl}^-) \times 27$ 

Common factor is a transfer of 54 e<sup>-</sup>.

$$54 e^{-} + 27 Cl_{2} \rightarrow 54 Cl^{-}$$
  
 $32 H_{2}O + 2 CrI_{3} \rightarrow 2 CrO_{4}^{2-} + 6 IO_{4}^{-} + 64 H^{+} + 54 e^{-}$ 

$$32 \text{ H}_2\text{O} + 2 \text{ CrI}_3 + 27 \text{ Cl}_2 \rightarrow 54 \text{ Cl}^- + 2 \text{ CrO}_4^{2-} + 6 \text{ IO}_4^- + 64 \text{ H}^+$$

Add 64 OH<sup>-</sup> to both sides and convert 64 H<sup>+</sup> into 64 H<sub>2</sub>O.

$$64 \text{ OH}^- + 32 \text{ H}_2\text{O} + 2 \text{ CrI}_3 + 27 \text{ Cl}_2 \rightarrow 54 \text{ Cl}^- + 2 \text{ CrO}_4^{2-} + 6 \text{ IO}_4^- + 64 \text{ H}_2\text{O}$$

Reducing gives:

$$64 \text{ OH}^{-}(\text{aq}) + 2 \text{ CrI}_{3}(\text{s}) + 27 \text{ Cl}_{2}(\text{g}) \rightarrow 54 \text{ Cl}^{-}(\text{aq}) + 2 \text{ CrO}_{4}^{2-}(\text{aq}) + 6 \text{ IO}_{4}^{-}(\text{aq}) + 32 \text{ H}_{2}\text{O(l)}$$

e. 
$$Ce^{4+} \rightarrow Ce(OH)_3$$
  
 $(e^- + 3 \text{ H}_2O + Ce^{4+} \rightarrow Ce(OH)_3 + 3 \text{ H}^+) \times 61$ 

$$Fe(CN)_6^{4-} \rightarrow Fe(OH)_3 + CO_3^{2-} + NO_3^{-}$$
  
 $Fe(CN)_6^{4-} \rightarrow Fe(OH)_3 + 6 CO_3^{2-} + 6 NO_3^{-}$ 

There are 39 extra O atoms on right. Add 39 H<sub>2</sub>O to left, then add 75 H<sup>+</sup> to right to balance H<sup>+</sup>.

$$39 \text{ H}_2\text{O} + \text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{OH})_3 + 6 \text{ CO}_3^{2-} + 6 \text{ NO}_3^{-} + 75 \text{ H}^+$$
  
net charge = 4- net charge = 57+

Add 61 e<sup>-</sup> to the product side, and then add the two balanced half-reactions with a common factor of 61 e<sup>-</sup> transferred.

$$39~H_2O + Fe(CN)_6^{4-} \rightarrow Fe(OH)_3 + 6~CO_3^- + 6~NO_3^- + 75~H^+ + 61~e^- \\ 61~e^- + 183~H_2O + 61~Ce^{4+} \rightarrow 61~Ce(OH)_3 + 183~H^+$$

$$\frac{1}{222 \text{ H}_2\text{O} + \text{Fe}(\text{CN})_6^{4-} + 61 \text{ Ce}^{4+} \rightarrow 61 \text{ Ce}(\text{OH})_3 + \text{Fe}(\text{OH})_3 + 6 \text{ CO}_3^{2-} + 6 \text{ NO}_3^{-} + 258 \text{ H}^{+}}$$

Adding 258 OH<sup>-</sup> to each side, and then reducing gives:

$$258 \; OH^{-}(aq) + Fe(CN)_{6}^{4-}(aq) + 61 \; Ce^{4+}(aq) \rightarrow 61 \; Ce(OH)_{3}(s) + Fe(OH)_{3}(s) \\ + 6 \; CO_{3}^{2-}(aq) + 6 \; NO_{3}^{-}(aq) + 36 \; H_{2}O(l)$$

72. Use the same method as with acidic solutions. After the final balanced equation, convert H<sup>+</sup> to OH<sup>-</sup> as described in section 4.11 of the text. The extra step involves converting H<sup>+</sup> into H<sub>2</sub>O by adding equal moles of OH<sup>-</sup> to each side of the reaction. This converts the reaction to a basic solution while keeping it balanced.

a. 
$$Al \rightarrow Al(OH)_4^ MnO_4^- \rightarrow MnO_2$$
  
 $4 H_2O + Al \rightarrow Al(OH)_4^- + 4 H^+$   $3 e^- + 4 H^+ + MnO_4^- \rightarrow MnO_2 + 2 H_2O$   
 $4 H_2O + Al \rightarrow Al(OH)_4^- + 4 H^+ + 3 e^-$   
 $4 H_2O + Al \rightarrow Al(OH)_4^- + 4 H^+ + 3 e^-$   
 $3 e^- + 4 H^+ + MnO_4^- \rightarrow MnO_2 + 2 H_2O$ 

$$2 \text{ H}_2\text{O}(1) + \text{Al}(s) + \text{MnO}_4(aq) \rightarrow \text{Al}(O\text{H})_4(aq) + \text{MnO}_2(s)$$

Because H<sup>+</sup> doesn't appear in the final balanced reaction, we are done.

b. 
$$Cl_2 \rightarrow Cl^-$$
  
 $2 e^- + Cl_2 \rightarrow 2 Cl^-$   
 $2 H_2O + Cl_2^- \rightarrow 2 ClO^- + 4 H^+ + 2 e^-$   
 $2 H_2O + Cl_2 \rightarrow 2 Cl^- + 4 H^+ + 2 e^-$   
 $2 H_2O + 2 Cl_2 \rightarrow 2 Cl^- + 2 ClO^- + 4 H^+$ 

Now convert to a basic solution. Add 4 OH<sup>-</sup> to both sides of the equation. The 4 OH<sup>-</sup> will react with the 4 H<sup>+</sup> on the product side to give 4 H<sub>2</sub>O. After this step, cancel identical species on both sides (2 H<sub>2</sub>O). Applying these steps gives 4 OH<sup>-</sup> + 2 Cl<sub>2</sub>  $\rightarrow$  2 Cl<sup>-</sup> + 2 ClO<sup>-</sup> + 2 H<sub>2</sub>O, which can be further simplified to:

$$2 OH^{-}(aq) + Cl_{2}(g) \rightarrow Cl^{-}(aq) + ClO^{-}(aq) + H_{2}O(l)$$

c. 
$$NO_2^- \rightarrow NH_3$$
  $Al \rightarrow AlO_2^-$   
 $6 e^- + 7 H^+ + NO_2^- \rightarrow NH_3 + 2 H_2O$   $(2 H_2O + Al \rightarrow AlO_2^- + 4 H^+ + 3 e^-) \times 2$ 

Common factor is a transfer of 6 e<sup>-</sup>.

$$6e^{-} + 7 H^{+} + NO_{2}^{-} \rightarrow NH_{3} + 2 H_{2}O$$
  
 $4 H_{2}O + 2 Al \rightarrow 2 AlO_{2}^{-} + 8 H^{+} + 6 e^{-}$ 

$$OH^- + 2 H_2O + NO_2^- + 2 Al \rightarrow NH_3 + 2 AlO_2^- + H^+ + OH^-$$

Reducing gives:  $OH^{-}(aq) + H_2O(1) + NO_2^{-}(aq) + 2 Al(s) \rightarrow NH_3(g) + 2 AlO_2^{-}(aq)$ 

d. 
$$S^{2-} \to S$$
  $MnO_4^- \to MnS$   
 $(S^{2-} \to S + 2 e^-) \times 5$   $MnO_4^- + S^{2-} \to MnS$   
 $(5 e^- + 8 H^+ + MnO_4^- + S^{2-} \to MnS + 4 H_2O) \times 2$ 

Common factor is a transfer of 10 e<sup>-</sup>.

$$5 \text{ S}^{2-} \rightarrow 5 \text{ S} + 10 \text{ e}^{-}$$
  
 $10 \text{ e}^{-} + 16 \text{ H}^{+} + 2 \text{ MnO}_{4}^{-} + 2 \text{ S}^{2-} \rightarrow 2 \text{ MnS} + 8 \text{ H}_{2}\text{O}$ 

$$\frac{}{16 \text{ OH}^{-} + 16 \text{ H}^{+} + 7 \text{ S}^{2-} + 2 \text{ MnO}_{4}^{-} \rightarrow 5 \text{ S} + 2 \text{ MnS} + 8 \text{ H}_{2}\text{O} + 16 \text{ OH}^{-}}$$

$$16 \text{ H}_2\text{O} + 7 \text{ S}^{2-} + 2 \text{ MnO}_4^- \rightarrow 5 \text{ S} + 2 \text{ MnS} + 8 \text{ H}_2\text{O} + 16 \text{ OH}^-$$

Reducing gives:

$$8 \text{ H}_2\text{O(1)} + 7 \text{ S}^{2-}(\text{aq}) + 2 \text{ MnO}_4^-(\text{aq}) \rightarrow 5 \text{ S(s)} + 2 \text{ MnS(s)} + 16 \text{ OH}^-(\text{aq})$$

e. 
$$CN^- \rightarrow CNO^-$$
  
 $(H_2O + CN^- \rightarrow CNO^- + 2 H^+ + 2 e^-) \times 3$ 

$$MnO_4^- \rightarrow MnO_2$$

$$(3 e^- + 4 H^+ + MnO_4^- \rightarrow MnO_2 + 2 H_2O) \times 2$$

Common factor is a transfer of 6 electrons.

$$3 \text{ H}_2\text{O} + 3 \text{ CN}^- \rightarrow 3 \text{ CNO}^- + 6 \text{ H}^+ + 6 \text{ e}^-$$
  
 $6 \text{ e}^- + 8 \text{ H}^+ + 2 \text{ MnO}_4^- \rightarrow 2 \text{ MnO}_2 + 4 \text{ H}_2\text{O}$ 

$$2 \text{ OH}^- + 2 \text{ H}^+ + 3 \text{ CN}^- + 2 \text{ MnO}_4^- \rightarrow 3 \text{ CNO}^- + 2 \text{ MnO}_2 + \text{H}_2\text{O} + 2 \text{ OH}^-$$

Reducing gives:

$$H_2O(1) + 3 \text{ CN}^-(aq) + 2 \text{ MnO}_4^-(aq) \rightarrow 3 \text{ CNO}^-(aq) + 2 \text{ MnO}_2(s) + 2 \text{ OH}^-(aq)$$

73. a. Review Section 4.11 of the text for rules on balancing by the half-reaction method. The first step is to separate the reaction into two half-reactions, and then balance each half-reaction separately.

$$(Cu \rightarrow Cu^{2+} + 2 e^{-}) \times 3$$
  $NO_{3}^{-} \rightarrow NO + 2 H_{2}O$   
 $(3 e^{-} + 4 H^{+} + NO_{3}^{-} \rightarrow NO + 2 H_{2}O) \times 2$ 

Adding the two balanced half-reactions so electrons cancel:

$$\begin{array}{c} 3 \text{ Cu} \rightarrow 3 \text{ Cu}^{2^{+}} + 6 \text{ e}^{-} \\ 6 \text{ e}^{-} + 8 \text{ H}^{+} + 2 \text{ NO}_{3}^{-} \rightarrow 2 \text{ NO} + 4 \text{ H}_{2}\text{O} \\ \hline 3 \text{ Cu(s)} + 8 \text{ H}^{+}(\text{aq}) + 2 \text{ NO}_{3}^{-}(\text{aq}) \rightarrow 3 \text{ Cu}^{2^{+}}(\text{aq}) + 2 \text{ NO(g)} + 4 \text{ H}_{2}\text{O(l)} \\ \text{b.} \quad (2 \text{ Cl}^{-} \rightarrow \text{Cl}_{2} + 2 \text{ e}^{-}) \times 3 \\ & \qquad \qquad \qquad \qquad \text{Cr}_{2}\text{O}_{7}^{2^{-}} \rightarrow 2 \text{ Cr}^{3^{+}} + 7 \text{ H}_{2}\text{O} \\ 6 \text{ e}^{-} + 14 \text{ H}^{+} + \text{Cr}_{2}\text{O}_{7}^{2^{-}} \rightarrow 2 \text{ Cr}^{3^{+}} + 7 \text{ H}_{2}\text{O} \end{array}$$

