

## Chapter 8

1. We can characterize a reaction's equilibrium position using the equilibrium constant for the reaction as written or the equilibrium constant for its reverse reaction; here we will use the  $K_{sp}$  for AgCl to characterize the equilibrium between  $\text{Ag}^+$ ,  $\text{Cl}^-$ , and  $\text{AgCl}(s)$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

For reactions 8.3–8.5, the equilibrium constant expressions are

$$K_1 = \frac{[\text{AgCl}(aq)]}{[\text{Ag}^+][\text{Cl}^-]}$$

$$K_2 = \frac{[\text{AgCl}_2^-]}{[\text{AgCl}(aq)][\text{Cl}^-]}$$

$$K_3 = \frac{[\text{AgCl}_3^{2-}]}{[\text{AgCl}_2^-][\text{Cl}^-]}$$

From equation 8.6, we know that the solubility of AgCl is defined in terms of the concentration of  $\text{Ag}^+$  in all its forms

$$S_{\text{AgCl}} = [\text{Ag}^+] + [\text{AgCl}(aq)] + [\text{AgCl}_2^-] + [\text{AgCl}_3^{2-}]$$

Solving each of these equilibrium constant expressions for the concentration of its particular form of  $\text{Ag}^+$ , such that each is defined as a function of equilibrium constants and  $[\text{Cl}^-]$  only

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]}$$

$$[\text{AgCl}(aq)] = K_1[\text{Ag}^+][\text{Cl}^-] = K_1K_{sp}$$

$$[\text{AgCl}_2^-] = K_2[\text{AgCl}(aq)][\text{Cl}^-] = K_1K_2K_{sp}[\text{Cl}^-]$$

$$[\text{AgCl}_3^{2-}] = K_3[\text{AgCl}_2^-][\text{Cl}^-] = K_1K_2K_3K_{sp}[\text{Cl}^-]^2$$

and substituting back into the equation for  $S_{\text{AgCl}}$

$$S_{\text{AgCl}} = \frac{K_{sp}}{[\text{Cl}^-]} + K_1K_{sp} + K_1K_2K_{sp}[\text{Cl}^-] + K_1K_2K_3K_{sp}[\text{Cl}^-]^2$$

leaves us with equation 8.7.

2. In equations 8.6 and 8.7, and in problem 8.1, we defined the solubility of AgCl in terms of the total concentration of  $\text{Ag}^+$  in all its forms. We also can express the solubility of AgCl in terms of the total concentration of  $\text{Cl}^-$  in all its form; thus

$$S_{\text{AgCl}} = [\text{Cl}^-] + [\text{AgCl}(aq)] + 2[\text{AgCl}_2^-] + 3[\text{AgCl}_3^{2-}]$$

where we multiply the concentration of  $\text{AgCl}_2^-$  by 2 and the concentration of  $\text{AgCl}_3^{2-}$  by 3 to account for chloride's stoichiometry in the

complex ions. Using the same equilibrium constant expressions from Problem 1

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$K_1 = \frac{[\text{AgCl}(aq)]}{[\text{Ag}^+][\text{Cl}^-]} = 1050$$

$$K_2 = \frac{[\text{AgCl}_2^-]}{[\text{AgCl}(aq)][\text{Cl}^-]} = 83.2$$

$$K_3 = \frac{[\text{AgCl}_3^{2-}]}{[\text{AgCl}_2^-][\text{Cl}^-]} = 6.03$$

we solve each for the concentration of its particular form of  $\text{Cl}^-$ , such that each is defined as a function of equilibrium constants and  $[\text{Ag}^+]$  only; thus

$$[\text{Cl}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]}$$

$$[\text{AgCl}(aq)] = K_1 [\text{Ag}^+][\text{Cl}^-] = K_1 K_{\text{sp}}$$

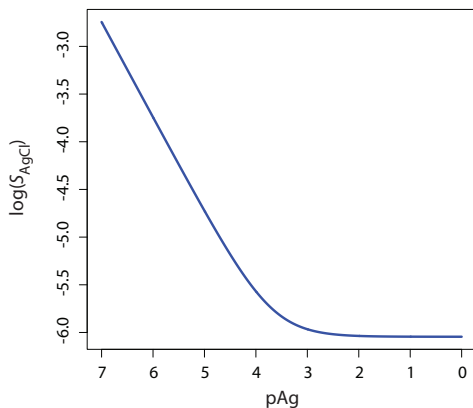
$$[\text{AgCl}_2^-] = K_2 [\text{AgCl}(aq)][\text{Cl}^-] = \frac{K_1 K_2 K_{\text{sp}}^2}{[\text{Ag}^+]}$$

$$[\text{AgCl}_3^{2-}] = K_3 [\text{AgCl}_2^-][\text{Cl}^-] = \frac{K_1 K_2 K_3 K_{\text{sp}}^3}{[\text{Ag}^+]^2}$$

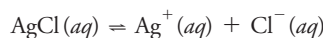
Substituting back into the equation for  $S_{\text{AgCl}}$  leaves us with our final equation for the solubility of AgCl

$$S_{\text{AgCl}} = \frac{K_{\text{sp}}}{[\text{Ag}^+]} + K_1 K_{\text{sp}} + \frac{2K_1 K_2 K_{\text{sp}}^2}{[\text{Ag}^+]} + \frac{3K_1 K_2 K_3 K_{\text{sp}}^3}{[\text{Ag}^+]^2}$$

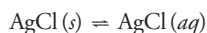
Figure SM8.1 shows a plot of  $\log(S_{\text{AgCl}})$  as a function of  $\text{pAg}$ . For smaller concentrations of  $\text{Ag}^+$ , the solubility of AgCl is determined by the  $K_{\text{sp}}$  reaction alone; thus, the solubility for  $\text{pAg} > 4$  is identical to that seen in Figure 8.1. The solubility of AgCl in the presence of a larger concentration of  $\text{Ag}^+$  is dominated by the formation of  $\text{AgCl}(aq)$ ; thus, the solubility shown for  $\text{pAg} < 4$  is independent of  $[\text{Ag}^+]$  and much less than that seen in Figure 8.1 where the higher concentration of  $\text{Cl}^-$  allows for the formation of the soluble  $\text{AgCl}_2^-$  and  $\text{AgCl}_3^{2-}$  ions.



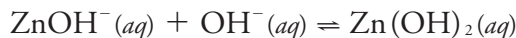
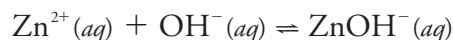
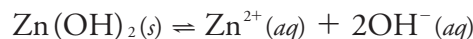
**Figure SM8.1** Solubility of AgCl as a function of  $\text{pAg}$  based on reaction 8.1 and reactions 8.3–8.5. Solubility is displayed on the  $y$ -axis in logarithmic form. For  $\text{pAg} > 4$ , solubility is controlled by the reaction



For  $\text{pAg} < 4$ , solubility is controlled by the reaction



3. The relevant equilibrium reactions are





for which the equilibrium constant expressions are

$$K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^-]^2 = 3.0 \times 10^{-16}$$

$$K_1 = \frac{[\text{ZnOH}^+]}{[\text{Zn}^{2+}][\text{OH}^-]} = 1.0 \times 10^5$$

$$K_2 = \frac{[\text{Zn}(\text{OH})_2(aq)]}{[\text{ZnOH}^+][\text{OH}^-]} = 1.3 \times 10^7$$

$$K_3 = \frac{[\text{Zn}(\text{OH})_3^-]}{[\text{Zn}(\text{OH})_2(aq)][\text{OH}^-]} = 320$$

$$K_4 = \frac{[\text{Zn}(\text{OH})_4^{2-}]}{[\text{Zn}(\text{OH})_3^-][\text{OH}^-]} = 16$$

