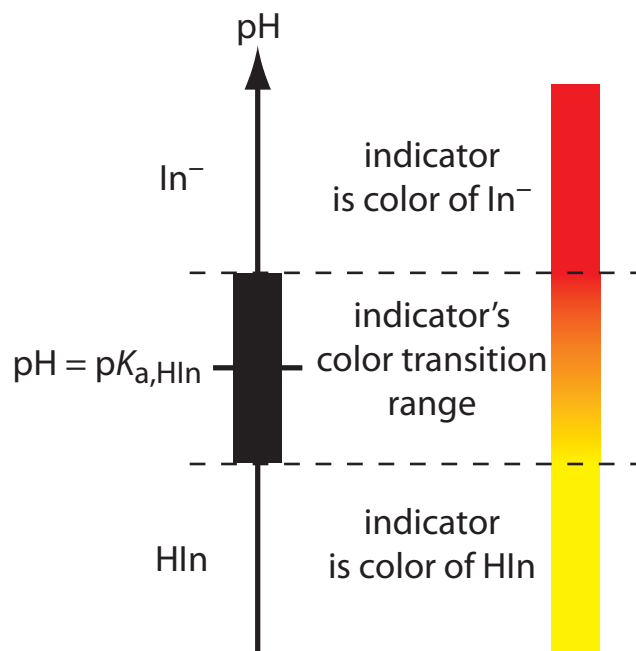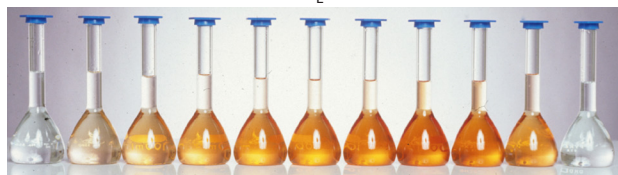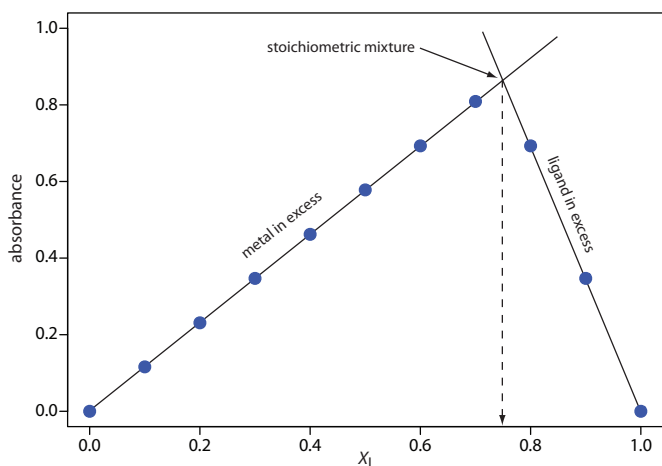# Analytical Chemistry 2.1
Solutions Manual

Production History

Print Version

Solutions Manual to Modern Analytical Chemistry by David Harvey
ISBN 0–697–39760–3
Copyright © 2000 by McGraw-Hill Companies
Copyright transferred to David Harvey, February 15, 2008

Electronic Version

Solutions Manual to Analytical Chemistry 2.1 by David Harvey (Summer 2016)

Copyright

Illustrations

All illustrations are original to this solutions manual and are covered by the copyright described in the previous section.

Table of Contents

Chapter 1

1. (a) A qualitative and a quantitative analysis is the best choice because we need to determine the identify of the possible contaminants and determine if their concentrations are greater than the expected background levels.

    (b) A forged work of art often contains compounds that are not present in authentic materials or contains a distribution of compounds that do not match the authentic materials. Either a qualitative analysis (to identify a compound that should not be present in authentic materials) or a quantitative analysis (to determine if the concentrations of compounds present do not match the distribution expected in authentic materials) is appropriate.

    (c) Because we are interested in detecting the presence of specific compounds known to be present in explosive materials, a qualitative analysis is the best choice.

    (d) A compound's structure is one of its characteristic properties; a characterization analysis, therefore, is the best approach.

    (e) In searching for a new acid–base indicator we are seeking to improve the performance of an existing analytical method, which requires a fundamental analysis of the method's properties.

    (f) A quantitative analysis is used to determine if an automobile emits too much carbon monoxide.

2. Answers to this problem will vary, but here is a list of important points that you might address:

    The goal of this research is to develop a fast, automated, and real-time instrumental method for determining a coffee's sensory profile that yields results similar to those from trained human sensory panels.

    One challenge the authors have to address is that a human sensory panelist reports results on a relative scale, typically 0–10, for characteristics that are somewhat arbitrary: What does it mean, for example, to say that a coffee is bitter? An instrumental method, on the other hand, reports results on an absolute scale and for a clearly defined signal; in this case, the signal is a raw count of the number of ions with a particular mass–to-charge ratio. Much of the mathematical processing described by the authors is used to transform the instrumental data into a relative form and to normalize the two sets of data to the same relative scale.