Add the two balanced half-reactions with six electrons transferred:

$$6 \text{ Cl}^{-} \rightarrow 3 \text{ Cl}_{2} + 6 \text{ e}^{-} 
6 \text{ e}^{-} + 14 \text{ H}^{+} + \text{Cr}_{2}\text{O}_{7}^{2-} \rightarrow 2 \text{ Cr}^{3+} + 7 \text{ H}_{2}\text{O}$$

$$14 \text{ H}^{+}(\text{aq}) + \text{Cr}_{2}\text{O}_{7}^{2-}(\text{aq}) + 6 \text{ Cl}^{-}(\text{aq}) \rightarrow 3 \text{ Cl}_{2}(\text{g}) + 2 \text{ Cr}^{3+}(\text{aq}) + 7 \text{ H}_{2}\text{O}(\text{l})$$

c. 
$$Pb \rightarrow PbSO_4$$
  $PbO_2 \rightarrow PbSO_4$   $PbO_2 \rightarrow PbSO_4$   $Pb + H_2SO_4 \rightarrow PbSO_4 + 2 H^+$   $PbO_2 + H_2SO_4 \rightarrow PbSO_4 + 2 H_2O$   $Pb + H_2SO_4 \rightarrow PbSO_4 + 2 H^+ + 2 e^ 2 e^- + 2 H^+ + PbO_2 + H_2SO_4 \rightarrow PbSO_4 + 2 H_2O$ 

Add the two half-reactions with two electrons transferred:

$$2 e^{-} + 2 H^{+} + PbO_{2} + H_{2}SO_{4} \rightarrow PbSO_{4} + 2 H_{2}O$$

$$Pb + H_{2}SO_{4} \rightarrow PbSO_{4} + 2 H^{+} + 2 e^{-}$$

$$Pb(s) + 2 H_{2}SO_{4}(aq) + PbO_{2}(s) \rightarrow 2 PbSO_{4}(s) + 2 H_{2}O(1)$$

This is the reaction that occurs in an automobile lead storage battery.

d. 
$$Mn^{2+} \rightarrow MnO_4^-$$
  
 $(4 \text{ H}_2\text{O} + Mn^{2+} \rightarrow MnO_4^- + 8 \text{ H}^+ + 5 \text{ e}^-) \times 2$   
 $NaBiO_3 \rightarrow Bi^{3+} + Na^+$   
 $6 \text{ H}^+ + NaBiO_3 \rightarrow Bi^{3+} + Na^+ + 3 \text{ H}_2\text{O}$   
 $(2 \text{ e}^- + 6 \text{ H}^+ + NaBiO_3 \rightarrow Bi^{3+} + Na^+ + 3 \text{ H}_2\text{O}) \times 5$   
 $8 \text{ H}_2\text{O} + 2 \text{ M}n^{2+} \rightarrow 2 \text{ M}nO_4^- + 16 \text{ H}^+ + 10 \text{ e}^-$   
 $10 \text{ e}^- + 30 \text{ H}^+ + 5 \text{ N}aBiO_3 \rightarrow 5 \text{ B}i^{3+} + 5 \text{ N}a^+ + 15 \text{ H}_2\text{O}$   
 $8 \text{ H}_2\text{O} + 30 \text{ H}^+ + 2 \text{ M}n^{2+} + 5 \text{ N}aBiO_3 \rightarrow 2 \text{ M}nO_4^- + 5 \text{ B}i^{3+} + 5 \text{ N}a^+ + 15 \text{ H}_2\text{O} + 16 \text{ H}^+$ 

Simplifying:

$$14 \; H^{\scriptscriptstyle +}(aq) \; + \; 2 \; Mn^{2^{\scriptscriptstyle +}}(aq) \; + \; 5 \; NaBiO_3(s) \; \\ \rightarrow \; 2 \; MnO_4^{\scriptscriptstyle -}(aq) \; + \; 5 \; Bi^{3^{\scriptscriptstyle +}}(aq) \; + \; 5 \; Na^{\scriptscriptstyle +}(aq) \; + \; 7 \; H_2O(l) \; \\ + \; 10 \; Mn^{2^{\scriptscriptstyle +}}(aq) \; + \; 10 \; Na^{\scriptscriptstyle +}(aq) \; + \;$$

e. 
$$H_3AsO_4 \rightarrow AsH_3$$
  $(Zn \rightarrow Zn^{2+} + 2 e^-) \times 4$   $H_3AsO_4 \rightarrow AsH_3 + 4 H_2O$   $8 e^- + 8 H^+ + H_3AsO_4 \rightarrow AsH_3 + 4 H_2O$ 

$$8 \, e^- + 8 \, H^+ + H_3 A S O_4 \rightarrow A s H_3 + 4 \, H_2 O \\ 4 \, Z n \rightarrow 4 \, Z n^{2+} + 8 \, e^- \\ \hline$$

$$8 \, H^+ (aq) + H_3 A s O_4 (aq) + 4 \, Z n (s) \rightarrow 4 \, Z n^{2+} (aq) + A s H_3 (g) + 4 \, H_2 O (l)$$

$$f. \qquad A s_2 O_3 \rightarrow H_3 A s O_4 \\ A s_2 O_3 \rightarrow 2 \, H_3 A s O_4 \\ (5 \, H_2 O + A s_2 O_3 \rightarrow 2 \, H_3 A s O_4 + 4 \, H^+ + 4 \, e^-) \times 3$$

$$NO_3^- \rightarrow NO + 2 \, H_2 O \\ 4 \, H^+ + NO_3^- \rightarrow NO + 2 \, H_2 O \\ (3 \, e^- + 4 \, H^+ + NO_3^- \rightarrow NO + 2 \, H_2 O) \times 4$$

$$12 \, e^- + 16 \, H^+ + 4 \, NO_3^- \rightarrow 4 \, NO + 8 \, H_2 O \\ 15 \, H_2 O + 3 \, A s_2 O_3 \rightarrow 6 \, H_3 A s O_4 + 12 \, H^+ + 12 \, e^- \\ \hline$$

$$7 \, H_2 O (l) + 4 \, H^+ (aq) + 3 \, A s_2 O_3 (s) + 4 \, NO_3^- (aq) \rightarrow 4 \, NO (g) + 6 \, H_3 A s O_4 (aq)$$

$$g. \qquad (2 \, B r^- \rightarrow B \, r_2 + 2 \, e^-) \times 5 \qquad \qquad MnO_4^- \rightarrow M n^{2+} + 4 \, H_2 O \\ (5 \, e^- + 8 \, H^+ + M nO_4^- \rightarrow M n^{2+} + 4 \, H_2 O) \times 2$$

$$10 \, B r^- \rightarrow 5 \, B r_2 + 10 \, e^- \\ 10 \, e^- + 16 \, H^+ + 2 \, M nO_4^- \rightarrow 2 \, M n^{2+} + 8 \, H_2 O$$

$$16 \, H^+ (aq) + 2 \, M nO_4^- (aq) + 10 \, B r^- (aq) \rightarrow 5 \, B r_2 (l) + 2 \, M n^{2+} (aq) + 8 \, H_2 O (l)$$

$$h. \qquad C H_3 O H \rightarrow C H_2 O \qquad C r_2 O_7^{2-} \rightarrow C r^{3+} + 7 \, H_2 O \\ 6 \, e^- + 14 \, H^+ + C r_2 O_7^{2-} \rightarrow 2 \, C r^{3+} + 7 \, H_2 O$$

$$3 \, C H_3 O H \rightarrow 3 \, C H_2 O + 6 \, H^+ + 6 \, e^- \\ 6 \, e^- + 14 \, H^+ + C r_2 O_7^{2-} \rightarrow 2 \, C r^{3+} + 7 \, H_2 O$$

74. The unbalanced reaction is:  $VO^{2+} + MnO_4^- \rightarrow V(OH)_4^+ + Mn^{2+}$ 

This is a redox reaction in acidic solution and must be balanced accordingly. The two half-reactions to balance are:  $VO^{2+} \rightarrow V(OH)_4^+$  and  $MnO_4^- \rightarrow Mn^{2+}$ 

 $\frac{1}{8 \text{ H}^{+}(\text{ag}) + 3 \text{ CH}_{3}\text{OH}(\text{ag}) + \text{Cr}_{2}\text{O}_{7}^{2-}(\text{ag}) \rightarrow 2 \text{ Cr}^{3+}(\text{ag}) + 3 \text{ CH}_{2}\text{O}(\text{ag}) + 7 \text{ H}_{2}\text{O}(1)}$ 

Balancing by the half-reaction method gives:

$$MnO_{4}^{-}(aq) + 5\ VO^{2+}(aq) + 11\ H_{2}O(l) \ \rightarrow 5\ V(OH)_{4}^{+}(aq) + Mn^{2+}(aq) + 2\ H^{+}(aq)$$

$$0.02645 \; L \times \frac{0.02250 mol \, MnO_4^{\; -}}{L} \times \frac{5 \; mol \, VO^{\; 2+}}{mol \, MnO_4^{\; -}} \times \frac{1 \; mol \, V}{mol \, VO^{\; 2+}} \times \frac{50.94 \, g \; V}{mol \, V} = 0.1516 \; g \; V$$

$$0.581 = \frac{0.1516 \text{g V}}{\text{mass of ore sample}}$$
,  $0.1516/0.581 = 0.261 \text{ g ore sample}$ 

75. 
$$(Fe^{2+} \to Fe^{3+} + e^{-}) \times 5$$

$$5 e^{-} + 8 H^{+} + MnO_{4}^{-} \to Mn^{2+} + 4 H_{2}O$$

$$8 H^{+}(aq) + MnO_{4}^{-}(aq) + 5 Fe^{2+}(aq) \to 5 Fe^{3+}(aq) + Mn^{2+}(aq) + 4 H_{2}O(1)$$

From the titration data we can get the number of moles of Fe<sup>2+</sup>. We then convert this to a mass of iron and calculate the mass percent of iron in the sample.

$$38.37 \times 10^{-3} \text{ L MnO}_{4}^{-} \times \frac{0.0198 \text{molMnO}_{4}^{-}}{\text{L}} \times \frac{5 \text{ molFe}^{2+}}{\text{molMnO}_{4}^{-}} = 3.80 \times 10^{-3} \text{ mol Fe}^{2+}$$

$$= 3.80 \times 10^{-3} \text{ mol Fe}^{2+}$$

$$= 3.80 \times 10^{-3} \text{ mol Fe}^{2+}$$

$$3.80 \times 10^{-3} \text{ mol Fe} \times \frac{55.85 \text{ g Fe}}{\text{mol Fe}} = 0.212 \text{ g Fe}$$

Mass % Fe = 
$$\frac{0.212 \,\text{g}}{0.6128 \,\text{g}} \times 100 = 34.6\%$$
 Fe

76. a. 
$$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}) \times 5$$
  $5e^{-} + 8H^{+} + MnO_{4}^{-} \rightarrow Mn^{2+} + 4H_{2}O_{4}^{-}$ 

The balanced equation is:

$$8 \text{ H}^+(aq) + \text{MnO}_4^-(aq) + 5 \text{ Fe}^{2+}(aq) \rightarrow 5 \text{ Fe}^{3+}(aq) + \text{Mn}^{2+}(aq) + 4 \text{ H}_2\text{O}(1)$$

$$20.62 \times 10^{-3} \text{ L soln} \times \frac{0.0216 \text{molMnO}_4^-}{\text{L soln}} \times \frac{5 \text{ molFe}^{2+}}{\text{molMnO}_4^-} = 2.23 \times 10^{-3} \text{ mol Fe}^{2+}$$