The solubility of  $\text{Zn}(\text{OH})_2$  is defined in terms of the total concentration of  $\text{Zn}^{2+}$  in all its form; thus

$$S_{\text{Zn}(\text{OH})_2} = [\text{Zn}^{2+}] + [\text{ZnOH}^+] + [\text{Zn}(\text{OH})_2(aq)] + [\text{Zn}(\text{OH})_3^-] + [\text{Zn}(\text{OH})_4^{2-}]$$

Solving each of the equilibrium constant expressions for the concentration of its particular form of  $\text{Zn}^{2+}$ , such that each is defined as a function of equilibrium constants and  $[\text{OH}^-]$  only, and substituting back into the equation for  $S_{\text{Zn}(\text{OH})_2}$  leaves us with our final equation for the solubility of  $\text{Zn}(\text{OH})_2$

$$S_{\text{Zn}(\text{OH})_2} = \frac{K_{\text{sp}}}{[\text{OH}^-]^2} + \frac{K_1 K_{\text{sp}}}{[\text{OH}^-]} + K_1 K_2 K_{\text{sp}} + K_1 K_2 K_3 K_{\text{sp}} [\text{OH}^-] + K_1 K_2 K_3 K_4 K_{\text{sp}} [\text{OH}^-]^2$$

Figure SM8.2 shows the solubility diagram for  $\text{Zn}(\text{OH})_2$ . The minimum solubility spans a range of pH levels from approximately 9 to 11, with solubility limited by the species  $\text{Zn}(\text{OH})_2(aq)$ .

4. We begin by solving HF's  $K_a$  expression for  $[\text{F}^-]$

$$[\text{HF}] = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{K_a}$$

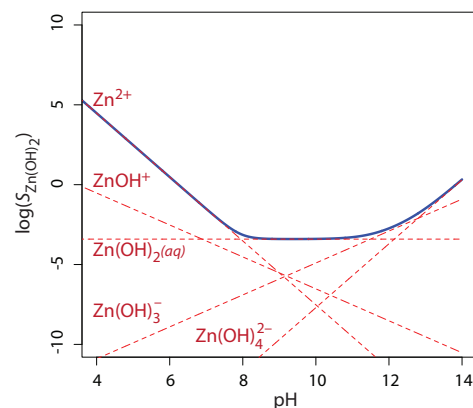
and substitute this into equation 8.10

$$[\text{Ca}^{2+}] = \frac{1}{2}\{[\text{F}^-] + [\text{HF}]\} = \frac{1}{2}\left([\text{F}^-] + \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{K_a}\right)$$

Next, we rewrite this equation so that we express the concentration of  $\text{F}^-$  in terms of the concentration of  $\text{Ca}^{2+}$

$$[\text{Ca}^{2+}] = \frac{1}{2}[\text{F}^-]\left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)$$

$$[\text{F}^-] = \frac{2[\text{Ca}^{2+}]}{\left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)}$$



**Figure SM8.2** Solubility of  $\text{Zn}(\text{OH})_2$  as a function of pH. The contribution of the various soluble forms of  $\text{Zn}^{2+}$  in solution are shown by the dashed red lines; the total solubility is given by the solid blue line; note that the minimum solubility occurs over a range of pH values because the concentration of  $\text{Zn}(\text{OH})_2(aq)$  is independent of pH.

Did you notice that equation 8.10 is a mass balance equation for calcium and for fluorine? Be sure you understand why this equation is correct.

and then substitute this back into the  $K_{sp}$  expression for reaction 8.8

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = [\text{Ca}^{2+}] \left\{ \frac{2[\text{Ca}^{2+}]}{\left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)} \right\}^2$$

Finally, we solve this equation for  $[\text{Ca}^{2+}]$

$$K_{sp} = [\text{Ca}^{2+}] \left\{ \frac{2[\text{Ca}^{2+}]}{\left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)} \right\}^2 = \frac{4[\text{Ca}^{2+}]^3}{\left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)^2}$$

$$[\text{Ca}^{2+}]^3 = \frac{K_{sp}}{4} \left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)^2$$

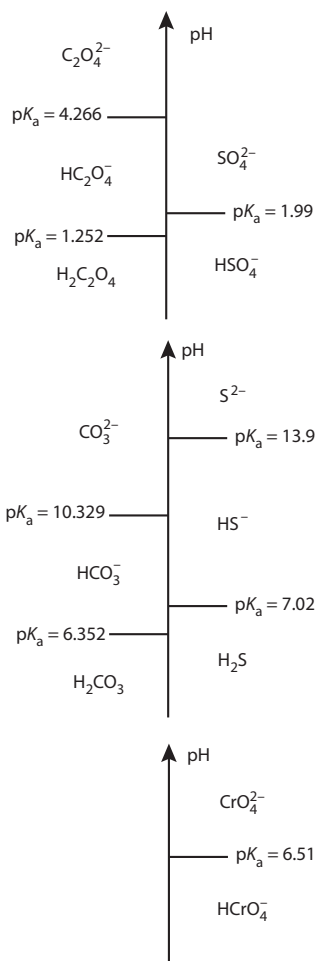
$$[\text{Ca}^{2+}] = \left\{ \frac{K_{sp}}{4} \left(1 + \frac{[\text{H}_3\text{O}^+]}{K_a}\right)^2 \right\}^{1/3}$$

which leaves us with equation 8.11.

5. Each of these precipitates has an anion that is a weak base, which means that each is more soluble at lower pHs where the anion is in its most basic form. Figure SM8.3 shows the ladder diagram for all five basic anions, which helps us in identifying the optimum pH range for each precipitate.

(a) To minimize the solubility of  $\text{CaC}_2\text{O}_4$ , the upper-left ladder diagram suggests that we maintain the pH above 4.27 where  $\text{C}_2\text{O}_4^{2-}$  is the only important form of oxalate. (b) For  $\text{PbCrO}_4$ , the ladder diagram at the bottom indicates that we must keep the pH level above 6.5 where  $\text{CrO}_4^{2-}$  is the only important form of chromate. (c) Examining the upper-right ladder diagram, we see that any pH greater than 2.0 is sufficient to minimize the solubility of  $\text{BaSO}_4$  as  $\text{SO}_4^{2-}$  is the only important form of sulfate. (d) The middle-left ladder diagram suggests that to minimize the solubility of  $\text{SrCO}_3$ , we must maintain a pH more basic than 10.33 to ensure that  $\text{CO}_3^{2-}$  is the only important form of carbonate. (e) Finally, as shown in the middle-right ladder diagram, we need to maintain a pH of greater than 13.9, where  $\text{S}^{2-}$  is the only important form of sulfide, to minimize the solubility of  $\text{ZnS}$ .

6. Pure  $\text{KClO}_4$  is white and pure  $\text{KMnO}_4$  is a dark purple; the presence of a purple color in a precipitate of  $\text{KClO}_4$  indicates that  $\text{KMnO}_4$  is present and the depth of the color is proportional to the amount of  $\text{KMnO}_4$  in the precipitate. In Experiment 1, the concentration of  $\text{MnO}_4^-$  is much greater than the concentration of  $\text{ClO}_4^-$ . As  $\text{KClO}_4$  precipitates, the high concentration of  $\text{MnO}_4^-$  makes more likely the formation of inclusions of  $\text{KMnO}_4$  that impart the deep purple color to the white precipitate of  $\text{KClO}_4$ . In experiment 2, the concentration of  $\text{MnO}_4^-$  is much smaller than that of  $\text{ClO}_4^-$ ; as a result, inclusions of  $\text{KMnO}_4$  are less likely and the precipitate's color is less intensely pink.