    The instrumental technique relies on gas chromatography equipped with a mass spectrometer as a detector. The specific details of the instrument are not important, but the characteristics the authors describe—low fragmentation, high time resolution, broad linear dy-

See Chapter 12 for a discussion of gas chromatography and for detection using a mass spectrometer.

namic range—are important. When a species enters a mass spectrometer it is ionized (the PTR—proton transfer reaction—in PTR-MS simply describes the method of ionization) and the individual ions, being unstable, may decompose into smaller ions. As a roasted coffee has more than 1000 volatile components, many of which do not contribute to the sensory profile, the authors wish to limit the number of ions produced in the mass spectrometer. In addition, they want to ensure that the origin of each ion traces back to just a small number of volatile compounds so that the signal for each ion carries information about a small number of compounds. Table 1, for example, shows that the 16 ions monitored in this study trace back to just 32 unique volatile compounds, and that, on average, each ion traces back to 3–4 unique volatile compounds with a range of one to eight.

The authors need high time resolution so that they can monitor the release of volatile species as a function of time, as seen in Figure 1, and so that they can report the maximum signal for each ion during the three-minute monitoring period. A rapid analysis also means they can monitor the production of coffee in real time on the production line instead of relying on a lengthy off-line analysis completed by a sensory panel. This is advantageous when it comes to quality control where time is important.

For a discussion of quality control and quality assurance, see Chapter 15.

A broad linear dynamic range simply means there is a linear relationship between the measured signal and the concentration of the compounds contributing to that signal over a wide range of concentrations. The assumption of a linear relationship between signal and concentration is important because a relative change in concentration has the same affect on the signal regardless of the original concentration. A broad range is important because it means the signal is sensitive to a very small concentration of a volatile compound and that the signal does not become saturated, or constant, at higher concentrations of the volatile compound; thus, the signal carries information about a much wider range of concentrations.

For a discussion of the relationship between signal and concentration, see Chapter 5.

To test their method, the authors divide their samples into two sets: a training set and a validation set. The authors use the training set to build a mathematical model that relates the normalized intensities of the 16 ions measured by the instrument to the eight normalized relative attributes evaluated by members of the sensory panel. The specific details of how they created the mathematical model are not important here, but the agreement between the panel's sensory profile and that predicted using the instrumental method generally is very good (see Figure 3; note that the results for Espresso No. 5 and No. 11 show the least agreement).

Any attempt to create a model that relates one measurement (results from the sensory panel) to a second measurement (results from the

instrumental analysis) is subject to a number of limitations, the most important of which is that the model works well for the data set used to build the model, but that it fails to work for other samples. To test the more general applicability of their model—what they refer to as a robust model—the authors use the model to evaluate the data in their validation set; the results, shown in Figure 4, suggest that the can apply their model both to coffees of the same type, but harvested in a different year, and to coffees of a different type.

See Chapter 14 for a discussion of robustness and other ways to characterize an analytical method.

Chapter 2

1. (a) 3 significant figures; (b) 3 significant figures; (c) 5 significant figures; (d) 3 significant figures; (e) 4 significant figures; (f) 3 significant figures

   For (d) and for (e), the zero in the tenths place is not a significant digit as its presence is needed only to indicate the position of the decimal point. If you write these using scientific notation, they are 9.03×10^{-2} and 9.030×10^{-2}, with three and four significant figures respectively.

2. (a) 0.894; (b) 0.893; (c) 0.894; (d) 0.900; (e) 0.0891

3. (a) 12.01; (b) 16.0; (c) 6.022×10^{23} mol^{-1}; (d) 9.65×10^{4} C/mol

4. a. $4.\mathbf{5}91 + 0.\mathbf{2}309 + 67.\mathbf{1} = 71.\mathbf{9}219 \approx 71.9$

   b. $31\mathbf{3} - 27\mathbf{3}.15 = 3\mathbf{9}.85 \approx 39.8$

   Note that for (b) we retain an extra significant figure beyond that suggested by our simple rules so that the uncertainty in the final answer (1 part out of 398) is approximately the same as the most uncertain of our two measurements (1 part out of 313). Reporting the answer as 40, or 4.0×10^{1}, as suggested by our simple rules, gives an uncertainty in the final result of 1 part out of 40, which is substantially worse than either of our two measurements.

   c. $712 \times \mathbf{8.6} = \mathbf{61}23.2 \approx 6.1 \times 10^{3}$

   d. $1.43/0.0\mathbf{26} = \mathbf{55}.00 \approx 55$

   e. $(8.314 \times \mathbf{298})/96\,485 = 0.0\mathbf{256}783 \approx 2.57 \times 10^{-2}$

   f. $\log(\mathbf{6.53} \times 10^{-5}) = -4.\mathbf{185}09 = -4.185$

   Note that when we take the logarithm of a number, any digits before the decimal point provide information on the original number's power of 10; thus, the 4 in –4.185 is not counted as a significant digit.