Molarity = 
$$\frac{2.23 \times 10^{-3} \text{ mol Fe}^{2+}}{50.00 \times 10^{-3} \text{ L}} = 4.46 \times 10^{-2} M \text{ Fe}^{2+}$$

b. 
$$(Fe^{2+} \rightarrow Fe^{3+} + e^{-}) \times 6$$
  $6e^{-} + 14H^{+} + Cr_{2}O_{7}^{2-} \rightarrow 2Cr^{3+} + 7H_{2}O_{7}^{2-}$ 

The balanced equation is:

$$14 \; H^{\scriptscriptstyle +}(aq) + C r_2 O_7^{\; 2 \scriptscriptstyle -}(aq) + 6 \; Fe^{2 \scriptscriptstyle +}(aq) \to 6 \; Fe^{3 \scriptscriptstyle +}(aq) + 2 \; C r^{3 \scriptscriptstyle +}(aq) + 7 \; H_2 O(l)$$

$$50.00\times10^{-3}\,L\times\frac{4.46\times10^{-2}\;molFe^{2+}}{L}\times\frac{1\,mol\,Cr_2O_7^{\ 2-}}{6\,mol\,Fe^{2+}}\times\frac{1\,L}{0.0150\,mol\,Cr_2O_7^{\ 2-}}$$

$$= 2.48 \times 10^{-2}$$
L or 24.8 mL

77. 
$$Mg(s) + 2 HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$3.00~g~Mg \times \frac{1\,mol\,Mg}{24.31\,g~Mg} \times \frac{2\,mol\,HCl}{mol\,Mg} \times \frac{1\,L~HCl}{5.0~mol\,HCl} = ~0.0494~L = 49.4~mL~HCl$$

78. a. 
$$16 e^{-} + 18 H^{+} + 3 IO_{3}^{-} \rightarrow I_{3}^{-} + 9 H_{2}O$$
  $(3 I^{-} \rightarrow I_{3}^{-} + 2 e^{-}) \times 8$ 

$$24 I^{-} \rightarrow 8 I_{3}^{-} + 16 e^{-}$$

$$16 e^{-} + 18 H^{+} + 3 IO_{3}^{-} \rightarrow I_{3}^{-} + 9 H_{2}O$$

$$\overline{18 H^{+} + 24 \Gamma + 3 IO_{3}^{-} \rightarrow 9 I_{3}^{-} + 9 H_{2}O}$$

Reducing:  $6 \text{ H}^+(aq) + 8 \text{ I}^-(aq) + \text{IO}_3^-(aq) \rightarrow 3 \text{ I}_3^-(aq) + 3 \text{ H}_2\text{O}(1)$ 

b. 
$$0.6013 \text{ g KIO}_3 \times \frac{1 \text{ mol KIO}_3}{214.0 \text{ g KIO}_3} = 2.810 \times 10^{-3} \text{ mol KIO}_3$$

$$2.810 \times 10^{-3} \text{ mol KIO}_3 \times \frac{8 \text{ mol KI}}{\text{mol KIO}_3} \times \frac{166.0 \text{ g KI}}{\text{mol KI}} = 3.732 \text{ g KI}$$

$$2.810 \times 10^{-3} \ mol \ KIO_{3} \times \ \frac{6 \ mol \ HCl}{mol \ KIO_{3}} \times \frac{1 \ L}{3.00 \ mol \ HCl} \ = 5.62 \times 10^{-3} \ L = 5.62 \ mL \ HCl$$

c. 
$$I_3^- + 2 e^- \rightarrow 3 I^ 2 S_2 O_3^{2-} \rightarrow S_4 O_6^{2-} + 2 e^-$$

Adding the balanced half-reactions gives:

$$2\; {S_2}{O_3}^{2\text{--}}(aq) + {I_3}^{\text{--}}(aq) \to 3\; {I}^{\text{--}}(aq) + {S_4}{O_6}^{2\text{--}}(aq)$$

$$d. \quad 25.00 \times 10^{-3} \ L \ KIO_3 \times \frac{0.0100 mol \ KIO_3}{L} \times \frac{3 \ mol \ I_3^-}{mol \ KIO_3} \times \frac{2 \ mol \ Na_2 S_2 O_3}{mol \ I_3^-} = \\ 1.50 \ \times 10^{-3} \ mol \ \ Na_2 S_2 O_3$$

$$M_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{1.50 \times 10^{-3} \text{ mol}}{32.04 \times 10^{-3} \text{ L}} = 0.0468 \text{ M Na}_2\text{S}_2\text{O}_3$$

e. 
$$0.5000 \text{ L} \times \frac{0.0100 \text{mol KIO}_3}{\text{L}} \times \frac{214.0 \text{ g KIO}_3}{\text{mol KIO}_3} = 1.07 \text{ g KIO}_3$$

Place 1.07 g KIO<sub>3</sub> in a 500-mL volumetric flask; add water to dissolve the KIO<sub>3</sub>; continue adding water to the 500.0-mL mark, with mixing along the way.

79. 
$$\operatorname{Mn} \to \operatorname{Mn}^{2+} + 2 e^{-} \qquad \operatorname{HNO_3} \to \operatorname{NO_2} \\ \operatorname{HNO_3} \to \operatorname{NO_2} + \operatorname{H_2O} \\ (e^{-} + \operatorname{H}^{+} + \operatorname{HNO_3} \to \operatorname{NO_2} + \operatorname{H_2O}) \times 2$$

$$\begin{array}{c} Mn \rightarrow Mn^{2+} + 2 \, e^{-} \\ 2 \, e^{-} + 2 \, H^{+} + 2 \, HNO_{3} \rightarrow 2 \, NO_{2} + 2 \, H_{2}O \\ \hline 2 \, H^{+}(aq) + Mn(s) + 2 \, HNO_{3}(aq) \rightarrow Mn^{2+}(aq) + 2 \, NO_{2}(g) + 2 \, H_{2}O(l) \, \, \, \text{or} \\ 4 \, H^{+}(aq) + Mn(s) + 2 \, NO_{3}^{-}(aq) \rightarrow Mn^{2+}(aq) + 2 \, NO_{2}(g) + 2 \, H_{2}O(l) \, \, \, (HNO_{3} \, \text{is a strong acid.}) \\ (4 \, H_{2}O + Mn^{2+} \rightarrow MnO_{4}^{-} + 8 \, H^{+} + 5 \, e^{-}) \times 2 \qquad (2 \, e^{-} + 2 \, H^{+} + IO_{4}^{-} \rightarrow IO_{3}^{-} + H_{2}O) \times 5 \\ 8 \, H_{2}O + 2 \, Mn^{2+} \rightarrow 2 \, MnO_{4}^{-} + 16 \, H^{+} + 10 \, e^{-} \\ 10 \, e^{-} + 10 \, H^{+} + 5 \, IO_{4}^{-} \rightarrow 5 \, IO_{3}^{-} + 5 \, H_{2}O \\ \hline 3 \, H_{2}O(l) + 2 \, Mn^{2+}(aq) + 5 \, IO_{4}^{-}(aq) \rightarrow 2 \, MnO_{4}^{-}(aq) + 5 \, IO_{3}^{-}(aq) + 6 \, H^{+}(aq) \\ \hline 80. \qquad (H_{2}C_{2}O_{4} \rightarrow 2 \, CO_{2} + 2 \, H^{+} + 2 \, e^{-}) \times 5 \qquad (5 \, e^{-} + 8 \, H^{+} + MnO_{4}^{-} \rightarrow Mn^{2+} + 4 \, H_{2}O) \times 2 \\ 5 \, H_{2}C_{2}O_{4} \rightarrow 10 \, CO_{2} + 10 \, H^{+} + 10 \, e^{-} \\ 10 \, e^{-} + 16 \, H^{+} + 2 \, MnO_{4}^{-} \rightarrow 2 \, Mn^{2+} + 8 \, H_{2}O \\ \hline 6 \, H^{+}(aq) + 5 \, H_{2}C_{2}O_{4}(aq) + 2 \, MnO_{4}^{-}(aq) \rightarrow 10 \, CO_{2}(g) + 2 \, Mn^{2+}(aq) + 8 \, H_{2}O(l) \\ \hline 0.1058 \, g \, H_{2}C_{2}O_{4} \times \frac{1 \, mol \, H_{2}C_{2}O_{4}}{90.034 \, g} \times \frac{2 \, mol \, MnO_{4}^{-}}{5 \, mol \, H_{2}C_{2}O_{4}} = 4.700 \times 10^{-4} \, mol \, MnO_{4}^{-} \\ Molarity = \frac{4.700 \times 10^{-4} \, mol \, MnO_{4}^{-}}{28.97 \, mL} \times \frac{1000 \, mL}{L} = 1.622 \times 10^{-2} \, M \, MnO_{4}^{-} \\ \hline \end{array}$$

## **Additional Exercises**

81. Mol of KHP used = 
$$0.4016 \text{ g} \times \frac{1 \text{ mol}}{204.22 \text{ g}} = 1.967 \times 10^{-3} \text{ mol KHP}$$

Because 1 mole of NaOH reacts completely with 1 mole of KHP, the NaOH solution contains  $1.967 \times 10^{-3}$  mol NaOH.

$$\mbox{Molarity of NaOH} = \frac{1.967 \times 10^{-3} \ mol}{25.06 \times 10^{-3} \ L} = \frac{7.849 \times 10^{-2} \ mol \ NaOH}{L}$$

$$\mbox{Maximum molarity} = \frac{1.967 \times 10^{-3} \ mol}{25.01 \times 10^{-3} \ L} = \frac{7.865 \times 10^{-2} \ mol \ NaOH}{L}$$

$$\mbox{Minimum molarity} = \frac{1.967 \times 10^{-3} \ mol}{25.11 \times 10^{-3} \ L} = \frac{7.834 \times 10^{-2} \ mol \ NaOH}{L}$$

We can express this as  $0.07849 \pm 0.00016 \, M$ . An alternate way is to express the molarity as  $0.0785 \pm 0.0002 \, M$ . This second way shows the actual number of significant figures in the molarity. The advantage of the first method is that it shows that we made all our individual measurements to four significant figures.

82. Desired uncertainty is 1% of 0.02, or  $\pm 0.0002$ . So we want the solution to be 0.0200  $\pm$  0.0002 M, or the concentration should be between 0.0198 and 0.0202 M. We should use a 1-L volumetric flask to make the solution. They are good to  $\pm 0.1\%$ . We want to weigh out between 0.0198 mol and 0.0202 mol of KIO<sub>3</sub>.

Molar mass of  $KIO_3 = 39.10 + 126.9 + 3(16.00) = 214.0 \text{ g/mol}$ 

$$0.0198 \text{ mol} \times \frac{214.0 \text{ g}}{\text{mol}} = 4.237 \text{ g}; \ 0.0202 \text{ mol} \times \frac{214.0 \text{ g}}{\text{mol}} = 4.323 \text{ g (carrying extra sig. figs.)}$$

We should weigh out between 4.24 and 4.32 g of  $KIO_3$ . We should weigh it to the nearest milligram or 0.1 mg. Dissolve the  $KIO_3$  in water, and dilute to the mark in a 1-liter volumetric flask. This will produce a solution whose concentration is within the limits and is known to at least the fourth decimal place.