**Figure SM8.3** Ladder diagrams for the weak base anions in Problem 8.5. Note that the ladder diagram for  $\text{SO}_4^{2-}$  does not include  $\text{H}_2\text{SO}_4$  because it is a strong acid, and that the ladder diagram for  $\text{CrO}_4^{2-}$  does not include  $\text{H}_2\text{CrO}_4$  because its  $pK_a$  of  $-0.2$  means that it is an important species only at pH levels that are negative.

7. The difference in these three experiments is in the relative supersaturation (RSS) of the analyte and of the precipitant. In Experiment 1, the high concentration of the analyte and the precipitant results in a large RSS that favors the rapid formation of small particles of precipitate; the result is the formation of a gelatinous precipitate. In Experiment 2, an intermediate RSS results in rapid precipitation, but the particles of precipitate are sufficiently large to give a less gelatinous and more substantive solid. Finally, in Experiment 3, the low RSS favors the slow growth particle growth, resulting in the formation of fewer particles that are larger in size.
8. (a) There are three ways that the procedure encourages the formation of larger particles of precipitate: (i) adding the precipitant drop-by-drop ensures that its concentration remains small, which decreases the RSS; (ii) heating the solution increases the precipitate's solubility, which decreases the RSS; and (iii) digesting the precipitate provides time to allow for additional particle growth.
- (b) If we isolate one mole of Al as  $\text{Al}(\text{OH})_3$ , we obtain 78.0 g of product, and if we isolate one mole of Al as  $\text{Al}_2\text{O}_3$ , we obtain 51.0 g of product. Failing to convert some of the  $\text{Al}(\text{OH})_3$  to  $\text{Al}_2\text{O}_3$  results in a larger than expected final mass—a positive determinate error—and we report a %w/w Al that is too high.
- (c) Both are added to help us control the solution's pH, which is important as  $\text{Al}(\text{OH})_3$  becomes more soluble at higher pHs due to the formation of complex ions, such as  $\text{Al}(\text{OH})_4^-$ . The presence of  $\text{NH}_4^+$  slows the rise in pH as it  $\text{NH}_3$  is added as they combine to form a buffer. The change in methyl red's color provides a visual indication that we have added sufficient  $\text{NH}_3$  to complete the precipitation of  $\text{Al}^{3+}$ .
- (d) If we isolate one mole of Al as  $\text{Al}_2\text{O}_3$ , we obtain 51.0 g of product, and if we isolate one mole of Al as  $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$ , we obtain 459 g of product. With a greater mass, isolating Al as  $\text{Al}(\text{C}_9\text{H}_6\text{NO})_3$  improves the method's sensitivity.
9. (a) At first glance, we might expect that  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  is a more desirable final product as it yields more grams of product per mole of Ca than does  $\text{CaCO}_3$ . Even though a precipitate may form with a well-defined stoichiometry between the underlying solid and the hydrated water, it often is difficult to dry the precipitate in a way that maintains this stoichiometry. Drying the precipitate at a temperature where it loses all hydrated water solves this problem.
- (b) If we isolate one mole of Ca as CaO, we obtain 56.1 g of product, and if we isolate one mole of Ca as  $\text{CaCO}_3$ , we obtain 100.1 g of product. If we accidentally convert some of the  $\text{CaCO}_3$  to CaO, the

Be sure to convince yourself that these values are correct. We will use this approach several times in the solution's to this chapter's problems.

final mass is less than expected—a negative determinate error—and we report a %w/w Ca that is too small.

(c) Adding the precipitant to a hot, acidic solution decreases the RSS by increasing the precipitate's solubility. This helps form larger particles of precipitate with fewer co-precipitated impurities.

10. (a) If we isolate one mole of Fe as  $\text{Fe}_3\text{O}_4$ , we obtain 77.2 g of product, and if we isolate one mole of Fe as  $\text{Fe}_2\text{O}_3$ , we obtain 79.8 g of product. As a result, if we isolate some of the Fe as  $\text{Fe}_3\text{O}_4$  instead of as  $\text{Fe}_2\text{O}_3$ , the final mass is less than expected—a negative determinate error—and we report a %w/w Fe that is too small.

(b) The  $\text{NH}_4\text{NO}_3$  is added to prevent peptization of the precipitate.

(c) Ammonia, which is a weak base, is the source of  $\text{OH}^-$  for precipitating  $\text{Fe}(\text{OH})_3$ . As  $\text{NH}_3$  is volatile and has a distinct odor, once all the  $\text{Fe}^{3+}$  is precipitated as  $\text{Fe}(\text{OH})_3$ , the excess  $\text{NH}_3$  is easy to detect.

(d) One way to test the filtrate for  $\text{Cl}^-$  is to use  $\text{Ag}^+$  and look for the formation of precipitate of  $\text{AgCl}$ . To carry out the test, we remove a small portion of the filtrate, add a small amount of acid to neutralize any  $\text{NH}_3$  present so it does not form the stable complex  $\text{Ag}(\text{NH}_3)_2^+$ , and then add a few drops of a  $\text{NaCl}$  solution. If a precipitate forms, then we need to continue rinsing the precipitate.

11. First, we need to calculate the expected mass of  $\text{MoO}_3$ . Starting with samples that contain 0.0770 g of Mo, we expect to obtain

$$0.0770 \text{ g Mo} \times \frac{143.96 \text{ g MoO}_3}{95.96 \text{ g Mo}} = 0.116 \text{ g MoO}_3$$

From the data, we see that at least 0.42 g of the precipitant are needed to ensure the quantitative precipitation of Mo. Any temperature between 30°C and 75°C appears acceptable; however, the highest temperature of 80°C appears to decrease the yield of  $\text{MoO}_3$ . The volume of  $\text{HCl}$  used is unimportant, at least within the range tested.

Given the reaction's stoichiometry, the quantitative precipitation of Mo requires that we use

$$0.077 \text{ g Mo} \times \frac{426.5 \text{ g C}_{13}\text{H}_{11}\text{NO}_2}{95.96 \text{ g Mo}} = 0.34 \text{ g C}_{13}\text{H}_{11}\text{NO}_2$$

of the precipitant. As we actually add 0.42 g of  $\text{C}_{13}\text{H}_{11}\text{NO}_2$ , the additional 0.08 g is in excess; this amounts to a minimum excess of

$$\frac{0.08 \text{ g}}{300 \text{ mL}} \times 100 = 0.027\% \text{w/v}$$

12. To ensure that we obtain at least 1.0 g of  $\text{Fe}_2\text{O}_3$ , we must take samples with a mass of at least

$$1.0 \text{ g Fe}_2\text{O}_3 \times \frac{111.7 \text{ g Fe}}{159.7 \text{ g Fe}_2\text{O}_3} \times \frac{1 \text{ g}}{0.55 \text{ g Fe}} = 1.3 \text{ g}$$

Be sure you are comfortable with the ratio 111.7 g Fe/159.7 g  $\text{Fe}_2\text{O}_3$ . Each mole (159.7 g) of  $\text{Fe}_2\text{O}_3$  contains two moles ( $2 \times 55.845 \text{ g} = 111.7 \text{ g}$ ) of Fe.