   g. $10^{-7.\mathbf{14}} = \mathbf{7.2}44 \times 10^{-8} \approx 7.2 \times 10^{-8}$

   Note that we take the antilog of a number, the digits before the decimal point provide information on the power of 10 for the resulting answer; thus, the 7 in –7.14 is not counted as a significant digit.

   h. $(\mathbf{6.51} \times 10^{-5}) \times (8.14 \times 10^{-9}) = \mathbf{5.29}914 \times 10^{-13} \approx 5.30 \times 10^{-13}$

5. To find the %w/w Ni, we first subtract the mass of Co from point B from the combined mass of Ni and Co from point B, and then divide by the mass of sample; thus

$$\frac{(0.2306 - 0.0813) \text{ g Ni}}{12.1374 \text{ g sample}} \times 100 =$$

$$\frac{0.1493 \text{ g Ni}}{12.1374 \text{ g sample}} = 1.230 \text{ \%w/w Ni}$$

In problem 4 we use a bold **red** font to help us keep track of significant figures. For example, in (a) we mark the last significant digit common to the numbers we are adding together, and in (e), where we are multiplying and dividing, we identify the number with the smallest number of significant digits.

For problems in this chapter, all formula weights are reported to the number of significant figures allowed by the atomic weights in Appendix 18. As a compound's formula weight rarely limits the uncertainty in a calculation, in later chapters usually we will round formula weights to a smaller number of significant figures, chosen such that it does not limit the calculation's uncertainty.

For problem 7 we include an extra significant figure in each of the calculation's first two steps to avoid the possibility of introducing a small error in the final calculation as a result of rounding. If we need to report the result for an intermediate calculation, then we round that result appropriately; thus, we need to isolate 3.61×10^{-3} mol of $BaCl_2$.

6. Using the atomic weights from Appendix 18, we find that the formula weight for $Ni(C_4H_{14}N_4O_4)_2$ is

$$(58.693) + (8 \times 12.011) + (14 \times 1.008) +$$
$$(4 \times 14.007) + (4 \times 15.999) = 288.917 \text{ g/mole}$$

7. First we convert the mass of Cl^- to moles of Cl^-

$$256 \text{ mg } Cl^- \times \frac{1 \text{ g } Cl^-}{1000 \text{ mg } Cl^-} \times$$
$$\frac{1 \text{ mol } Cl^-}{35.45 \text{ g } Cl^-} = 7.221 \times 10^{-3} \text{ mol } Cl^-$$

and then the moles of Cl^- to the moles of $BaCl_2$

$$7.221 \times 10^{-3} \text{ mol } Cl^- \times \frac{1 \text{ mol } BaCl_2}{2 \text{ mol } Cl^-} = 3.610 \times 10^{-3} \text{ mol } BaCl_2$$

and finally the moles of $BaCl_2$ to the volume of our $BaCl_2$ solution

$$3.610 \times 10^{-3} \text{ mol } BaCl_2 \times$$
$$\frac{1 \text{ L}}{0.217 \text{ mol } BaCl_2} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 16.6 \text{ mL}$$

8. We can express a part per million in several ways—this is why some organizations recommend against using the abbreviation ppm—but here we must assume that the density of the solution is 1.00 g/mL and that ppm means mg/L or µg/mL. As molarity is expressed as mol/L, we will use mg/L as our starting point; thus

$$\frac{0.28 \text{ mg } Pb}{L} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol } Pb}{207.2 \text{ g } Pb} = 1.4 \times 10^{-6} \text{ M } Pb$$

9. (a) The molarity of 37.0% w/w HCl is

$$\frac{37.0 \text{ g } HCl}{1.00 \times 10^2 \text{ g solution}} \times \frac{1.18 \text{ g solution}}{\text{ml solution}} \times$$
$$\frac{1000 \text{ mL}}{L} \times \frac{1 \text{ mol } HCl}{36.46 \text{ g } HCl} = 12.0 \text{ M } HCl$$

(b) To calculate the mass and volume of solution we begin with the molarity calculated in part (a). To avoid any errors due to rounding the molarity down to three significant, we will return one additional significant figure, taking the molarity as 11.97 M.

$$0.315 \text{ mol } HCl \times \frac{1 \text{ L}}{11.97 \text{ mol } HCl} \times$$
$$\frac{1000 \text{ mL}}{L} \times \frac{1.18 \text{ g solution}}{\text{mL}} = 31.1 \text{ g}$$

$$0.315 \text{ mol } HCl \times \frac{1 \text{ L}}{11.97 \text{ mol } HCl} \times \frac{1000 \text{ mL}}{L} = 26.3 \text{ mL}$$