83. 
$$H_2SO_4(aq) + 2 NaOH(aq) \rightarrow Na_2SO_4(aq) + 2 H_2O(1)$$

$$0.02844 \text{ L} \times \frac{0.1000 \text{mol NaOH}}{\text{L}} \times \frac{1 \text{ mol H}_2 \text{SO}_4}{2 \text{ mol NaOH}} \times \frac{1 \text{ mol SO}_2}{\text{mol H}_2 \text{SO}_4} \times \frac{32.07 \text{ g S}}{\text{mol SO}_2}$$

$$= 4.560 \times 10^{-2} \text{ g S}$$

Mass % S = 
$$\frac{0.04560g}{1.325g} \times 100 = 3.442\%$$

84. 
$$3 (NH_4)_2 CrO_4(aq) + 2 Cr(NO_2)_3(aq) \rightarrow 6 NH_4 NO_2(aq) + Cr_2 (CrO_4)_3(s)$$

$$0.203~L \times \frac{0.307\,mol}{L} = 6.23 \times 10^{-2}~mol~(NH_4)_2 CrO_4$$

$$0.137 \text{ L} \times \frac{0.269 \, \text{mol}}{\text{L}} = 3.69 \times 10^{-2} \, \text{mol Cr(NO}_2)_3$$

0.0623 mol/0.0369 mol = 1.69 (actual); the balanced reaction requires a 3/2 = 1.5 to 1 mole ratio between  $(NH_4)_2CrO_4$  and  $Cr(NO_2)_3$ . Actual > required, so  $Cr(NO_2)_3$  (the denominator) is limiting.

$$3.69\times10^{-2}\ mol\ Cr(NO_2)_3\times\ \frac{1\,mol\ Cr_2(CrO_4)_3}{2\,mol\ Cr(NO_2)_3}\times \frac{452.00\,g\ Cr_2(CrO_4)_3}{mol\ Cr_2(CrO_4)_3}=8.34\ g\ Cr_2(CrO_4)_3$$

$$0.880 = \frac{\text{actual yield}}{8.34 \,\text{g}}$$
, actual yield =  $(8.34 \,\text{g})(0.880) = 7.34 \,\text{g Cr}_2(\text{CrO}_4)_3$  isolated

85. a. 
$$MgCl_2(aq) + 2 AgNO_3(aq) \rightarrow 2 AgCl(s) + Mg(NO_3)_2(aq)$$

$$0.641~g~AgCl \times \frac{1\,mol\,AgCl}{143.4~g~AgCl} \times \frac{1\,mol\,MgCl_2}{2\,mol\,AgCl} \times \frac{95.21\,g}{mol\,MgCl_2} = 0.213~g~MgCl_2$$

$$\frac{0.213g \ MgCl_2}{1.50g \ mixture} \times 100 = 14.2\% \ MgCl_2$$

$$b. \quad 0.213 \text{ g MgCl}_2 \times \frac{1 \operatorname{molMgCl}_2}{95.21 \text{ g}} \times \frac{2 \operatorname{molAgNO}_3}{\operatorname{molMgCl}_2} \times \frac{1 L}{0.500 \operatorname{molAgNO}_3} \times \frac{1000 \mathrm{mL}}{1 L} \\ = 8.95 \text{ mL AgNO}_3$$

86. 
$$Al(NO_3)_3(aq) + 3 KOH(aq) \rightarrow Al(OH)_3(s) + 3 KNO_3(aq)$$

$$0.0500 \text{ L} \times \frac{0.200 \, \text{mol Al(NO}_3)_3}{\text{L}} = 0.0100 \, \text{mol Al(NO}_3)_3$$

$$0.2000 \text{ L} \times \frac{0.100 \, \text{mol KOH}}{L} = 0.0200 \, \text{mol KOH}$$

From the balanced equation, 3 moles of KOH are required to react with 1 mole of  $Al(NO_3)_3$  (3 : 1 mole ratio). The actual KOH to  $Al(NO_3)_3$  mole ratio present is 0.0200/0.0100 = 2 (2 : 1). Because the actual mole ratio present is less than the required mole ratio, KOH is the limiting reagent.

$$0.0200 \; mol \; KOH \times \; \frac{1 \; mol \; Al(OH)_3}{3 \; mol \; KOH} \times \; \frac{78.00 \; g \; Al(OH)_3}{mol \; Al(OH)_3} \; = 0.520 \; g \; Al(OH)_3$$

87. 
$$Cr(NO_3)_3(aq) + 3 NaOH(aq) \rightarrow Cr(OH)_3(s) + 3 NaNO_3(aq)$$

$$\label{eq:molNaOH} \begin{aligned} &\text{Mol NaOH used} = 2.06 \text{ g Cr(OH)}_3 \times \frac{1 \, mol\, Cr(OH)_3}{103.02 \, g} \times \frac{3 \, mol\, NaOH}{mol\, Cr(OH)_3} = 6.00 \times 10^{-2} \, mol \, to \, form \, precipitate \end{aligned}$$

$$NaOH(aq) + HCl(aq) \ \rightarrow NaCl(aq) + H_2O(l)$$

$$\label{eq:mol_NaOH} \begin{aligned} &\text{Mol NaOH used} = 0.1000 \ L \times \frac{0.400 \, mol \, HCl}{L} \times \frac{1 \, mol \, NaOH}{mol \, HCl} = \ 4.00 \times 10^{-2} \, mol \, to \, react \, with \, HCl \end{aligned}$$

$$M_{\text{NaOH}} = \frac{\text{totalmol NaOH}}{\text{volume}} = \frac{6.00 \times 10^{-2} \text{ mol} + 4.00 \times 10^{-2} \text{ mol}}{0.0500 \text{L}} = 2.00 M \text{ NaOH}$$

88. a. 
$$Fe^{3+}(aq) + 3 OH^{-}(aq) \rightarrow Fe(OH)_{3}(s)$$

$$Fe(OH)_3$$
:  $55.85 + 3(16.00) + 3(1.008) = 106.87 g/mol$ 

$$0.107 \text{ g Fe(OH)}_3 \times \frac{55.85 \text{ g Fe}}{106.9 \text{ g Fe(OH)}_3} = 0.0559 \text{ g Fe}$$

b.  $Fe(NO_3)_3$ : 55.85 + 3(14.01) + 9(16.00) = 241.86 g/mol

$$0.0559 \text{ g Fe} \times \frac{241.9 \text{ g Fe}(\text{NO}_3)_3}{55.85 \text{ g Fe}} = 0.242 \text{ g Fe}(\text{NO}_3)_3$$

- c. Mass % Fe(NO<sub>3</sub>)<sub>3</sub> =  $\frac{0.242 \,\text{g}}{0.456 \,\text{g}} \times 100 = 53.1\%$
- 89.  $Mol\ CaCl_2\ present = 0.230\ L\ CaCl_2 \times \frac{0.275\,mol\,CaCl_2}{L\ CaCl_2} = 6.33 \times 10^{-2}\ mol\ CaCl_2$

The volume of CaCl<sub>2</sub> solution after evaporation is:

$$6.33 \times 10^{-2} \ mol \ CaCl_2 \times \frac{1 \ L \ CaCl_2}{1.10 \ mol \ CaCl_2} = 5.75 \times 10^{-2} \ L = 57.5 \ mL \ CaCl_2$$

Volume  $H_2O$  evaporated = 230.  $mL - 57.5 mL = 173 mL H_2O$  evaporated

- 90. There are other possible correct choices for the following answers. We have listed only three possible reactants in each case.
  - a. AgNO<sub>3</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, and Hg<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> would form precipitates with the Cl<sup>-</sup> ion.

$$\begin{array}{ll} Ag^+(aq) + Cl^-(aq) & \rightarrow AgCl(s); & Pb^{2+}(aq) + 2 \ Cl^-(aq) & \rightarrow PbCl_2(s) \\ Hg_2^{\ 2+}(aq) + 2 \ Cl^-(aq) & \rightarrow Hg_2Cl_2(s) \end{array}$$

b. Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>3</sub>PO<sub>4</sub> would form precipitates with the Ca<sup>2+</sup> ion.

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s); Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
  
3  $Ca^{2+}(aq) + 2 PO_4^{3-}(aq) \rightarrow Ca_3(PO_4)_2(s)$ 

c. NaOH, Na<sub>2</sub>S, and Na<sub>2</sub>CO<sub>3</sub> would form precipitates with the Fe<sup>3+</sup> ion.

$$Fe^{3+}(aq) + 3 OH^{-}(aq) \rightarrow Fe(OH)_{3}(s); 2 Fe^{3+}(aq) + 3 S^{2-}(aq) \rightarrow Fe_{2}S_{3}(s)$$

$$2\;Fe^{3+}(aq)+3\;CO_3^{\;2-}(aq) \rightarrow Fe_2(CO_3)_3(s)$$

d.  $BaCl_2$ ,  $Pb(NO_3)_2$ , and  $Ca(NO_3)_2$  would form precipitates with the  $SO_4^{\ 2-}$  ion.

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s); Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$$

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s)$$

e. Na<sub>2</sub>SO<sub>4</sub>, NaCl, and NaI would form precipitates with the Hg<sub>2</sub><sup>2+</sup> ion.

$$H{g_2}^{2+}(aq) + S{O_4}^{2-}(aq) \to H{g_2}S{O_4}(s); \ H{g_2}^{2+}(aq) + 2\ Cl^-(aq) \to \ H{g_2}Cl_2(s)$$

$$Hg_2^{2+}(aq) + 2 \Gamma(aq) \to Hg_2I_2(s)$$

f. NaBr, Na<sub>2</sub>CrO<sub>4</sub>, and Na<sub>3</sub>PO<sub>4</sub> would form precipitates with the Ag<sup>+</sup> ion.

$$Ag^{+}(aq) + Br^{-}(aq) \rightarrow AgBr(s); 2 Ag^{+}(aq) + CrO_{4}^{2-}(aq) \rightarrow Ag_{2}CrO_{4}(s)$$
  
 $3 Ag^{+}(aq) + PO_{4}^{3-}(aq) \rightarrow Ag_{3}PO_{4}(s)$ 

91. a. 
$$0.308 \text{ g AgCl} \times \frac{35.45 \text{ g Cl}}{143.4 \text{ g AgCl}} = 0.0761 \text{ g Cl}; \% \text{ Cl} = \frac{0.0761 \text{ g}}{0.256 \text{ g}} \times 100 = 29.7\% \text{ Cl}$$

Cobalt(III) oxide,  $Co_2O_3$ : 2(58.93) + 3(16.00) = 165.86 g/mol

$$0.145 \text{ g Co}_2\text{O}_3 \times \frac{117.86 \text{ g Co}}{165.86 \text{ g Co}_2\text{O}_3} = 0.103 \text{ g Co}; \text{ \% Co} = \frac{0.103 \text{ g}}{0.416 \text{ g}} \times 100 = 24.8\% \text{ Co}$$

The remainder, 100.0 - (29.7 + 24.8) = 45.5%, is water.