13. To report the concentration of arsenic as %w/w  $\text{As}_2\text{O}_3$ , we first need to convert the mass of  $\text{Mg}_2\text{As}_2\text{O}_7$  recovered into an equivalent mass of  $\text{As}_2\text{O}_3$ ; thus

$$0.1065 \text{ g Mg}_2\text{As}_2\text{O}_7 \times \frac{197.84 \text{ g As}_2\text{O}_3}{310.45 \text{ g Mg}_2\text{As}_2\text{O}_7} = 0.0679 \text{ g As}_2\text{O}_3$$

which leave us with a %w/w  $\text{As}_2\text{O}_3$  of

$$\frac{0.0679 \text{ g As}_2\text{O}_3}{1.627 \text{ g sample}} \times 100 = 4.17\% \text{w/w As}_2\text{O}_3$$

14. If the alum is pure, then the mass of Al in a 1.2931-g sample is

$$1.2931 \text{ g alum} \times \frac{53.96 \text{ g Al}}{948.77 \text{ g alum}} = 0.07354 \text{ g Al}$$

The mass of Al recovered is

$$0.1357 \text{ g Al}_2\text{O}_3 \times \frac{53.96 \text{ g Al}}{101.96 \text{ g Al}_2\text{O}_3} = 0.07182 \text{ g Al}$$

Thus, the purity of the alum is

$$\frac{0.07182 \text{ g Al}}{0.07354 \text{ g Al}} \times 100 = 97.7\%$$

15. First we convert the mass of  $\text{Fe}_2\text{O}_3$  to an equivalent mass of iron and then convert the mass of Fe to the mass of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in the original sample; thus

$$0.355 \text{ g Fe}_2\text{O}_3 \times \frac{111.69 \text{ g Fe}}{159.69 \text{ g Fe}_2\text{O}_3} = 0.2483 \text{ g Fe}$$

$$0.2483 \text{ g Fe} \times \frac{278.01 \text{ g FeSO}_4 \cdot 7\text{H}_2\text{O}}{55.845 \text{ g Fe}} = 1.236 \text{ g FeSO}_4 \cdot 7\text{H}_2\text{O}$$

The mass of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per tablet, therefore, is

$$\frac{1.236 \text{ g FeSO}_4 \cdot 7\text{H}_2\text{O}}{3.116 \text{ g}} \times \frac{20.505 \text{ g}}{15 \text{ tablets}} = 0.542 \frac{\text{g FeSO}_4 \cdot 7\text{H}_2\text{O}}{\text{tablet}}$$

16. Because we isolate iron in a form,  $\text{Fe}_2\text{O}_3$ , identical to how we report its concentration, the calculation is straightforward

$$\frac{0.0357 \text{ g Fe}_2\text{O}_3}{1.4639 \text{ g sample}} \times 100 = 2.44\% \text{w/w Fe}_2\text{O}_3$$

For calcium, we isolate it as  $\text{CaSO}_4$  but report it as  $\text{CaO}$ ; thus

$$1.4058 \text{ g CaSO}_4 \times \frac{56.08 \text{ g CaO}}{136.14 \text{ g CaSO}_4} = 0.5791 \text{ g CaO}$$

$$\frac{0.5791 \text{ g CaO}}{1.4639 \text{ g sample}} \times 100 = 39.56\% \text{w/w CaO}$$

For magnesium, we isolate it as  $\text{Mg}_2\text{P}_2\text{O}_7$  but report it as  $\text{MgO}$ ; thus

$$0.0672 \text{ g Mg}_2\text{P}_2\text{O}_7 \times \frac{48.61 \text{ g Mg}}{222.55 \text{ g Mg}_2\text{P}_2\text{O}_7} \\ \times \frac{40.30 \text{ g MgO}}{24.305 \text{ g Mg}} = 0.02434 \text{ g MgO} \\ \frac{0.02434 \text{ g MgO}}{1.4639 \text{ g sample}} \times 100 = 1.663\% \text{ MgO}$$

17. We begin by converting the mass of AgI produced in the second reaction to the moles of HI consumed in the first reaction

$$0.1478 \text{ g AgI} \times \frac{1 \text{ mol HI}}{234.77 \text{ g AgI}} = 6.296 \times 10^{-4} \text{ mol HI}$$

Next, we note that each mole of  $\text{R}(\text{OCH}_2\text{CH}_3)_x$  consumes  $x$  moles of HI, which means there are

$$6.296 \times 10^{-4} \text{ mol HI} \times \frac{\text{mol R}(\text{OCH}_2\text{CH}_3)_x}{x \text{ mol HI}} \\ = \frac{(6.296 \times 10^{-4}) \text{ mol R}(\text{OCH}_2\text{CH}_3)_x}{x}$$

in the 0.03692 g sample. Given that the molecular weight is reported as 176 g/mol, we know that

$$\frac{0.03692 \text{ g R}(\text{OCH}_2\text{CH}_3)_x}{(6.296 \times 10^{-4}) \text{ mol R}(\text{OCH}_2\text{CH}_3)_x} = \frac{176 \text{ g R}(\text{OCH}_2\text{CH}_3)_x}{\text{mol R}(\text{OCH}_2\text{CH}_3)_x}$$

which we solve to find that  $x = 3.00$ .

18. Because the mixture contains only  $\text{K}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ , we know that

$$x + y = 0.5167 \text{ g}$$

where  $x$  is the mass of  $\text{K}_2\text{SO}_4$  and  $y$  is the mass of  $(\text{NH}_4)_2\text{SO}_4$ . With one equation and two unknowns, we need an additional equation to define the system. Because  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{BaSO}_4$  each contain a single mole of  $\text{SO}_4^{2-}$ , we know that

$$\text{mol BaSO}_4 = \text{mol K}_2\text{SO}_4 + \text{mol (NH}_4)_2\text{SO}_4$$

which we can rewrite in terms of each compound's mass and formula weight

$$\frac{0.8635 \text{ g BaSO}_4}{233.39 \frac{\text{g BaSO}_4}{\text{mol}}} = \frac{x}{174.26 \frac{\text{g K}_2\text{SO}_4}{\text{mol}}} + \frac{y}{132.14 \frac{\text{g (NH}_4)_2\text{SO}_4}{\text{mol}}}$$

With two equations we have sufficient information to grind through the algebra and determine the mass of  $\text{K}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  in the sample. Using the first equation, we solve for the mass of  $(\text{NH}_4)_2\text{SO}_4$  in terms of  $\text{K}_2\text{SO}_4$



$$y = 0.5167 g - x$$

substitute it into the second equation

$$\frac{0.8635}{233.39} = \frac{x}{174.26} + \frac{0.5167 g - x}{132.14}$$

and solve for the mass of  $K_2SO_4$  and the %w/w  $K_2SO_4$  in the sample.

$$0.003700 = 0.005739x + 0.003910 - 0.007568x$$

$$0.001829x = 2.1 \times 10^{-4}$$

$$x = 0.1148 \text{ g } K_2SO_4$$

$$\frac{0.1148 \text{ g } K_2SO_4}{0.5167 \text{ g sample}} \times 100 = 22.22\% \text{w/w } K_2SO_4$$