10. A volume of 1.0×10^3 mL is equivalent to 1.0 L; thus

$$1.0\,L \times \frac{0.036\ mol\ NH_3}{L} \times \frac{17.031\ g\ NH_3}{mol\ NH_3} \times$$

$$\frac{1.00 \times 10^2\ g\ solution}{28.0\ g\ NH_3} \times \frac{1.00\ mL}{0.899\ g\ solution} = 2.4\ mL$$

11. As we have information about the solution's volume and no informa-tion about its density, we will assume that ppm and ppb are expressed as a mass of analyte per unit volume; thus,

$$\frac{45.1\ \mu g}{250.0\ ml} \times \frac{1\ g}{1 \times 10^6\ \mu g} \times 100 = 1.80 \times 10^{-5}\ \%\ w/w$$

$$\frac{45.1\ \mu g}{250.0\ ml} = 0.180\ ppm$$

$$\frac{45.1\ \mu g}{250.0\ ml} \times \frac{1000\ mL}{L} = 1.80 \times 10^2\ ppb$$

12. To obtain a total concentration of 1.6 ppm F^- we must add sufficient NaF such that we increase the concentration of F^- by 1.4 ppm; thus

$$1\,gal \times \frac{3.785\ L}{gal} \times \frac{1.4\ mg\ F^-}{L} \times$$

$$\frac{41.988\ mg\ NaF}{18.998\ mg\ F^-} = 12\ mg\ NaF$$

Note that "per gallon" implies that 1 gal is an exact number that does not limit the number of significant figures in our final answer.

13. $pH = -\log[H^+] = -\log(6.92\times10^{-6}) = 5.160$

$[H_3O^+] = 10^{-pH} = 10^{-8.923} = 1.19\times10^{-9}\ M$

14. When using a 25-mL graduated cylinder to measure 15 mL, the ab-solute uncertainty is $\pm1\%$ of 25 mL, or ±0.25 mL and the relative uncertainty is

$$\frac{\pm0.25\ mL}{15\ mL} \times 100 = \pm1.7\%$$

When using a 50-mL graduated cylinder to measure 15 mL, the ab-solute uncertainty is $\pm1\%$ of 50 mL, or ±0.50 mL and the relative uncertainty is

$$\frac{\pm0.50\ mL}{15\ mL} \times 100 = \pm3.3\%$$

15. First, we calculate the moles of $K_2Cr_2O_7$

$$9.67\ g\ K_2Cr_2O_7 \times \frac{1\ mol\ K_2Cr_2O_7}{294.181\ g\ K_2Cr_2O_7} = 0.03287\ mol\ K_2Cr_2O_7$$

and then we calculate the solution's molarity

$$\frac{0.03287\ mol\ K_2Cr_2O_7}{0.1000\ L} = 0.329\ M\ K_2Cr_2O_7$$

16. Given that the uncertainty in the volume and in the concentration is 1% (1.0 L $\pm$ 0.1 L or 0.10 M $\pm$ 0.01 M), we can prepare these

Given the uncertainty in the volume and in the concentration, there is no advantage to taking the extra time needed to measure the solid's mass to three or four decimal places, to quantitatively transfer the solid to a volumetric flask, and dilute to volume.

solution by weighing out the appropriate amount of solid to two significant figures, place it in a 1-L beaker or bottle, and dissolve in 1000 mL of water. What remains is to calculate the amount of reagent for each solution; thus: (a) for KCl we have

$$1.0\,L \times \frac{0.10\,mol\,K^+}{L} \times \frac{1\,mol\,KCl}{mol\,K^+} \times \frac{74.55\,g\,KCl}{mol\,KCl} = 7.5\,g\,KCl$$

$$1.0\,L \times \frac{1.0 \times 10^2\,mg\,K^+}{L} \times \frac{1\,g\,K^+}{1000\,mg\,K^+}$$

$$\times \frac{74.55\,g\,KCl}{39.098\,g\,K^+} = 0.19\,g\,KCl$$

$$1.0\,L \times \frac{1000\,mL}{L} \times \frac{1.0\,g\,K^+}{1.0 \times 10^2\,mL}$$

$$\times \frac{74.55\,g\,KCl}{39.098\,g\,K^+} = 19\,g\,KCl$$

and (b) for K_2SO_4 we have

$$1.0\,L \times \frac{0.10\,mol\,K^+}{L} \times \frac{1\,mol\,K_2SO_4}{2\,mol\,K^+}$$

$$\times \frac{174.25\,g\,K_2SO_4}{mol\,K_2SO_4} = 8.7\,g\,K_2SO_4$$

$$1.0\,L \times \frac{1.0 \times 10^2\,mg\,K^+}{L} \times \frac{1\,g\,K^+}{1000\,mg\,K^+}$$

$$\times \frac{174.25\,g\,K_2SO_4}{78.196\,g\,K^+} = 0.22\,g\,K_2SO_4$$

$$1.0\,L \times \frac{1000\,mL}{L} \times \frac{1.0\,g\,K^+}{1.0 \times 10^2\,mL}$$