Assuming 100.0 g of compound:

$$45.5 \text{ g H}_2\text{O} \times \frac{2.016 \text{ g H}}{18.02 \text{ g H}_2\text{O}} = 5.09 \text{ g H}; \text{ \% H} = \frac{5.09 \text{ g H}}{100.0 \text{ g compound}} \times 100 = 5.09 \text{ M}$$

$$45.5 \text{ g H}_2\text{O} \times \frac{16.00 \text{ g O}}{18.02 \text{ g H}_2\text{O}} = 40.4 \text{ g O}; \text{ \% O} = \frac{40.4 \text{ g O}}{100.0 \text{ g compound}} \times 100 = 40.4 \text{ \% O}$$

The mass percent composition is 24.8% Co, 29.7% Cl, 5.09% H, and 40.4% O.

b. Out of 100.0 g of compound, there are:

$$24.8 \text{ g Co} \times \frac{1 \text{ mol}}{58.93 \text{ g Co}} = 0.421 \text{ mol Co}; \ 29.7 \text{ g Cl} \times \frac{1 \text{ mol}}{35.45 \text{ g Cl}} = 0.838 \text{ mol Cl}$$

$$5.09 \text{ g H} \times \frac{1 \text{ mol}}{1.008 \text{ g H}} = 5.05 \text{ mol H}; \ 40.4 \text{ g O} \times \frac{1 \text{ mol}}{16.00 \text{ g O}} = 2.53 \text{ mol O}$$

Dividing all results by 0.421, we get CoCl<sub>2</sub>•6H<sub>2</sub>O for the empirical formula, which is also the molecular formula.

c. 
$$CoCl_2 \bullet 6H_2O(aq) + 2 AgNO_3(aq) \rightarrow 2 AgCl(s) + Co(NO_3)_2(aq) + 6 H_2O(l)$$

$$CoCl_2 \bullet 6H_2O(aq) + 2 NaOH(aq) \rightarrow Co(OH)_2(s) + 2 NaCl(aq) + 6 H_2O(l)$$

 $Co(OH)_2 \rightarrow Co_2O_3$  This is an oxidation-reduction reaction. Thus we also need to include an oxidizing agent. The obvious choice is  $O_2$ .

$$4 \text{ Co(OH)}_2(s) + O_2(g) \rightarrow 2 \text{ Co}_2O_3(s) + 4 \text{ H}_2O(l)$$

92. a. Assume 100.00 g of material.

$$42.23 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 3.516 \text{ mol C}; 55.66 \text{ g F} \times \frac{1 \text{ mol F}}{19.00 \text{ g F}} = 2.929 \text{ mol F}$$

$$2.11 \text{ g B} \times \frac{1 \text{ mol B}}{10.81 \text{ g B}} = 0.195 \text{ mol B}$$

Dividing by the smallest number: 
$$\frac{3.516}{0.195} = 18.0$$
;  $\frac{2.929}{0.195} = 15.0$ 

The empirical formula is  $C_{18}F_{15}B$ .

b. 
$$0.3470 \text{ L} \times \frac{0.01267 \text{mol}}{\text{L}} = 4.396 \times 10^{-3} \text{ mol BARF}$$

Molar mass of BARF =  $\frac{2.251 \text{g}}{4.396 \times 10^{-3} \text{ mol}} = 512.1 \text{ g/mol}$ 

The empirical formula mass of BARF is 511.99 g. Therefore, the molecular formula is the same as the empirical formula,  $C_{18}F_{15}B$ .

93. 
$$Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$$
; let  $x = mol NaCl and  $y = mol KCl$ .$ 

$$(22.90 \times 10^{-3} \text{ L}) \times 0.1000 \text{ mol/L} = 2.290 \times 10^{-3} \text{ mol Ag}^+ = 2.290 \times 10^{-3} \text{ mol Cl}^- \text{ total}$$
  
 $x + y = 2.290 \times 10^{-3} \text{ mol Cl}^-, \ x = 2.290 \times 10^{-3} - y$ 

Because the molar mass of NaCl is 58.44 g/mol and the molar mass of KCl is 74.55 g/mol:

$$(58.44)x + (74.55)y = 0.1586 g$$

$$58.44(2.290 \times 10^{-3} - y) + (74.55)y = 0.1586, (16.11)y = 0.0248, \ y = 1.54 \times 10^{-3} \text{ mol KCl}$$

Mass % KCl = 
$$\frac{1.54 \times 10^{-3} \text{ mol} \times 74.55 \text{ g/mol}}{0.1586 \text{g}} \times 100 = 72.4\% \text{ KCl}$$

$$\%$$
 NaCl =  $100.0 - 72.4 = 27.6\%$  NaCl

94. Using HA as an abbreviation for the monoprotic acid acetylsalicylic acid:

$$HA(aq) + NaOH(aq) \rightarrow H_2O(1) + NaA(aq)$$

$$Mol~HA = 0.03517~L~NaOH \times \frac{0.5065mol~NaOH}{L~NaOH} \times \frac{1~mol~HA}{mol~NaOH} = 1.781 \times 10^{-2}~mol~HA$$

From the problem, 3.210 g HA was reacted, so:

molar mass = 
$$\frac{3.210 \text{ g HA}}{1.781 \times 10^{-2} \text{ mol HA}} = 180.2 \text{ g/mol}$$

95. 
$$\operatorname{Mol} C_6 H_8 O_7 = 0.250 \text{ g } C_6 H_8 O_7 \times \frac{1 \operatorname{mol} C_6 H_8 O_7}{192.1 \operatorname{g} C_6 H_8 O_7} = 1.30 \times 10^{-3} \operatorname{mol} C_6 H_8 O_7$$

Let  $H_xA$  represent citric acid, where x is the number of acidic hydrogens. The balanced neutralization reaction is:

$$H_xA(aq) + x OH^-(aq) \rightarrow x H_2O(1) + A^{x-}(aq)$$

Mol OH<sup>-</sup> reacted = 
$$0.0372 \text{ L} \times \frac{0.105 \text{ mol OH}^{-}}{\text{L}} = 3.91 \times 10^{-3} \text{ mol OH}^{-}$$

$$x = \frac{\text{molOH}^{-}}{\text{molcitricacid}} = \frac{3.91 \times 10^{-3} \text{ mol}}{1.30 \times 10^{-3} \text{ mol}} = 3.01$$

Therefore, the general acid formula for citric acid is  $H_3A$ , meaning that citric acid has three acidic hydrogens per citric acid molecule (citric acid is a triprotic acid).

### **Challenge Problems**

96. Mol CuSO<sub>4</sub> = 87.6 mL × 
$$\frac{1 \text{ L}}{1000 \text{ mL}}$$
 ×  $\frac{0.500 \text{ mol}}{\text{L}}$  = 0.0439 mol

$$Mol \; Fe = \, 2.00 \, g \, \times \, \frac{1 \, mol \, Fe}{55.85 \, g} \, = 0.0358 \; mol$$

The two possible reactions are:

I. 
$$CuSO_4(aq) + Fe(s) \rightarrow Cu(s) + FeSO_4(aq)$$

II. 
$$3 \text{ CuSO}_4(aq) + 2 \text{ Fe}(s) \rightarrow 3 \text{ Cu}(s) + \text{Fe}_2(SO_4)_3(aq)$$

If reaction I occurs, Fe is limiting, and we can produce:

$$0.0358 \text{ mol Fe} \times \frac{1 \text{ mol Cu}}{1 \text{ mol Fe}} \times \frac{63.55 \text{ g Cu}}{\text{mol Cu}} = 2.28 \text{ g Cu}$$

If reaction II occurs, CuSO<sub>4</sub> is limiting, and we can produce:

$$0.0439 \text{ mol CuSO}_4 \times \frac{3 \text{ mol Cu}}{3 \text{ mol CuSO}_4} \times \frac{63.55 \text{ g Cu}}{\text{mol Cu}} = 2.79 \text{ g Cu}$$

Assuming 100% yield, reaction I occurs because it fits the data best.

97.  $Zn(s) + 2 AgNO_2(aq) \rightarrow 2 Ag(s) + Zn(NO_2)_2(aq)$ 

Let x = mass of Ag and y = mass of Zn after the reaction has stopped. Then x + y = 29.0 g. Because the moles of Ag produced will equal two times the moles of Zn reacted:

$$(19.0 - y) \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.38 \text{ g Zn}} \times \frac{2 \text{ mol Ag}}{1 \text{ mol Zn}} = x \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.9 \text{ g Ag}}$$

Simplifying:

$$3.059 \times 10^{-2}(19.0 - y) = (9.268 \times 10^{-3})x$$

Substituting x = 29.0 - y into the equation gives:

$$3.059 \times 10^{-2}(19.0 - y) = 9.268 \times 10^{-3}(29.0 - y)$$

Solving:

$$0.581 - (3.059 \times 10^{-2})y = 0.269 - (9.268 \times 10^{-3})y$$
,  $(2.132 \times 10^{-2})y = 0.312$ ,  $y = 14.6$  g Zn

14.6 g Zn are present, and 29.0 - 14.6 = 14.4 g Ag are also present after the reaction is stopped.

98. 
$$2(6 e^{-} + 14 H^{+} + Cr_{2}O_{7}^{2-} \rightarrow 2 Cr^{3+} + 7 H_{2}O)$$
$$3 H_{2}O + C_{2}H_{5}OH \rightarrow 2 CO_{2} + 12 H^{+} + 12 e^{-}$$

$$16 \text{ H}^+ + 2 \text{ Cr}_2 \text{O}_7^{2-} + \text{ C}_2 \text{H}_5 \text{OH} \rightarrow 4 \text{ Cr}^{3+} + 2 \text{ CO}_2 + 11 \text{ H}_2 \text{O}$$

$$0.03105 L \left( \frac{0.0600 \text{molCr}_2 \text{O}_7^{2-}}{L} \right) \left( \frac{1 \text{molC}_2 \text{H}_5 \text{OH}}{2 \text{molCr}_2 \text{O}_7^{2-}} \right) \left( \frac{46.07 \text{ g}}{\text{molC}_2 \text{H}_5 \text{OH}} \right) = 0.0429 \text{ g C}_2 \text{H}_5 \text{OH}$$

$$\frac{0.0429 \text{g C}_2 \text{H}_5 \text{OH}}{30.0 \text{ g blood}} \times 100 = 0.143\% \text{ C}_2 \text{H}_5 \text{OH}$$

99. Molar masses: KCl, 39.10 + 35.45 = 74.55 g/mol; KBr, 39.10 + 79.90 = 119.00 g/mol, AgCl, 107.9 + 35.45 = 143.4 g/mol; AgBr, 107.9 + 79.90 = 187.8 g/mol

Let x = number of moles of KCl in mixture and y = number of moles of KBr in mixture. Ag<sup>+</sup> + Cl<sup>-</sup>  $\rightarrow$  AgCl and Ag<sup>+</sup> + Br<sup>-</sup>  $\rightarrow$  AgBr; so, x = moles AgCl and y = moles AgBr.

Setting up two equations from the given information:

$$0.1024 \text{ g} = (74.55)x + (119.0)y \text{ and } 0.1889 \text{ g} = (143.4)x + (187.8)y$$

Multiply the first equation by  $\frac{187.8}{119.0}$ , and then subtract from the second.

$$0.1889 = (143.4)x + (187.8)y$$

$$-0.1616 = -(117.7)x - (187.8)y$$

$$0.0273 = (25.7)x, x = 1.06 \times 10^{-3} \text{ mol KCl}$$

$$1.06 \times 10^{-3} \text{ mol KCl} \times \frac{74.55 \text{g KCl}}{\text{mol KCl}} = 0.0790 \text{ g KCl}$$

Mass % KCl = 
$$\frac{0.0790g}{0.1024g} \times 100 = 77.1\%$$
, % KBr =  $100.0 - 77.1 = 22.9\%$ 

100. Let 
$$x = \text{mass of NaCl}$$
, and let  $y = \text{mass } K_2SO_4$ . So  $x + y = 10.00$ .

Two reactions occur: 
$$Pb^{2+}(aq) + 2 Cl^{-}(aq) \rightarrow PbCl_2(s)$$
 and  $Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$ 

Molar mass of NaCl = 58.44 g/mol; molar mass of  $K_2SO_4$  = 174.27 g/mol; molar mass of  $PbCl_2$  = 278.1 g/mol; molar mass of  $PbSO_4$  = 303.3 g/mol

$$\frac{x}{58.44}$$
 = moles NaCl;  $\frac{y}{174.27}$  = moles K<sub>2</sub>SO<sub>4</sub>

mass of PbCl<sub>2</sub> + mass PbSO<sub>4</sub> = total mass of solid 
$$\frac{x}{5844}(1/2)(278.1) + \frac{y}{17427}(303.3) = 21.75$$

We have two equations:

$$(2.379)x + (1.740)y = 21.75$$
 and  $x + y = 10.00$ . Solving:

$$x = 6.81 \text{ g NaCl}; \frac{6.81 \text{ g NaCl}}{10.00 \text{ g mixture}} \times 100 = 68.1\% \text{ NaCl}$$