19. To make equations more compact and easier to read, we will let HL represent the ligand  $C_9H_7NO$ . From the first part of the analysis, we know that

$$g \text{ FeL}_3 + g \text{ MnL}_2 = 0.8678 \text{ g}$$

and from the second part of the analysis, we know that

$$g \text{ L}_{\text{Fe}} + g \text{ L}_{\text{Mn}} = 5.276 \times 10^{-3} \text{ mol L} \times \frac{144.15 \text{ g L}}{\text{mol L}} = 0.7605 \text{ g}$$

where  $L_{\text{Fe}}$  is the ligand bound to iron and  $L_{\text{Mn}}$  is the ligand bound to manganese. At this point we have two equations and four unknowns, which means we need to identify two additional equations that relate the unknowns to each other. Two useful equations are the stoichiometric relationships between Fe and  $\text{FeL}_3$

$$g \text{ L}_{\text{Fe}} = g \text{ FeL}_3 \times \frac{1 \text{ mol FeL}_3}{488.30 \text{ g FeL}_3} \times \frac{3 \text{ mol L}_{\text{Fe}}}{\text{mol FeL}_3} \times \frac{144.15 \text{ g L}_{\text{Fe}}}{\text{mol L}_{\text{Fe}}}$$

$$g \text{ L}_{\text{Fe}} = g \text{ FeL}_3 \times 0.8856$$

and between Mn and  $\text{MnL}_2$

$$g \text{ L}_{\text{Mn}} = g \text{ MnL}_2 \times \frac{1 \text{ mol MnL}_2}{343.24 \text{ g MnL}_2} \times \frac{2 \text{ mol L}_{\text{Mn}}}{\text{mol MnL}_2} \times \frac{144.15 \text{ g L}_{\text{Mn}}}{\text{mol L}_{\text{Mn}}}$$

$$g \text{ L}_{\text{Mn}} = g \text{ MnL}_2 \times 0.8399$$

Substituting back leaves us with two equations and two unknowns that we can solve simultaneously

$$g \text{ FeL}_3 \times 0.8856 + g \text{ MnL}_2 \times 0.8399 = 0.7605 \text{ g}$$

$$g \text{ FeL}_3 + g \text{ MnL}_2 = 0.8678 \text{ g}$$

Multiplying the second equation by 0.8399 and subtracting from the first equation

$$\text{g FeL}_3 \times 0.0457 = 0.0316$$

and solving gives the mass of  $\text{FeL}_3$  as 0.6915 g. Substituting back gives the mass of  $\text{MnL}_2$  as 0.1763 g.

Finally, we convert the mass of  $\text{FeL}_3$  and the mass of  $\text{MnL}_2$  into the mass of Fe and the mass of Mn

$$0.6915 \text{ g FeL}_3 \times \frac{55.845 \text{ g Fe}}{488.30 \text{ g FeL}_3} = 0.07908 \text{ g Fe}$$

$$0.1763 \text{ g MnL}_2 \times \frac{54.938 \text{ g Mn}}{343.24 \text{ g MnL}_2} = 0.02822 \text{ g Mn}$$

which leaves us with weight percents of

$$\frac{0.07908 \text{ g Fe}}{0.1273 \text{ g sample}} \times 100 = 62.12\% \text{w/w Fe}$$

$$\frac{0.02822 \text{ g Mn}}{0.1273 \text{ g sample}} \times 100 = 22.17\% \text{w/w Mn}$$

20. We begin with the following three equations

$$\text{g NaBr} + \text{g NaI} + \text{g NaNO}_3 = 0.8612 \text{ g}$$

$$\text{g AgBr} + \text{g AgI} = 1.0186 \text{ g}$$

$$(\text{g AgCl})_{\text{AgBr}} + (\text{g AgCl})_{\text{AgI}} = 0.7125 \text{ g}$$

where, in the last equation, the notation  $(\text{g AgCl})_x$  indicates the source of the AgCl. At this point we have three equations and seven unknowns, which means we need to identify four additional equations that relate the unknowns to each other. Two useful equations are the stoichiometric relationships between the mass of AgCl created from AgBr and from AgI; thus

$$\begin{aligned} (\text{g AgCl})_{\text{AgBr}} &= \text{g AgBr} \times \frac{1 \text{ mol AgBr}}{187.77 \text{ g AgBr}} \times \\ &\frac{1 \text{ mol (AgCl)}_{\text{AgBr}}}{\text{mol AgBr}} \times \frac{143.32 \text{ g (AgCl)}_{\text{AgBr}}}{\text{mol (AgCl)}_{\text{AgBr}}} = \text{g AgBr} \times 0.7633 \end{aligned}$$

$$\begin{aligned} (\text{g AgCl})_{\text{AgI}} &= \text{g AgI} \times \frac{1 \text{ mol AgI}}{234.77 \text{ g AgI}} \times \\ &\frac{1 \text{ mol (AgCl)}_{\text{AgI}}}{\text{mol AgI}} \times \frac{143.32 \text{ g (AgCl)}_{\text{AgI}}}{\text{mol (AgCl)}_{\text{AgI}}} = \text{g AgI} \times 0.6105 \end{aligned}$$

Substituting back leaves us with two equations and two unknowns that we can solve simultaneously

$$\text{g AgBr} \times 0.7633 + \text{g AgI} \times 0.6105 = 0.7125 \text{ g}$$

$$\text{g AgBr} + \text{g AgI} = 1.0186 \text{ g}$$

Multiplying the second equation by 0.6105 and subtracting from the first equation

$$0.1528 \times \text{g AgBr} = 0.09065$$

and solving gives the mass of AgBr as 0.5933 g. Substituting back gives the mass of AgI as 0.4253 g.

Now that we have the mass of AgBr and the mass of AgI, we can use simple stoichiometry to convert them to the equivalent amount of NaBr and of NaI; thus

$$0.5933 \text{ g AgBr} \times \frac{102.80 \text{ g NaBr}}{187.77 \text{ g AgBr}} = 0.3248 \text{ g NaBr}$$

$$0.4253 \text{ g AgI} \times \frac{149.80 \text{ g NaI}}{234.77 \text{ g AgI}} = 0.2714 \text{ g NaI}$$

Finally, the mass of  $\text{NaNO}_3$  is

$$0.8612 \text{ g} - 0.3248 \text{ g NaBr} - 0.2714 \text{ g NaI} = 0.2650 \text{ g NaNO}_3$$

and the mass percent of  $\text{NaNO}_3$  is

$$\frac{0.2650 \text{ g NaNO}_3}{0.8612 \text{ g sample}} \times 100 = 30.77\% \text{ w/s NaNO}_3$$

21. We begin by calculating the moles of AgBr formed

$$12.53112 \text{ g AgBr} \times \frac{1 \text{ mol AgBr}}{187.772 \text{ g AgBr}} = 0.0667358 \text{ mol AgBr}$$

and then convert this to the moles of  $\text{MnBr}_2$

$$0.0667358 \text{ mol AgBr} \times \frac{1 \text{ mol MnBr}_2}{2 \text{ mol AgBr}} = 0.0333679 \text{ mol MnBr}_2$$

The formula weight for  $\text{MnBr}_2$  is

$$\frac{7.16539 \text{ g MnBr}_2}{0.0333679 \text{ g MnBr}_2} = 214.739 \text{ g/mol}$$

Subtracting out the contribution of bromine gives the atomic weight of Mn as 54.931 g/mol.

22. Figure 8.16 shows six precipitates, for which two are yellow and four are white; these precipitates are:

AgCl (white)    AgI (yellow)    BaSO<sub>4</sub> (white)

PbCl<sub>2</sub> (white)    PbI<sub>2</sub> (yellow)    PbSO<sub>4</sub> (white)

We identify solution C as KI because I<sup>-</sup> is the only species that forms two yellow precipitates. Solution E is BaCl<sub>2</sub> as it is the only solution that forms three white precipitates (one that contains Ba<sup>2+</sup> and two that contain SO<sub>4</sub><sup>2-</sup>). The yellow precipitates when KI (solution C) is mixed with solutions A and B tell us that one of these solutions

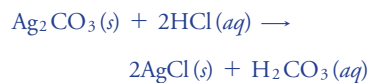
contains  $\text{Ag}^+$  and that the other contains  $\text{Pb}^{2+}$ ; because  $\text{Pb}(\text{NO}_3)_2$  forms two white precipitates, we know that it is solution B, which leaves solution A as  $\text{AgNO}_3$ . Finally, the one remaining solution, D, is  $\text{Na}_2\text{SO}_4$ .