$$\times \frac{174.25\,g\,K_2SO_4}{78.196\,g\,K^+} = 22\,g\,K_2SO_4$$

and (c) for $K_3Fe(CN)_6$ we have

$$1.0\,L \times \frac{0.10\,mol\,K^+}{L} \times \frac{1\,mol\,K_3Fe(CN)_6}{3\,mol\,K^+}$$

$$\times \frac{329.247\,g\,K_3Fe(CN)_6}{mol\,K_3Fe(CN)_6} = 11\,g\,K_3Fe(CN)_6$$

$$1.0\,L \times \frac{1.0 \times 10^2\,mg\,K^+}{L} \times \frac{1\,g\,K^+}{1000\,mg\,K^+}$$

$$\times \frac{329.247\,g\,K_3Fe(CN)_6}{117.294\,g\,K^+} = 0.28\,g\,K_3Fe(CN)_6$$

$$1.0\,L \times \frac{1000\,mL}{L} \times \frac{1.0\,g\,K^+}{1.0 \times 10^2\,mL}$$

$$\times \frac{329.247\,g\,K_3Fe(CN)_6}{117.294\,g\,K^+} = 28\,g\,K_3Fe(CN)_6$$

17. For a serial dilution, we need the concentration of solution A to calculate the concentration of solution B, and the concentration of solution B to calculate the concentration of solution A; thus

$$\text{Solution A: } 0.100 \text{ M} \times \frac{10.00 \text{ mL}}{250.0 \text{ mL}} = 4.00 \times 10^{-3} \text{ M}$$

$$\text{Solution B: } 4.00 \times 10^{-3} \text{ M} \times \frac{25.00 \text{ mL}}{100.0 \text{ mL}} = 1.00 \times 10^{-3} \text{ M}$$

$$\text{Solution C: } 1.00 \times 10^{-3} \text{ M} \times \frac{20.00 \text{ mL}}{500.0 \text{ mL}} = 4.00 \times 10^{-5} \text{ M}$$

18. When we dissolve 1.917 g NaCl in 50 mL of water measured using a graduated cylinder, the reported concentration of NaCl is limited to just two significant figures because the uncertainty for the graduated cylinder is approximately 1%, or 1 part in 50; thus

$$\frac{1.917 \text{ g NaCl} \times \dfrac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}}}{0.050 \text{ L}} = 0.66 \text{ M NaCl}$$

When we quantitatively transfer this solution to a 250.0 mL volumetric flask and dilute to volume, we can report the concentration of NaCl to four significant figures because the uncertainty in the volumetric flask is ± 0.01 mL, or 1 part in 2500; thus

$$\frac{1.917 \text{ g NaCl} \times \dfrac{1 \text{ mol NaCl}}{58.44 \text{ g NaCl}}}{0.2500 \text{ L}} = 0.1312 \text{ M NaCl}$$

Note that the second calculation does not begin with the concentration from the previous calculation, as we did in problem 17 for a serial dilution. A quantitative transfer is not a serial dilution; instead, all 1.917 g of NaCl added to the 50-mL beaker is transfered to the 250.0 mL volumetric flask, so we begin our calculation with this mass of NaCl.

As we are interested only in the concentration of NaCl in our final solution, there is no particular reason for us to complete the intermediate calculation; we did so here simply to make this point: The uncertainty in a calculated result is determined by the measurements that contribute to the calculation only, and is not affected by other measurements that we happen to make. What matters in this case is that 1.917 g of NaCl are dissolved in 250.0 mL of water. If we fail to complete a quantitative transfer, then our calculated concentration is in error, but this is an error in the accuracy of our work, not an uncertainty in the inherent precision of the balance or volumetric pipet. We will have more to say about accuracy and precision in Chapter 4.

19. First, we calculate the moles of NO_3^- in 50.0 mL of 0.050 M KNO_3 and in 40.0 mL of 0.075 M KNO_3.

$$0.0500 \text{ L} \times \frac{0.050 \text{ mol NO}_3^-}{\text{L}} = 2.50 \times 10^{-3} \text{ mol NO}_3^-$$

$$0.0400 \text{ L} \times \frac{0.075 \text{ mol NO}_3^-}{\text{L}} = 3.00 \times 10^{-3} \text{ mol NO}_3^-$$

Next, we add together these results to obtain the total moles of NO_3^- in the combined solutions, and then divide by the total volume to find the concentration of NO_3^- and pNO_3^-.

$$\frac{2.50 \times 10^{-3} \text{ mol NO}_3^- + 3.00 \times 10^{-3} \text{ mol NO}_3^-}{0.0500 \text{ L} + 0.0400 \text{ L}} = 0.061 \text{ M NO}_3^-$$

$$pNO_3^- = -\log(NO_3^-) = -\log(0.061) = 1.21$$

Here, again, we keep an extra significant figure through the intermediate steps of our calculation.