101. a. Flow rate = 
$$5.00 \times 10^4 \text{ L/s} + 3.50 \times 10^3 \text{ L/s} = 5.35 \times 10^4 \text{ L/s}$$

b. 
$$C_{HCl} = \frac{3.50 \times 10^3 (65.0)}{5.35 \times 10^4} = 4.25 \text{ ppm HCl}$$

c. 1 ppm = 1 mg/kg  $H_2O = 1$  mg/L (assuming density = 1.00 g/mL)

$$8.00 \text{ h} \times \frac{60 \text{ min}}{\text{h}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{1.80 \times 10^4 \text{ L}}{\text{s}} \times \frac{4.25 \text{ mg HCl}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{mg}} = 2.20 \times 10^6 \text{ g HCl}$$

$$2.20 \times 10^6 \text{ g HCl} \times \frac{1 \text{ molHCl}}{36.46 \text{ g HCl}} \times \frac{1 \text{ molCaO}}{2 \text{ molHCl}} \times \frac{56.08 \text{ g Ca}}{\text{molCaO}} = 1.69 \times 10^6 \text{ g CaO}$$

d. The concentration of Ca<sup>2+</sup> going into the second plant was:

$$\frac{5.00 \times 10^4 (10.2)}{5.35 \times 10^4} = 9.53 \text{ ppm}$$

The second plant used:  $1.80 \times 10^4$  L/s  $\times$  ( $8.00 \times 60 \times 60$ ) s =  $5.18 \times 10^8$  L of water.

$$1.69 \times 10^6 \ g \ CaO \ \times \ \frac{40.08 \ g \ Ca^{2+}}{56.08 \ g \ CaO} = 1.21 \times 10^6 \ g \ Ca^{2+} \ was \ added \ to \ this \ water.$$

$$C_{Ca^{2+}}$$
 (plant water) = 9.53 +  $\frac{1.21 \times 10^9 \text{ mg}}{5.18 \times 10^8 \text{ L}}$  = 9.53 + 2.34 = 11.87 ppm

Because 90.0% of this water is returned,  $(1.80 \times 10^4) \times 0.900 = 1.62 \times 10^4$  L/s of water with 11.87 ppm Ca<sup>2+</sup> is mixed with  $(5.35 - 1.80) \times 10^4 = 3.55 \times 10^4$  L/s of water containing 9.53 ppm Ca<sup>2+</sup>.

$$C_{\text{Ca}^{2+}}(\text{final}) = \ \frac{(1.62 \times 10^4 \ \text{L/s})(11.87 \ \text{ppm}) \ + \ (3.55 \times 10^4 \ \text{L/s})(9.53 \ \text{ppm})}{1.62 \times 10^4 \ \text{L/s} \ + \ 3.55 \times 10^4 \ \text{L/s}} = 10.3 \ \text{ppm}$$

102.  $0.2750 \text{ L} \times 0.300 \text{ mol/L} = 0.0825 \text{ mol H}^+$ ; let y = volume (L) delivered by Y and z = volume (L) delivered by Z.

$$H^{+}(aq) + OH^{-}(aq) \rightarrow H_{2}O(1); \underbrace{y(0.150 \text{ mol/L}) + z(0.250 \text{ mol/L})}_{\text{mol OH}^{-}} = 0.0825 \text{ mol H}^{+}$$

$$0.2750 L + y + z = 0.655 L$$
,  $y + z = 0.380$ ,  $z = 0.380 - y$ 

$$y(0.150) + (0.380 - y)(0.250) = 0.0825$$
, solving:  $y = 0.125$  L,  $z = 0.255$  L

Flow rate for 
$$Y = \frac{125 \text{ mL}}{60.65 \text{ min}} = 2.06 \text{ mL/min}$$
; flow rate for  $Z = \frac{255 \text{ mL}}{60.65 \text{ min}} = 4.20 \text{ mL/min}$ 

103. a. Let x = mass of Mg, so 10.00 - x = mass of Zn. Ag<sup>+</sup>(aq) + Cl<sup>-</sup>(aq)  $\rightarrow$  AgCl(s).

From the given balanced equations, there is a 2:1 mole ratio between mol Mg and mol  $Cl^-$ . The same is true for Zn. Because mol  $Ag^+ = mol \ Cl^-$  present, one can setup an equation relating mol  $Cl^-$  present to mol  $Ag^+$  added.

$$x \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} \times \frac{2 \text{ mol Cl}^{-}}{\text{mol Mg}} + (10.00 - x) \text{ g Zn} \times \frac{1 \text{ mol Zn}}{65.38 \text{ g Zn}} \times \frac{2 \text{ mol Cl}^{-}}{\text{mol Zn}}$$

$$= 0.156 \text{ L} \times \frac{3.00 \text{ mol Ag}^{+}}{\text{L}} \times \frac{1 \text{ mol Cl}^{-}}{\text{mol Ag}^{+}} = 0.468 \text{ mol Cl}^{-}$$

$$\frac{2x}{24.31} + \frac{2(10.00 - x)}{65.38} = 0.468, \ 24.31 \times 65.38 \left( \frac{2x}{24.31} + \frac{20.00 - 2x}{65.38} = 0.468 \right)$$

(130.8)x + 486.2 - (48.62)x = 743.8 (carrying 1 extra significant figure)

$$(82.2)x = 257.6$$
,  $x = 3.13$  g Mg; % Mg =  $\frac{3.13$  g Mg}{10.00 g mixture  $\times 100 = 31.3$ % Mg

b. 
$$0.156 \text{ L} \times \frac{3.00 \, \text{mol Ag}^+}{\text{L}} \times \frac{1 \, \text{mol Cl}^-}{\text{mol Ag}^+} = 0.468 \, \text{mol Cl}^- = 0.468 \, \text{mol HCl added}$$

$$M_{\text{HCl}} = \frac{0.468 \text{mol}}{0.0780 \text{L}} = 6.00 \, M \, \text{HCl}$$

104. 
$$Pb^{2+}(aq) + 2 Cl^{-}(aq) \rightarrow PbCl_{2}(s)$$

$$3.407 \text{ g PbCl}_2 \times \frac{1 \, \text{molPbCl}_2}{278.1 \, \text{g PbCl}_2} \times \frac{1 \, \text{molPbCl}_2}{\text{molPbCl}_2} = 0.01225 \, \text{mol Pb}^{2+}$$

$$\frac{0.01225 \text{mol}}{2.00 \times 10^{-3} \text{ L}} = 6.13 \text{ M Pb}^{2+} = 6.13 \text{ M Pb}(\text{NO}_3)_2$$

This is also the Pb(NO<sub>3</sub>)<sub>2</sub> concentration in the 80.0 mL of evaporated solution.

Original concentration = 
$$\frac{\text{moles Pb(NO}_3)_2}{\text{original volume}} = \frac{0.0800\text{L} \times 6.13\,\text{mol/L}}{0.1000\text{L}} = 4.90\,M\,\text{Pb(NO}_3)_2$$

105. a. 
$$C_{12}H_{10-n}Cl_n + n Ag^+ \rightarrow n AgCl$$
; molar mass of AgCl = 143.4 g/mol

Molar mass of PCB = 
$$12(12.01) + (10 - n)(1.008) + n(35.45) = 154.20 + (34.44)n$$

Because n mol AgCl are produced for every 1 mol PCB reacted, n(143.4) g of AgCl will be produced for every [154.20 + (34.44)n] g of PCB reacted.

$$\frac{\text{Mass of AgCl}}{\text{Mass of PCB}} = \frac{(143.4)n}{154.20 + (34.44)n} \text{ or } \text{mass}_{\text{AgCl}}[154.20 + (34.44)n] = \text{mass}_{\text{PCB}}(143.4)n$$

b. 
$$0.4971[154.20 + (34.44)n] = 0.1947(143.4)n$$
,  $76.65 + (17.12)n = (27.92)n$ 

$$76.65 = (10.80)n, n = 7.097$$

106. Mol BaSO<sub>4</sub> = 0.2327 g × 
$$\frac{1 \text{ mol}}{233.4 \text{ g}}$$
 = 9.970 × 10<sup>-4</sup> mol BaSO<sub>4</sub>

The moles of the sulfate salt depends on the formula of the salt. The general equation is:

$$M_x(SO_4)_v(aq) + y Ba^{2+}(aq) \rightarrow y BaSO_4(s) + x M^{z+}$$

Depending on the value of y, the mole ratio between the unknown sulfate salt and BaSO<sub>4</sub> varies. For example, if Pat thinks the formula is TiSO<sub>4</sub>, the equation becomes:

$$TiSO_4(aq) + Ba^{2+}(aq) \ \rightarrow \ BaSO_4(s) + Ti^{2+}(aq)$$

Because there is a 1 : 1 mole ratio between mol BaSO<sub>4</sub> and mol TiSO<sub>4</sub>, you need  $9.970 \times 10^{-4}$  mol of TiSO<sub>4</sub>. Because 0.1472 g of salt was used, the compound would have a molar mass of (assuming the TiSO<sub>4</sub> formula):

$$0.1472 \text{ g/9.970} \times 10^{-4} \text{ mol} = 147.6 \text{ g/mol}$$

From atomic masses in the periodic table, the molar mass of TiSO<sub>4</sub> is 143.95 g/mol. From just these data, TiSO<sub>4</sub> seems reasonable.

Chris thinks the salt is sodium sulfate, which would have the formula Na<sub>2</sub>SO<sub>4</sub>. The equation is:

$$Na_2SO_4(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s) + 2 Na^+(aq)$$

As with TiSO<sub>4</sub>, there is a 1:1 mole ratio between mol BaSO<sub>4</sub> and mol Na<sub>2</sub>SO<sub>4</sub>. For sodium sulfate to be a reasonable choice, it must have a molar mass of about 147.6 g/mol. Using atomic masses, the molar mass of Na<sub>2</sub>SO<sub>4</sub> is 142.05 g/mol. Thus Na<sub>2</sub>SO<sub>4</sub> is also reasonable.

Randy, who chose gallium, deduces that gallium should have a 3+ charge (because it is in column 3A), and the formula of the sulfate would be  $Ga_2(SO_4)_3$ . The equation would be:

$$Ga_2(SO_4)_3(aq) + 3 Ba^{2+}(aq) \rightarrow 3 BaSO_4(s) + 2 Ga^{3+}(aq)$$

The calculated molar mass of  $Ga_2(SO_4)_3$  would be:

$$\frac{0.1472 \, \text{Ga}_{\,2}(\text{SO}_{\,4})_{3}}{9.970 \times 10^{-4} \, \text{mol} \, \text{BaSO}_{\,4}} \times \frac{3 \, \text{mol} \, \text{BaSO}_{\,4}}{\text{mol} \, \text{Ga}_{\,2}(\text{SO}_{\,4})_{3}} = 442.9 \, \, \text{g/mol}$$

Using atomic masses, the molar mass of  $Ga_2(SO_4)_3$  is 427.65 g/mol. Thus  $Ga_2(SO_4)_3$  is also reasonable.

Looking in references, sodium sulfate  $(Na_2SO_4)$  exists as a white solid with orthorhombic crystals, whereas gallium sulfate  $Ga_2(SO_4)_3$  is a white powder. Titanium sulfate exists as a green powder, but its formula is  $Ti_2(SO_4)_3$ . Because this has the same formula as gallium sulfate, the calculated molar mass should be around 443 g/mol. However, the molar mass of  $Ti_2(SO_4)_3$  is 383.97 g/mol. It is unlikely, then, that the salt is titanium sulfate.

To distinguish between  $Na_2SO_4$  and  $Ga_2(SO_4)_3$ , one could dissolve the sulfate salt in water and add NaOH.  $Ga^{3+}$  would form a precipitate with the hydroxide, whereas  $Na_2SO_4$  would not. References confirm that gallium hydroxide is insoluble in water.