23. We know that the initial precipitate is completely soluble in dilute  $\text{HNO}_3$ , which means the precipitate contains one or more of the following compounds



and that it cannot include  $\text{AgCl}$  or  $\text{BaSO}_4$  as neither is soluble in acid; note that this means that the original sample cannot contain both  $\text{AgNO}_3$  and  $\text{ZnCl}_2$ , nor can it contain both  $\text{MgSO}_4$  and  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

Although the initial precipitate is soluble in  $\text{HNO}_3$ , at least one of its constituents does not dissolve in  $\text{HCl}$ . The solid that remains must be  $\text{AgCl}$ , as  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ba}^{2+}$  form soluble chloride salts; this also means that the original sample must include  $\text{AgNO}_3$  and  $\text{K}_2\text{CO}_3$ , and that it cannot include  $\text{ZnCl}_2$ .



The filtrate that remains after adding  $\text{HCl}$  to the initial precipitate forms a precipitate with  $\text{NH}_3$ , which is a source of  $\text{OH}^-$ . The only possible precipitate is  $\text{Mg}(\text{OH})_2$  as  $\text{Zn}^{2+}$  forms a soluble complex of  $\text{Zn}(\text{OH})_4^{2-}$ ; thus,  $\text{MgSO}_4$  is present in the original sample. Because  $\text{MgSO}_4$  is present, we know that  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$  is not present.

Finally, we have insufficient information to determine whether  $\text{NH}_4\text{NO}_3$  is present.

24. When we analyze for the sulfur in pyrite, the relationship between the mass of analyte,  $\text{FeS}_2$ , and the mass of the precipitate,  $\text{BaSO}_4$ , is

$$\begin{aligned} \text{g BaSO}_4 &= \text{g FeS}_2 \times \frac{2 \text{ mol S}}{119.96 \text{ g FeS}_2} \times \frac{233.39 \text{ g BaSO}_4}{1 \text{ mol S}} \\ \text{g BaSO}_4 &= 3.89 \times \text{g FeS}_2 \end{aligned}$$

When we analyze for the iron in pyrite, the relationship between the mass of analyte,  $\text{FeS}_2$ , and the mass of the final product,  $\text{Fe}_2\text{O}_3$ , is

$$\begin{aligned} \text{g Fe}_2\text{O}_3 &= \text{g FeS}_2 \times \frac{1 \text{ mol Fe}}{119.96 \text{ g FeS}_2} \times \frac{159.69 \text{ g Fe}_2\text{O}_3}{2 \text{ mol Fe}} \\ \text{g Fe}_2\text{O}_3 &= 0.666 \times \text{g FeS}_2 \end{aligned}$$

Based on these results, we see that the more sensitive analysis is to precipitate the sulfur in  $\text{FeS}_2$  as  $\text{BaSO}_4$  as this yields the greater mass of product for a given mass of  $\text{FeS}_2$ . This assumes, of course, that  $\text{FeS}_2$  is the only source of sulfur in the sample.

25. From Problem 24 we know that

$$\text{g BaSO}_4 = 3.89 \times \text{g FeS}_2$$

To form 1.0 g of BaSO<sub>4</sub>, therefore, requires a sample that contains

$$\text{g FeS}_2 = \frac{1.0 \text{ g BaSO}_4}{3.89} = 0.257 \text{ g FeS}_2$$

Given that the lower limit on purity is 90% FeS<sub>2</sub>, we need to collect samples that have a mass of at least

$$0.257 \text{ g FeS}_2 \times \frac{100 \text{ g sample}}{90 \text{ g FeS}_2} = 0.286 \text{ g} \approx 0.3 \text{ g}$$

26. To decide on the volume of AgNO<sub>3</sub> to use, we first need to determine which analyte has the greatest amount of Cl<sup>-</sup> on a per gram basis. This is easy to determine if we compare the %w/w Cl<sup>-</sup> in each compound

$$\text{KCl: } \frac{35.45 \text{ g Cl}^-}{74.55 \text{ g KCl}} \times 100 = 47.6\% \text{w/w Cl}^-$$

$$\text{NaCl: } \frac{35.45 \text{ g Cl}^-}{58.44 \text{ g NaCl}} \times 100 = 60.7\% \text{w/w Cl}^-$$

$$\text{NH}_4\text{Cl: } \frac{35.45 \text{ g Cl}^-}{53.49 \text{ g NH}_4\text{Cl}} \times 100 = 66.3\% \text{w/w Cl}^-$$

Because NH<sub>4</sub>Cl has the greatest %w/w Cl<sup>-</sup>, we assume that the sample contains only NH<sub>4</sub>Cl and calculate the volume of AgNO<sub>3</sub> needed

$$0.5 \text{ g NH}_4\text{Cl} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.49 \text{ g NH}_4\text{Cl}} \times \frac{1 \text{ mol AgNO}_3}{\text{mol NH}_4\text{Cl}} \times \frac{169.87 \text{ g AgNO}_3}{\text{mol AgNO}_3} \times \frac{100 \text{ mL}}{5 \text{ g AgNO}_3} = 31.8 \text{ mL} \approx 32 \text{ mL}$$

27. (a) If the reaction is stoichiometric, then the mass of PbCrO<sub>4</sub> obtained for each gram of Pb is

$$1.000 \text{ g Pb} \times \frac{323.2 \text{ g PbCrO}_4}{207.2 \text{ g Pb}} = 1.560 \text{ g PbCrO}_4$$

(b) To find the actual stoichiometric ratio we calculate the moles of Pb in 1.000 g of Pb and the moles of CrO<sub>4</sub><sup>2-</sup> in 1.568 g of precipitate, and then examine the mole ratio; thus

$$1.000 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2 \text{ g Pb}} = 4.826 \times 10^{-3} \text{ mol Pb}$$

$$1.568 \text{ g PbCrO}_4 \times \frac{1 \text{ mol CrO}_4^{2-}}{323.2 \text{ g PbCrO}_4} = 4.852 \times 10^{-4} \text{ mol CrO}_4^{2-}$$

$$\frac{4.852 \times 10^{-4} \text{ mol CrO}_4^{2-}}{4.826 \times 10^{-3} \text{ mol Pb}} = 1.005$$

we find that the apparent stoichiometry is Pb(CrO<sub>4</sub>)<sub>1.005</sub>.

(c) The effect of the non-stoichiometric ratio between  $\text{Pb}^{2+}$  and  $\text{CrO}_4^{2-}$  is to increase the apparent mass of precipitate, which means we report a %w/w Pb that is too large; the result, therefore, is a positive determine error.

28. To complete a propagation of uncertainty, we first write a single equation that defines the %w/w  $\text{Fe}_3\text{O}_4$  in a sample in terms of the measurements we make, formula weights, and constants. Looking at the solution to Example 8.1, we combine the two calculations into one equation

$$\%w/w \text{Fe}_3\text{O}_4 = \frac{2 \times m_{\text{Fe}_2\text{O}_3} \times FW_{\text{Fe}_3\text{O}_4}}{3 \times m_{\text{sample}} \times FW_{\text{Fe}_2\text{O}_3}} \times 100$$

where 2 and 3 account for the stoichiometry of iron in  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ,  $m_x$  is the mass of compound  $x$ , and  $FW_x$  is the formula weight of compound  $x$ . The uncertainty,  $u_m$ , for both the mass of  $\text{Fe}_2\text{O}_3$  and the mass of  $\text{Fe}_3\text{O}_4$  takes into account the need to tare the balance

$$u_m = \sqrt{(0.0001)^2 + (0.0001)^2} = 0.00014 \text{ g}$$

The mass of  $\text{Fe}_2\text{O}_3$  is  $0.8525 \pm 0.00014$  g and the mass of  $\text{Fe}_3\text{O}_4$  is  $1.5419 \pm 0.00014$  g. For the formula weights, we will report them to three decimal places, one more than in the solution to Example 8.1, and assume an uncertainty of  $\pm 0.001$  g/mol; thus, for  $\text{Fe}_2\text{O}_3$  the formula weight is  $159.691 \pm 0.001$  g/mol, and for  $\text{Fe}_3\text{O}_4$  the formula weight is  $231.537 \pm 0.001$  g/mol.