20. First, we calculate the moles of Cl^- in 25.0 mL of 0.025 M NaCl and in 35.0 mL of 0.050 M $BaCl_2$.

$$0.0250 \text{ L} \times \frac{0.025 \text{ mol NaCl}}{\text{L}} \times \frac{1 \text{ mol Cl}^-}{\text{mol NaCl}} = 6.25 \times 10^{-4} \text{ mol Cl}^-$$

$$0.0350 \text{ L} \times \frac{0.050 \text{ mol BaCl}_2}{\text{L}} \times \frac{2 \text{ mol Cl}^-}{\text{mol BaCl}_2} = 3.50 \times 10^{-3} \text{ mol Cl}^-$$

Next, we add together these results to obtain the total moles of Cl^- in the combined solutions, and then divide by the total volume to find the concentration of Cl^- and pCl.

$$\frac{6.25 \times 10^{-4} \text{ mol Cl}^- + 3.50 \times 10^{-3} \text{ mol Cl}^-}{0.0250 \text{ L} + 0.0350 \text{ L}} = 0.069 \text{ M Cl}^-$$

$$\text{pCl}^- = -\log(\text{Cl}^-) = -\log(0.069) = 1.16$$

21. The concentration is

$$0.0844 \text{ M ethanol} \times \frac{0.500 \text{ L}}{0.0050 \text{ L}} = 8.44 \text{ M ethanol}$$

Chapter 3

1. In a total analysis technique the signal is proportional to the absolute amount of analyte, in grams or in moles, in the original sample. If we double the amount of sample, then the signal also doubles. For this reason, an accurate analysis requires that we recover all analyte present in the original sample, which is accomplished here in two key ways: (a) the beaker in which the digestion is carried out is rinsed several times and the rinsings are passed through the filter paper, and (b) the filter paper itself is rinsed several times. The volume of solvent used in the digestion and the volumes used to rinse the beaker and the filter paper are not critical because they do not affect the mass or moles of analyte in the filtrate.

    In a concentration technique the signal is proportional to the relative amount, or concentration of analyte, which means our treatment of the sample must not change the analyte's concentration or it must allow us to do so in a precise way. Having completed the digestion, we need to ensure that the concentration of analyte in the beaker and the concentration of analyte in the filtrate are the same, which is accomplished here by not washing the beaker or the filter paper, which would dilute the analyte's concentration, and by taking a precisely measured volume of the filtrate to the next step in the procedure. Because we know precisely the original volume of sample (25.00 mL) and the volume of filtrate taken (5.00 mL), we can work back from the concentration of analyte in the filtrate to the absolute amount of analyte in the original sample.

2. (a) Here we must assume that a part per billion is expressed as a mass per unit volume, which, in this case, is best expressed as ng/mL; thus

    $$\frac{10 \text{ ng}}{\text{mL}} \times 0.5 \text{ mL} = 5 \text{ ng}$$

    (b) A concentration of 10% w/v is equivalent to 10 g of analyte per 100 mL of sample or 10^8 ng/mL. Because the final concentration is 10 ng/mL, we must dilute the sample by a factor of 10^7, which we can accomplish, for example, by diluting 0.1 µL of sample to a final volume of 1 L.

    (c) A concentration of 10% w/w is equivalent to 10 g of analyte per 100 g of sample. To prepare the solution we need to take

    $$1000 \text{ mL} \times \frac{10 \text{ ng analyte}}{\text{mL}} \times \frac{1 \text{ g analyte}}{10^9 \text{ ng analyte}} \times$$

    $$\frac{100 \text{ g sample}}{10 \text{ g analyte}} = 1 \times 10^{-4} \text{ g sample}$$

    or 0.1 mg of sample.

(d) This method is not particularly suited for a major analyte because we must dissolve a very small amount of sample (0.1 µL or 0.1 mg) in a large volume of solution (1000 mL), which is difficult to do with precision and with accuracy. We might consider a serial dilution from an initial solution that is more concentrated; however, multiple dilutions increase the opportunity for introducing error.

3. (a) The analyte's sensitivity, k_A, is

$$k_A = \frac{S_A}{C_A} = \frac{23.3}{15 \text{ ppm}} = 1.55 \text{ ppm}^{-1} \approx 1.6 \text{ ppm}^{-1}$$

(b) The interferent's sensitivity, k_I, is

$$k_I = \frac{S_I}{C_I} = \frac{13.7}{25 \text{ ppm}} = 0.548 \text{ ppm}^{-1} \approx 0.55 \text{ ppm}^{-1}$$

(c) The selectivity coefficient, $K_{A,I}$, is

$$K_{A,I} = \frac{k_I}{k_A} = \frac{0.548 \text{ ppm}^{-1}}{1.55 \text{ ppm}^{-1}} = 0.354 \approx 0.35$$

(d) Because k_A is greater than k_I, which makes $K_{A,I}$ less than one, we know that the method is more selective for the analyte than for the interferent.