107. There are three unknowns so we need three equations to solve for the unknowns. Let  $x = \max \text{ AgNO}_3$ ,  $y = \max \text{ CuCl}_2$ , and  $z = \max \text{ FeCl}_3$ . Then x + y + z = 1.0000 g. The Cl<sup>-</sup> in CuCl<sub>2</sub> and FeCl<sub>3</sub> will react with the excess AgNO<sub>3</sub> to form the precipitate AgCl(s). Assuming silver has an atomic mass of 107.90:

Mass of Cl in mixture = 1.7809 g AgCl × 
$$\frac{35.45 \text{ g Cl}}{143.35 \text{ g AgCl}}$$
 = 0.4404 g Cl

Mass of Cl from 
$$CuCl_2 = y$$
 g  $CuCl_2 \times \frac{2(35.45) \text{ g Cl}}{134.45 \text{ g CuCl}_2} = (0.5273)y$ 

Mass of Cl from FeCl<sub>3</sub> = 
$$z$$
 g FeCl<sub>3</sub> ×  $\frac{3(35.45) \text{ g Cl}}{162.20 \text{ g FeCl}_3}$  =  $(0.6557)z$ 

The second equation is: 0.4404 g Cl = (0.5273)y + (0.6557)z

Similarly, let's calculate the mass of metals in each salt.

Mass of Ag in AgNO<sub>3</sub> = 
$$x$$
 g AgNO<sub>3</sub> ×  $\frac{107.9 \text{ g Ag}}{169.91 \text{ g AgNO}_3}$  =  $(0.6350)x$ 

For CuCl<sub>2</sub> and FeCl<sub>3</sub>, we already calculated the amount of Cl in each initial amount of salt; the remainder must be the mass of metal in each salt.

Mass of Cu in 
$$CuCl_2 = y - (0.5273)y = (0.4727)y$$

Mass of Fe in FeCl<sub>3</sub> = 
$$z - (0.6557)z = (0.3443)z$$

The third equation is: 0.4684 g metals = (0.6350)x + (0.4727)y + (0.3443)z

We now have three equations with three unknowns. Solving:

$$-0.6350 (1.0000 = x + y + z)$$

$$0.4684 = (0.6350)x + (0.4727)y + (0.3443)z$$

$$-0.1666 = -(0.1623)y - (0.2907)z$$

$$\frac{0.5273}{0.1623}[-0.1666 = -(0.1623)y - (0.2907)z]$$

$$0.4404 = (0.5273)y + (0.6557)z$$

$$-0.1009 = -(0.2888)z, z = \frac{0.1009}{0.2888} = 0.3494 \text{ g FeCl}_3$$

$$0.4404 = (0.5273)y + 0.6557(0.3494), y = 0.4007 \text{ g CuCl}_2$$

$$x = 1.0000 - y - z = 1.0000 - 0.4007 - 0.3494 = 0.2499 \text{ g AgNO}_3$$

Mass % 
$$AgNO_3 = \frac{0.2499g}{1.0000g} \times 100 = 24.99\% \ AgNO_3$$

Mass % 
$$CuCl_2 = \frac{0.4007g}{1.0000g} \times 100 = 40.07\% \ CuCl_2$$
; mass %  $FeCl_3 = 34.94\%$ 

108. a. 
$$7 \text{ H}_2\text{O} + 2 \text{ Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 14 \text{ H}^+ + 6 \text{ e}^-$$
$$(2 \text{ e}^- + \text{S}_2\text{O}_8^{2-} \rightarrow 2 \text{ SO}_4^{2-}) \times 3$$

$$\frac{}{7 \text{ H}_2\text{O}(1) + 2 \text{ Cr}^{3+}(\text{aq}) + 3 \text{ S}_2\text{O}_8^{2-}(\text{aq}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{ H}^+(\text{aq}) + 6 \text{ SO}_4^{2-}(\text{aq})}$$

$$(Fe^{2+} \to Fe^{3+} + e^{-}) \times 6$$
 6  $e^{-}$  + 14  $H^{+}$  +  $Cr_{2}O_{7}^{2-}$   $\to$  2  $Cr^{3+}$  + 7  $H_{2}O$ 

$$\frac{14 \text{ H}^{+}(\text{aq}) + 6 \text{ Fe}^{2+}(\text{aq}) + \text{Cr}_{2}\text{O}_{7}^{2-}(\text{aq}) \rightarrow 2 \text{ Cr}^{3+}(\text{aq}) + 6 \text{ Fe}^{3+}(\text{aq}) + 7 \text{ H}_{2}\text{O}(1)}{14 \text{ H}^{+}(\text{aq}) + 6 \text{ Fe}^{2+}(\text{aq}) + 7 \text{ H}_{2}\text{O}(1)}$$

b. 
$$8.58 \times 10^{-3} \text{ L} \times \frac{0.0520 \text{mol} \text{Cr}_2 \text{O}_7^{2-}}{\text{L}} \times \frac{6 \text{ mol} \text{Fe}^{2+}}{\text{mol} \text{Cr}_2 \text{O}_7^{2-}} = 2.68 \times 10^{-3} \text{ mol of excess Fe}^{2+}$$

$$Fe^{2+} \text{ (total)} = 3.000 \text{ g Fe}(NH_4)_2 (SO_4)_2 \bullet 6H_2O \times \frac{1 \text{ mol}}{392.17 \text{ g}} = 7.650 \times 10^{-3} \text{ mol Fe}^{2+}$$

 $7.650\times10^{-3}-2.68\times10^{-3}$  =  $4.97\times10^{-3}$  mol  $Fe^{2+}$  reacted with  $Cr_2O_7^{\ 2-}$  generated from the Cr plating.

The Cr plating contained:

$$4.97 \times 10^{-3} \text{ mol Fe}^{2+} \times \frac{1 \, \text{mol} \, \text{Cr}_2 \text{O}_7^{2-}}{6 \, \text{mol} \, \text{Fe}^{2+}} \times \frac{2 \, \text{mol} \, \text{Cr}^{3+}}{\text{mol} \, \text{Cr}_2 \text{O}_7^{2-}} = 1.66 \times 10^{-3} \, \text{mol} \, \text{Cr}^{3+}$$
 
$$= 1.66 \times 10^{-3} \, \text{mol} \, \text{Cr}$$

$$1.66 \times 10^{-3} \text{ mol Cr} \times \frac{52.00 \text{ g Cr}}{\text{mol Cr}} = 8.63 \times 10^{-2} \text{ g Cr}$$

Volume of Cr plating = 
$$8.63 \times 10^{-2}$$
 g  $\times \frac{1 \text{ cm}^3}{7.19 \text{ g}} = 1.20 \times 10^{-2}$  cm<sup>3</sup> = area × thickness

Thickness of Cr plating = 
$$\frac{1.20 \times 10^{-2} \text{ cm}^3}{40.0 \text{ cm}^2} = 3.00 \times 10^{-4} \text{ cm} = 300. \ \mu\text{m}$$

109. a.  $YBa_2Cu_3O_{6.5}$ :

$$+3 + 2(+2) + 3x + 6.5(-2) = 0$$

$$7 + 3x - 13 = 0$$
,  $3x = 6$ ,  $x = +2$  Only Cu<sup>2+</sup> present.

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>:

$$+3 + 2(+2) + 3x + 7(-2) = 0$$
,  $x = +2.1/3$  or 2.33

This corresponds to two Cu<sup>2+</sup> and one Cu<sup>3+</sup> present.

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>8</sub>:

$$+3 + 2(+2) + 3x + 8(-2) = 0$$
,  $x = +3$ ; Only Cu<sup>3+</sup> present.

b. 
$$(e^{-} + Cu^{2+} + \Gamma \to CuI) \times 2$$
  $2 e^{-} + Cu^{3+} + \Gamma \to CuI$   $3\Gamma \to I_3^{-} + 2 e^{-}$   $3\Gamma \to I_3^{-} + 2 e^{-}$   $2 Cu^{2+}(aq) + 5 \Gamma(aq) \to 2 CuI(s) + I_3^{-}(aq)$   $Cu^{3+}(aq) + 4 \Gamma(aq) \to CuI(s) + I_3^{-}(aq)$   $2 S_2O_3^{2-} \to S_4O_6^{2-} + 2 e^{-}$   $2 e^{-} + I_3^{-} \to 3 \Gamma$   $2 S_2O_3^{2-}(aq) + I_3^{-}(aq) \to 3 \Gamma(aq) + S_4O_6^{2-}(aq)$ 

c. Step II data: All Cu is converted to Cu<sup>2+</sup>. *Note*: Superconductor abbreviated as "123."

$$22.57 \times 10^{-3} \text{ L} \times \frac{0.1000 \text{molS}_2 \text{O}_3^{2^-}}{\text{L}} \times \frac{1 \, \text{molI}_3^-}{2 \, \text{molS}_2 \text{O}_3^{2^-}} \times \frac{2 \, \text{molCu}^{2^+}}{\text{molI}_3^-} \\ = 2.257 \times 10^{-3} \, \text{mol Cu}^{2^+}$$

$$2.257 \times 10^{-3} \text{ mol Cu} \times \frac{1 \text{ mol "}123"}{3 \text{ mol Cu}} = 7.523 \times 10^{-4} \text{ mol "}123"$$

Molar mass of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> = 
$$\frac{0.5402g}{7.523 \times 10^{-4} \text{ mol}} = 670.2 \text{ g/mol}$$

$$670.2 = 88.91 + 2(137.3) + 3(63.55) + x(16.00), 670.2 = 554.2 + x(16.00)$$

x = 7.250; formula is YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.25</sub>.

Check with Step I data: Both Cu<sup>2+</sup> and Cu<sup>3+</sup> present.

$$37.77 \times 10^{-3} \text{ L} \times \frac{0.1000 \text{mol} S_2 O_3^{2^-}}{\text{L}} \times \frac{1 \, \text{mol} \, I_3^{--}}{2 \, \text{mol} \, S_2 O_3^{2^-}} = 1.889 \times 10^{-3} \, \text{mol} \, \, I_3^{--}$$

We get 1 mol  $I_3^-$  per mol  $Cu^{3+}$  and 1 mol  $I_3^-$  per 2 mol  $Cu^{2+}$ . Let  $n_{Cu^{3+}} = \text{mol } Cu^{3+}$  and  $n_{Cu^{2+}} = \text{mol } Cu^{2+}$ , then:

$$n_{\text{Cu}^{3+}} + \frac{n_{\text{Cu}^{2+}}}{2} = 1.889 \times 10^{-3} \text{ mol}$$

In addition:  $\frac{0.5625 \text{g}}{670.2 \text{ g/mol}} = 8.393 \times 10^{-4} \text{ mol "123"}$ ; this amount of "123" contains:  $3(8.393 \times 10^{-4}) = 2.518 \times 10^{-3} \text{ mol Cu total} = n_{\text{Cu}^{3+}} + n_{\text{Cu}^{2+}}$ 

Solving by simultaneous equations:

$$n_{\text{Cu}^{3+}} + n_{\text{Cu}^{2+}} = 2.518 \times 10^{-3}$$
$$-n_{\text{Cu}^{3+}} - \frac{n_{\text{Cu}^{2+}}}{2} = -1.889 \times 10^{-3}$$
$$\frac{n_{\text{Cu}^{2+}}}{2} = 6.29 \times 10^{-4}$$

$$n_{\mathrm{Cu}^{2+}}^{} = 1.26 \times 10^{-3} \; \mathrm{mol} \; \mathrm{Cu}^{2+}; \; \; n_{\mathrm{Cu}^{3+}}^{} = 2.518 \times 10^{-3} - 1.26 \times 10^{-3} = 1.26 \; \times 10^{-3} \; \mathrm{mol} \; \mathrm{Cu}^{3+}$$

This sample of superconductor contains equal moles of  $Cu^{2+}$  and  $Cu^{3+}$ . Therefore, 1 mole of  $YBa_2Cu_3O_x$  contains 1.50 mol  $Cu^{2+}$  and 1.50 mol  $Cu^{3+}$ . Solving for x using oxidation states:

$$+3 + 2(+2) + 1.50(+2) + 1.50(+3) + x(-2) = 0$$
,  $14.50 = 2x$ ,  $x = 7.25$ 

The two experiments give the same result, x = 7.25 with formula YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.25</sub>.

Average oxidation state of Cu:

$$+3 + 2(+2) + 3(x) + 7.25(-2) = 0$$
,  $3x = 7.50$ ,  $x = +2.50$ 

As determined from Step I data, this superconductor sample contains equal moles of Cu<sup>2+</sup> and Cu<sup>3+</sup>, giving an average oxidation state of +2.50.