The %w/w  $\text{Fe}_2\text{O}_3$  in the sample is

$$\frac{2 \times 0.8525 \times 231.537}{3 \times 1.5419 \times 159.691} \times 100 = 53.44\%w/w \text{Fe}_3\text{O}_4$$

and the estimated relative uncertainty in this value is

$$\frac{u_R}{R} = \sqrt{\left(\frac{0.00014}{0.8525}\right)^2 + \left(\frac{0.00014}{1.5419}\right)^2 + \left(\frac{0.001}{159.691}\right)^2 + \left(\frac{0.001}{231.537}\right)^2} = 1.878 \times 10^{-4}$$

or an estimated uncertainty of approximately 0.019%. The estimated relative uncertainty is a factor of 10 better than the expected range of 0.1–0.2%. One explanation for the difference is that the propagation of uncertainty did not account for uncertainty in forming and in handling the precipitate, including variations in contaminants, such as inclusions, and in solubility losses.

29. The change in mass for the standard sample of  $\text{KO}_3$  is

$$\frac{7.10 \text{ mg lost}}{38.63 \text{ mg KO}_3} \times 100 = 18.38\%$$

which we can use to determine the mg of  $\text{KO}_3$  in the impure sample

Although you do not need to know the product of this volatilization reaction to determine the sample's purity, you do have sufficient information to determine the balanced reaction. Work out the details; you can check your answer at the top of the next page.

$$4.86 \text{ mg lost} \times \frac{100 \text{ mg KO}_3}{18.38 \text{ mg lost}} = 26.44 \text{ mg KO}_3$$

The sample's purity, therefore, is

$$\frac{26.44 \text{ mg KO}_3}{29.6 \text{ mg sample}} \times 100 = 89.3\%$$

The formula weight of  $\text{KO}_3$  is 87.1 g/mol, which means that an 18.3% reduction in mass is equivalent to 16.0 g/mol. As this is the mass of a single oxygen atom, the most likely reaction is



30. The change in mass of 329.6 mg is the mass of water released during the drying process; thus, the percentage of water in the sample is

$$\frac{329.6 \text{ mg H}_2\text{O}}{875.4 \text{ mg sample}} \times 100 = 37.65\% \text{w/w H}_2\text{O}$$

31. In Representative Method 8.2, silicon is present in the sample as  $\text{SiO}_2$ , all of which is lost during the volatilization step. For each mole of  $\text{SiO}_2$  there is one mole of Si; thus

$$0.21 \text{ g SiO}_2 \times \frac{28.08 \text{ g Si}}{60.08 \text{ g SiO}_2} = 0.0981 \text{ g Si} \approx 0.10 \text{ g SiO}_2$$

32. (a) The %w/w Fe in the compound is

$$0.2091 \text{ g Fe}_2\text{O}_3 \times \frac{111.69 \text{ g Fe}}{159.69 \text{ g Fe}_2\text{O}_3} = 0.1462 \text{ g Fe}$$

$$\frac{0.1462 \text{ g Fe}}{0.4873 \text{ g sample}} \times 100 = 30.00\% \text{w/w Fe}$$

(b) To find the compound's empirical formula, we first need to determine the weight-percent of Fe, C, and H in the compound. We have the %w/w for Fe already; thus, we need to determine the %w/w C and the %w/w H.

$$1.2119 \text{ g CO}_2 \times \frac{12.011 \text{ g C}}{44.009 \text{ g CO}_2} = 0.3308 \text{ g C}$$

$$\frac{0.3308 \text{ g C}}{0.5123 \text{ g sample}} \times 100 = 64.57\% \text{w/w C}$$

$$0.2482 \text{ g H}_2\text{O} \times \frac{2.016 \text{ g H}}{18.015 \text{ g H}_2\text{O}} = 0.0278 \text{ g H}$$

$$\frac{0.0278 \text{ g H}}{0.5123 \text{ g sample}} \times 100 = 5.43\% \text{w/w H}$$

For each gram of the compound we have 0.3000 g Fe, 0.6457 g C, and 0.0543 g H, which correspond to

$$0.3000 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.845 \text{ g Fe}} = 5.37 \times 10^{-3} \text{ mol Fe}$$

$$0.6457 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g C}} = 5.38 \times 10^{-2} \text{ mol C}$$

$$0.0543 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 5.39 \times 10^{-2} \text{ mol H}$$

and mole ratios of

$$\frac{5.38 \times 10^{-2} \text{ mol C}}{5.37 \times 10^{-3} \text{ mol Fe}} = 10 \text{ C:1Fe}$$

$$\frac{5.39 \times 10^{-2} \text{ mol H}}{5.37 \times 10^{-3} \text{ mol Fe}} = 10 \text{ H:1Fe}$$

The compound's empirical formula, therefore, is  $\text{FeC}_{10}\text{H}_{10}$ .

33. (a) For each analysis, the %w/w ash is

$$\%w/w \text{ ash} = \frac{m_{\text{ash}}}{m_{\text{polymer}}} \times 100 = \frac{m_{\text{crucible} + \text{ash}} - m_{\text{crucible}}}{m_{\text{crucible} + \text{polymer}} - m_{\text{crucible}}} \times 100$$

The following table summarizes the results for each replicate of each sample.

polymer A	$m_{\text{polymer}}$ (g)	$m_{\text{ash}}$ (g)	%w/w ash
1	2.0829	0.6259	30.05
2	2.0329	0.6117	30.09
3	1.9608	0.5917	30.18

polymer B	$m_{\text{polymer}}$ (g)	$m_{\text{ash}}$ (g)	%w/w ash
1	1.9236	0.5730	29.79
2	2.1282	0.6336	29.77
3	1.9841	0.5914	29.81

The mean and the standard deviation for polymer A are 30.11%w/w ash and 0.0666%w/w ash, respectively, and for polymer B the mean and the standard deviation are 29.79%w/w ash and 0.0200%w/w ash, respectively.

(b) To compare the means for the two samples, we use an unpaired  $t$ -test with the following null and alternative hypotheses

$$H_0: \bar{X}_A = \bar{X}_B \quad H_A: \bar{X}_A \neq \bar{X}_B$$

Before we can complete the  $t$ -test, we must determine if we can pool the standard deviations for the two samples, which we accomplish using an  $F$ -test and the following null and alternative hypotheses

$$H_0: s_A^2 = s_B^2 \quad H_A: s_A^2 \neq s_B^2$$

finding that  $F_{\text{exp}}$

$$F_{\text{exp}} = \frac{(0.0666)^2}{(0.0200)^2} = 11.1$$

is less than the critical value for  $F(0.05, 2, 2)$  of 39.00; thus, we retain the null hypothesis and calculate a pooled standard deviation



$$s_{\text{pool}} = \sqrt{\frac{2 \times (0.0666)^2 + 2 \times (0.0200)^2}{4}} = 0.0492$$

The experimental value for  $t$  is

$$t_{\text{exp}} = \frac{30.11 - 29.79}{0.0492} \sqrt{\frac{3 \times 3}{3 + 3}} = 7.97$$

Because  $t_{\text{exp}}$  is greater than the critical value for  $t(0.05,4)$  of 2.776, we accept the alternative hypothesis that the difference between the %w/w ash for polymer A and for polymer B is significant at  $\alpha = 0.05$ .