(e) To achieve an error of less than 1% we know that

$$K_{A,I} \times C_I < 0.01 \times C_A$$

Rearranging for the ratio C_I/C_A and solving gives

$$\frac{C_I}{C_A} < \frac{0.01}{K_{A,I}} = \frac{0.01}{0.354} = 0.028 \approx 0.03$$

Thus, the interferent can be present with a concentration that is no more than 3% of the analyte's concentration.

4. We know that $S_{total} = S_A + S_{reag} = k_A C_A + S_{reag}$. Making appropriate substitutions

$$35.2 = (17.2 \text{ ppm}^{-1}) \times C_A + 0.06$$

and solving for C_A gives the analyte's concentration as 2.01 ppm.

5. A relative error of –2.0% means that

$$K_{Ca,Zn} \times C_{Zn} = -0.020 \times C_{Ca}$$

We know that the concentrations of Ca and Zn are in a 50:1 ratio, so it is convenient to assign a concentration of 50 to Ca and a concentration of 1 to Zn; making appropriate substitutions

$$K_{Ca,Zn} \times 1 = -0.02 \times 50$$

and solving for $K_{Ca,Zn}$ gives its value as –1.0. Note that an absolute value for $K_{Ca,Zn}$ of one implies the method is equally sensitive to the analyte, Ca, and the interferent, Zn, and that the negative sign for

$K_{Ca,Zn}$ implies the interferent, Zn, decreases the signal. A sample for which $C_{Ca} = C_{Zn}$ will have $S_{samp} = 0$!

6. In the absence of ascorbic acid the signal is

$$S_1 = k_{GL} \times C_{GL} = k_{GL} \times (10.0 \text{ ppb})$$

where GL represents glutathione. In the presence of ascorbic acid, AA, the signal is

$$S_2 = k_{GL}(C_{GL} + K_{GL,AA} \times C_{AA}) = k_{GL}(10.0 \text{ ppb} + K_{GL,AA} \times 1.5 \text{ ppb})$$

We know that the signal in the presence of ascorbic acid, S_1, is $5.43\times$ the signal in the absence of ascorbic acid, S_2; thus

$$\frac{S_2}{S_1} = 5.43 = \frac{k_{GL}(10.0 \text{ ppb} + K_{GL,AA} \times 1.5 \text{ ppb})}{k_{GL} \times (10.0 \text{ ppb})}$$

$$5.43 = \frac{10.0 \text{ ppb} + K_{GL,AA} \times 1.5 \text{ ppb}}{10.0 \text{ ppb}}$$

$$54.3 \text{ ppb} = 10.0 \text{ ppb} + K_{GL,AA} \times (1.5 \text{ ppb})$$

Solving for $K_{GL,AA}$ gives its value as 3.0×10^1. When the interferent is methionine, which we abbreviate as ME, we have

$$\frac{S_2}{S_1} = 0.906 = \frac{k_{GL}(10.0 \text{ ppb} + K_{GL,ME} \times 3.5 \times 10^2 \text{ ppb})}{k_{GL} \times (10.0 \text{ ppb})}$$

$$\frac{S_2}{S_1} = 0.906 = \frac{10.0 \text{ ppb} + K_{GL,ME} \times 3.5 \times 10^2 \text{ ppb}}{10.0 \text{ ppb}}$$

$$9.06 \text{ ppb} = 10.0 \text{ ppb} + K_{GL,ME} \times (3.50 \times 10^2 \text{ ppb})$$

which gives $K_{GL,ME}$ as -0.0027. There are two important differences between these two interferents. First, although the method is more sensitive for that analyte glutathione than it is for the interferent methionine (the absolute value for $K_{GL,ME}$ is less than one), it is more sensitive for the interferent ascorbic acid than it is for the analyte glutathione ($K_{GL,AA}$ is greater than one). Second, the positive value for $K_{GL,AA}$ indicates that ascorbic acid increases the total signal and the negative value for $K_{GL,ME}$ indicates that methionine decreases the total signal.

7. (a) In the absence of ascorbic acid the signal is

$$S_1 = k_{GA} C_{GA}$$

where GA represents glycolic acid, and in the presence of ascorbic acid, AA, the signal is

$$S_2 = k_{GA}(C_{GA} + K_{GA,AA} \times C_{AA})$$

We know that the signal in the presence of ascorbic acid, S_1, is $1.44\times$ the signal in the absence of ascorbic acid, S_2; thus

$$1.44 = \frac{k_{GA}(C_{GA} + K_{GA,AA} \times C_{AA})}{k_{GA} C_{GA}} = \frac{C_{GA} + K_{GA,AA} \times C_{AA}}{C_{GA}}$$

$$1.44 = \frac{(1 \times 10^{-4} \text{ M}) + K_{GA,AA} \times (1 \times 10^{-5} \text{ M})}{1 \times 10^{-4} \text{ M}}$$

Solving for $K_{GA,AA}$ gives its value as 4.4.