110. 0.298 g BaSO<sub>4</sub> × 
$$\frac{96.07 \text{ g SO}_4^{2^-}}{233.4 \text{ g BaSO}_4} = 0.123 \text{ g SO}_4^{2^-}$$
; % sulfate =  $\frac{0.123 \text{ g SO}_4^{2^-}}{0.205 \text{ g}} = 60.0\%$ 

Assume we have 100.0 g of the mixture of Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>. There are:

$$60.0 \text{ g SO}_4^{2-} \times \frac{1 \text{ mol}}{96.07 \text{ g}} = 0.625 \text{ mol SO}_4^{2-}$$

There must be  $2 \times 0.625 = 1.25$  mol of 1+ cations to balance the 2- charge of  $SO_4^{2-}$ .

Let x = number of moles of  $K^+$  and y = number of moles of  $Na^+$ ; then x + y = 1.25.

The total mass of  $Na^+$  and  $K^+$  must be 40.0 g in the assumed 100.0 g of mixture. Setting up an equation:

$$x \text{ mol } K^+ \times \frac{39.10 \,\mathrm{g}}{\mathrm{mol}} + y \text{ mol } \mathrm{Na}^+ \times \frac{22.99 \,\mathrm{g}}{\mathrm{mol}} = 40.0 \,\mathrm{g}$$

So, we have two equations with two unknowns: x + y = 1.25 and (39.10)x + (22.99)y = 40.0

$$x = 1.25 - y$$
, so  $39.10(1.25 - y) + (22.99)y = 40.0$ 

$$48.9 - (39.10)v + (22.99)v = 40.0$$
,  $-(16.11)v = -8.9$ 

$$y = 0.55 \text{ mol Na}^+ \text{ and } x = 1.25 - 0.55 = 0.70 \text{ mol K}^+$$

Therefore:

$$0.70 \text{ mol } K^{\scriptscriptstyle +} \times \ \frac{1 \, mol \, K_2 SO_4}{2 \, mol \, K^{\scriptscriptstyle +}} = 0.35 \, mol \, K_2 SO_4; \\ 0.35 \, mol \, K_2 SO_4 \times \frac{174.27 \, g}{mol} \\ = 61 \, g \, K_2 SO_4$$

We assumed 100.0 g; therefore, the mixture is 61% K<sub>2</sub>SO<sub>4</sub> and 39% Na<sub>2</sub>SO<sub>4</sub>.

## **Marathon Problems**

111. 
$$M(CHO_2)_2(aq) + Na_2SO_4(aq) \rightarrow MSO_4(s) + 2 NaCHO_2(aq)$$

From the balanced molecular equation, the moles of  $M(CHO_2)_2$  present initially must equal the moles of  $MSO_4(s)$  formed. Because moles = mass/molar mass and letting  $A_M$  = the atomic mass of M:

$$mol\ MSO_4 = \frac{mass\ MSO_4}{molar\ mass\ of\ MSO_4} = \frac{9.9392g}{A_M + 96.07}$$

mol M(CHO<sub>2</sub>)<sub>2</sub> = 
$$\frac{\text{mass M(CHO}_2)_2}{\text{molar mass of M(CHO}_2)_2} = \frac{9.7416\text{g}}{\text{A}_M + 90.04}$$

Because mol  $MSO_4 = mol M(CHO_2)_2$ :

$$\frac{9.9392}{A_M + 96.07} = \frac{9.7416}{A_M + 90.04}, (9.9392)A_M + 894.9 = (9.7416)A_M + 935.9$$

$$A_{\rm M} = \frac{41.0}{0.1976} = 207$$
; from the periodic table, the unknown element M is Pb.

From the information in the second paragraph, we can determine the concentration of the  $KMnO_4$  solution. Using the half-reaction method, the balanced reaction between  $MnO_4^-$  and  $C_2O_4^{-2-}$  is:

$$5~C_2O_4^{~2-}(aq) + 2~MnO_4^{~-}(aq) + 16~H^+(aq) \rightarrow 10~CO_2(g) + 2~Mn^{2+}(aq) + 8~H_2O(l)$$

$$Mol\ MnO_4^- = 0.9234\ g\ Na_2C_2O_4 \times \frac{1\ mol\ Na_2C_2O_4}{134.00\ g} \times \frac{1\ mol\ C_2O_4^{2-}}{1\ mol\ Na_2C_2O_4} \times \frac{2\ mol\ MnO_4^{--}}{5\ mol\ C_2O_4^{2--}}$$

$$= 2.756 \times 10^{-3} \text{ mol MnO}_4^{-1}$$

$$M_{\text{KMnO}_4} = M_{\text{MnO}_4^-} = \frac{\text{mol MnO}_4^-}{\text{volume}} = \frac{2.756 \times 10^{-3} \text{ mol}}{0.01855 \text{L}} = 0.1486 \text{ mol/L}$$

From the third paragraph, the standard  $KMnO_4$  solution reacts with formate ions from the filtrate. We must determine the moles of  $CHO_2^-$  ions present in order to determine volume of  $KMnO_4$  solution. The moles of  $CHO_2^-$  ions present initially are:

$$9.7416 \text{ g Pb(CHO}_2)_2 \times \frac{\text{molPb(CHO}_2)_2}{297.2 \text{ g}} \times \frac{2 \text{ molCHO}_2^{-}}{1 \text{ molPb(CHO}_2)_2} = 6.556 \times 10^{-2} \text{ mol CHO}_2^{-}$$

The moles of CHO<sub>2</sub> present in 10.00 mL of diluted solution are:

$$0.01000~L \times \frac{6.556 \times 10^{-2}~molCHO_2^{-}}{0.2500L} = 2.622 \times 10^{-3}~mol~CHO_2^{-}$$

Using the half-reaction method in basic solution, the balanced reaction between  $CHO_2^-$  and  $MnO_4^-$  is:

$$3 \text{ CHO}_2^-(aq) + 2 \text{ MnO}_4^-(aq) + \text{OH}^-(aq) \rightarrow 3 \text{ CO}_3^{2-}(aq) + 2 \text{ MnO}_2(s) + 2 \text{ H}_2\text{O}(1)$$

Determining the volume of MnO<sub>4</sub><sup>-</sup> solution:

$$2.622 \times 10^{-3} \text{ mol CHO}_{2}^{-} \times \frac{2 \text{ mol MnO}_{4}^{-}}{3 \text{ mol CHO}_{2}^{-}} \times \frac{1 \text{ L}}{0.1486 \text{ mol MnO}_{4}^{-}} = 1.176 \times 10^{-2} \text{ L}$$

$$= 11.76 \text{ mL}$$

The titration requires 11.76 mL of the standard KMnO<sub>4</sub> solution.

112. a. Compound A = M(NO<sub>3</sub>)<sub>x</sub>; in 100.00 g of compd.: 8.246 g N × 
$$\frac{48.00 \text{ g O}}{14.01 \text{ g N}}$$
 = 28.25 g O

Thus the mass of nitrate in the compound = 8.246 + 28.25 g = 36.50 g (if x = 1).

If 
$$x = 1$$
: mass of M =  $100.00 - 36.50$  g =  $63.50$  g

Mol M = mol N = 
$$\frac{8.246g}{14.01g/mol}$$
 = 0.5886 mol

Molar mass of metal M = 
$$\frac{63.50 \, \text{g}}{0.5886 \text{mol}}$$
 = 107.9 g/mol (This is silver, Ag.)

If 
$$x = 2$$
: mass of M =  $100.00 - 2(36.50) = 27.00$  g

Mol M = 
$$\frac{1}{2}$$
 mol N =  $\frac{0.5886$ mol  $2$  = 0.2943 mol

Molar mass of metal M = 
$$\frac{27.00 \text{ g}}{0.2943 \text{mol}} = 91.74 \text{ g/mol}$$

This is close to Zr, but Zr does not form stable 2+ ions in solution; it forms stable 4+ ions. Because we cannot have x=3 or more nitrates (three nitrates would have a mass greater than 100.00 g), compound A must be AgNO<sub>3</sub>.

Compound B:  $K_2CrO_x$  is the formula. This salt is composed of  $K^+$  and  $CrO_x^{2-}$  ions. Using oxidation states, 6 + x(-2) = -2, x = 4. Compound B is  $K_2CrO_4$  (potassium chromate).

b. The reaction is:

$$2 \text{ AgNO}_3(aq) + \text{K}_2\text{CrO}_4(aq) \rightarrow \text{Ag}_2\text{CrO}_4(s) + 2 \text{ KNO}_3(aq)$$

The blood red precipitate is  $Ag_2CrO_4(s)$ .

c. 331.8 g Ag<sub>2</sub>CrO<sub>4</sub> formed; this is equal to the molar mass of Ag<sub>2</sub>CrO<sub>4</sub>, so 1 mole of precipitate formed. From the balanced reaction, we need 2 mol AgNO<sub>3</sub> to react with 1 mol K<sub>2</sub>CrO<sub>4</sub> to produce 1 mol (331.8 g) of Ag<sub>2</sub>CrO<sub>4</sub>.

$$2.000 \text{ mol AgNO}_3 \times \frac{169.9 \text{ g}}{\text{mol}} = 339.8 \text{ g AgNO}_3$$

$$1.000 \text{ mol } K_2CrO_4 \times \frac{194.2 \text{ g}}{\text{mol}} = 194.2 \text{ g } K_2CrO_4$$

The problem says that we have equal masses of reactants. Our two choices are 339.8 g  $AgNO_3 + 339.8$  g  $K_2CrO_4$  or 194.2 g  $AgNO_3 + 194.2$  g  $K_2CrO_4$ . If we assume the 194.2 g quantities are correct, then when 194.2 g  $K_2CrO_4$  (1 mol) reacts, 339.8 g  $AgNO_3$  (2.0 mol) must be present to react with all the  $K_2CrO_4$ . We only have 194.2 g  $AgNO_3$  present; this cannot be correct. Instead of  $K_2CrO_4$  limiting,  $AgNO_3$  must be limiting, and we have reacted 339.8 g  $AgNO_3$  and 339.8 g  $K_2CrO_4$ .

Solution A: 
$$\frac{2.000 \,\text{mol Ag}^+}{0.5000 \,\text{L}} = 4.000 \,M\,\text{Ag}^+; \,\frac{2.000 \,\text{mol NO}_3^-}{0.5000 \,\text{L}} = 4.000 \,M\,\text{NO}_3^-$$

Solution B: 339.8 g 
$$K_2CrO_4 \times \frac{1 \, mol}{194.2 \, g} = 1.750 \, mol \, K_2CrO_4$$

$$\frac{2 \times 1.750 \,\text{mol}\,\text{K}^{+}}{0.5000 \,\text{L}} = 7.000 \,M\,\text{K}^{+}; \quad \frac{1.750 \,\text{mol}\,\text{CrO}_{4}^{\,2-}}{0.5000 \,\text{L}} = 3.500 \,M\,\text{CrO}_{4}^{\,2-}$$

d. After the reaction, moles of K<sup>+</sup> and moles of NO<sub>3</sub><sup>-</sup> remain unchanged because they are spectator ions. Because Ag<sup>+</sup> is limiting, its concentration will be 0 *M* after precipitation is complete.

$$2 \text{ Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{s})$$

$$M_{\text{K}^+} = \frac{2 \times 1.750 \,\text{mol}}{1.0000 \,\text{L}} = 3.500 \,M \,\text{K}^+; \quad M_{\text{NO}_3^-} = \frac{2.000 \,\text{mol}}{1.0000 \,\text{L}} = 2.000 \,M \,\text{NO}_3^-$$

$$M_{\text{CrO}_4^{2-}} = \frac{0.750 \,\text{mol}}{1.0000 \,\text{L}} = 0.750 \,M \,\text{CrO}_4^{2-}; \,M_{\text{Ag+}} = 0 \,M \,\text{(the limiting reagent)}$$