34. The density of surface hydroxyls,  $d$ , is

$$d = \frac{\text{mol H}_2\text{O}}{\text{m}^2}$$

$$d = \frac{0.006 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g H}_2\text{O}} \times \frac{2 \text{ mol OH}^-}{\text{mol H}_2\text{O}} \times \frac{10^6 \mu\text{mol}}{\text{mol}}}{1 \text{ g ZrO}_2 \times \frac{33 \text{ m}^2}{\text{g ZrO}_2}}$$

$$d = 20 \mu\text{mol/m}^2$$

35. The total volume of air sampled is

$$20 \text{ min} \times \frac{1 \text{ hr}}{60 \text{ min}} \times \frac{75 \text{ m}^3}{\text{hr}} = 25 \text{ m}^3$$

which gives the concentration of particular material as

$$\frac{345.2 \text{ mg}}{25 \text{ m}^3} = 13.8 \text{ mg/m}^3 \approx 14 \text{ mg/m}^3$$

$$13.8 \text{ mg/m}^3 \times \left(\frac{1 \text{ m}}{10^2 \text{ cm}}\right)^3 \times \frac{1000 \text{ cm}^3}{\text{L}} = 0.014 \text{ mg/L}$$

36. (a) The %w/w fat is defined as

$$\%w/w \text{ fat} = \frac{m_{\text{initial}} - m_{\text{final}}}{m_{\text{initial}}} \times 100$$

which gives the following set of results: 20.65%, 21.08%, 21.36%, 22.13%, and 21.17%. The mean and the standard deviation for this set of data are 21.28%w/w and 0.545%w/w, respectively.

(b) To determine if there is evidence for a determinate error, we use a  $t$ -test of the experimental mean,  $\bar{X}$ , to the expected mean,  $\mu$ , for which the null and alternative hypotheses are

$$H_0: \bar{X} = \mu \quad H_A: \bar{X} \neq \mu$$

The experimental value for  $t$  is

$$t_{\text{exp}} = \frac{|21.28 - 22.7| \sqrt{5}}{0.543} = 5.85$$

which is greater than the critical value for  $t(0.05,4)$  of 2.776; thus, we accept the alternative hypothesis that the difference between the experimental result and the expected result is significant at  $\alpha = 0.05$ .

37. To calculate the %w/w organic matter we must determine the mass of the sample and the mass of organic matter found in the sample. The mass of the sample is the difference between the weight of the dry sediment and the combined weight of the filter paper and the evaporating dish. Using the first increment as an example, the mass of the sample is

$$m_{\text{sample}} = 52.10 \text{ g} - (43.21 \text{ g} + 1.590 \text{ g}) = 7.300 \text{ g}$$

The mass of organic matter is the difference between the weight of the dry sample and the combined weight of the filter paper and the sample after ashing. Using the first increment as an example, the mass of organic matter is

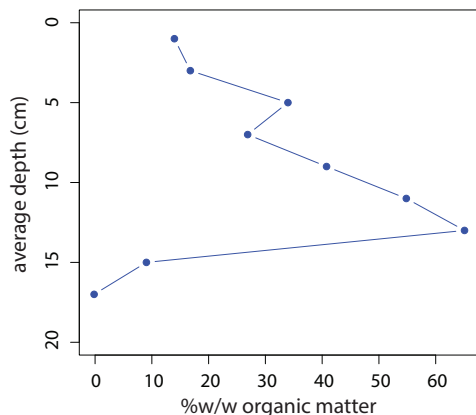
$$m_{\text{organic}} = 52.10 \text{ g} - (49.49 \text{ g} + 1.590 \text{ g}) = 1.020 \text{ g}$$

The %w/w organic matter for the first increment is

$$\frac{m_{\text{organic}}}{m_{\text{sample}}} \times 100 = \frac{1.020 \text{ g}}{7.300 \text{ g}} \times 100 = 13.97\% \text{w/w organic}$$

The results for each increment are gathered in the following table; note that results are reported for the average depth of each increment.

avg. depth (cm)	$m_{\text{sample}}$ (g)	$m_{\text{organic}}$ (g)	%w/w organic
1	7.300	1.020	13.97
3	6.465	1.085	16.78
5	10.011	3.401	33.97
7	6.879	1.849	26.88
9	6.602	2.692	40.78
11	4.582	2.522	54.82
13	3.207	2.087	65.08
15	12.720	1.150	9.04
17	9.374	-0.016	—



**Figure SM8.4** Sediment profile showing the concentration of organic matter as a function of depth. Although normally we plot the dependent variable (%w/w organic matter, in this case) on the  $y$ -axis, we flip the axes here so that depth is aligned vertically as it is in a sediment column; note that we also display the  $y$ -axis as increasing from top-to-bottom so that the bottom of the sediment column—that is, the greatest depth in our data—falls at the bottom of the  $y$ -axis.

Figure SM8.4 shows a plot of depth on the  $y$ -axis versus the concentration of organic matter on the  $x$ -axis. There is a general increase in the concentration of organic matter with depth, followed by a sharp decrease in concentration between 14 cm and 16 cm; presumably the sediment is largely inorganic below a depth of 17 cm.

38. (a) A 100- $\mu\text{L}$  sample weighs approximately 0.1 g, assuming a density of approximately 1 g/mL, which places the sample at the boundary between a macro and a meso sample. The concentration of thiourea is approximately  $10^{-6}$  M (using the midrange of the standards), or a %w/w concentration of

$$\begin{aligned} 1 \times 10^{-6} \text{ M} \times \frac{76.12 \text{ g}}{\text{mol}} \times \frac{1 \text{ L}}{1000 \text{ g}} \times 100 \\ = 7.6 \times 10^{-6} \% \text{w/w thiourea} \end{aligned}$$

which makes thiourea a trace level analyte.

(b) Figure SM8.5 shows the calibration curve for which the calibration equation is

$$\Delta f = 7.97 + 2.18 \times 10^8 [\text{thiourea}]$$

(c) Substituting the sample's response into the equation for the calibration curve gives the concentration of thiourea as

$$[\text{thiourea}] = \frac{176 - 7.97}{2.18 \times 10^8} = 7.71 \times 10^{-7} \text{ M}$$

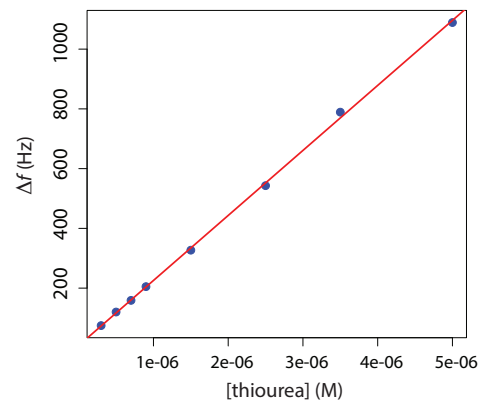
(d) To calculate the 95% confidence interval, we first calculate the standard deviation in the concentration using equation 5.25

$$s_{C_A} = \frac{9.799}{2.18 \times 10^8} \sqrt{\frac{1}{1} + \frac{1}{8} + \frac{(176 - 413.3)^2}{(2.18 \times 10^8)^2 (1.96 \times 10^{-11})}} = 4.89 \times 10^{-8}$$

where the standard deviation of the regression,  $s_r$ , is 9.799. The 95% confidence interval is

$$7.71 \times 10^{-7} \text{ M} \pm (2.447)(4.89 \times 10^{-8} \text{ M})$$

$$7.71 \times 10^{-7} \text{ M} \pm 1.20 \times 10^{-7} \text{ M}$$



**Figure SM8.5** Calibration curve for the data in Problem 8.38.

You can calculate  $s_r$  by hand using equation 5.19 in Chapter 5, or you can determine its value using Excel or R; the latter option is assumed here.