(b) The method is more selective for the interferent, ascorbic acid, than it is for the analyte, glycolic acid, because $K_{GA,AA}$ is greater than one.

(c) To avoid an error of more than 1%, we require that

$$K_{GA,AA} \times C_{AA} < 0.01 \times C_{GA}$$

which requires that

$$C_{GA} > \frac{K_{GA,AA} \times C_{AA}}{0.01} = \frac{4.4 \times (1.0 \times 10^{-5} \text{ M})}{0.01} = 4.4 \times 10^{-3} \text{ M}$$

8. (a) To determine the sensitivity for the analyte, we begin with the equation $S_{samp} = k_A C_A$ and solve for k_A; thus

$$k_A = \frac{S_{samp}}{C_A} = \frac{7.45 \times 10^{-5} \text{ A}}{1.12 \times 10^{-6} \text{ M}} = 66.5 \text{ A/M}$$

(b) In the presence of an interferent, the signal is

$$S_{samp} = k_A(C_A + K_{A,I} \times C_I)$$

Rearranging to solve for $K_{A,I}$ and making appropriate substitutions

$$K_{A,I} = \frac{S_{samp} - k_A C_A}{k_A C_I}$$

$$= \frac{4.04 \times 10^{-5} \text{ A} - (66.5 \text{ A/M}) \times (1.12 \times 10^{-6} \text{ M})}{(66.5 \text{ A/M}) \times (6.5 \times 10^{-5} \text{ M})}$$

gives -7.9×10^{-3} as the value for $K_{A,I}$.

(c) The method is more selective for the analyte, hypoxanthine, than for the interferent, ascorbic acid, because the absolute value of $K_{A,I}$ is less than one.

(d) To avoid an error of 1.0% requires that $K_{A,I} \times C_I < -0.01 \times C_A$, where we use a relative error of -0.010 because the interferent decreases the signal (note that $K_{A,I}$ is negative). Rearranging and making appropriate substitutions gives

$$C_I < \frac{-0.010 C_A}{K_{A,I}} = \frac{-0.010 \times (1.12 \times 10^{-6} \text{ M})}{-7.9 \times 10^{-3}}$$

or a concentration of ascorbic acid less than 1.4×10^{-6} M.

9. Answers will vary with the selected procedure, but what follows is an example of a typical response.

Surfactants are compounds that decrease the surface tension between normally immiscble compounds, allowing them to mix together. Common examples of surfactants, which have many practical applications, include detergents and emulsifiers. Many surfactants consist of a long non-polar hydrocarbon chain of 10–20 carbon atoms with a polar functional group on one end that either carries a charge (anionic or cationic) or is neutral. Although surfactants themselves generally are not a health hazard, their presence in the environment may help solubilize other, more harmful compounds. One method for determining the concentration of anionic surfactants in water is the Methylene Blue Method for Methylene-Blue-Active Substances (MBAS), which is Method 5540 C in *Standard Methods for the Examination of Water and Wastewater*.

This method relies on the reaction of methylene blue (MB), which is a cationic dye, with anionic surfactants to form a neutral complex. The aqueous sample is made slightly basic, a strongly acidic solution of MB is added, and the resulting complex extracted into chloroform. When the extraction is complete, the chloroform layer is isolated and then washed with an acidic solution of water to remove interferents. The intensity of the complex's color in chloroform is proportional to the concentration of anionic surfactants in the original sample.

The absorbance of the surfactant-MB complex is measured in a spectrophotometer using a cell with a 1-cm pathlength at a wavelength of 652 nm. A blank consisting of chloroform is used to calibrate the spectrophotometer.

Although a sample will contain a variety of different anionic surfactants, the method is standardized using a single, standard reference material of linear alkylbenzene sulfonates (LAS). A stock standard solution is prepared that is 1.00 g LAS/L, which is used to prepare a working standard solution that is 10.0 μg LAS/mL. At least five calibration standards are prepared from the working standard with concentrations of LAS in the range of 0.10 μg/mL to 2.0 μg/L.

The method is sensitive to a variety of interferents. If cationic surfactants are present, they will compete with methylene blue for the anionic surfactants, decreasing the reported concentration of MBAS; when present, their concentration is minimized by first passing the sample through a cation-exchange column. Some organic anions, such as chloride ions and organic sulfates, form complexes with methylene blue that also extract into chloroform, increasing the reported concentration of MBAS; these interferences are minimized by the acidic wash that follows the extraction step.

The volume of sample taken for the analysis is based on the expected MBAS concentration as follows: 400 mL if the expected concentra-

Not all anionic surfactants react with MB, which is why the procedure's name includes the qualifying statement "methylene-blue-active substances. (MBAS)" The most important class of MBAS surfactants are linear alkylbenzene sulfonates (LAS) with the general formula $R–C_6H_4SO_3^-$ where R is an linear alkyl chain of 10–14 carbons.

See Chapter 7 for more details on solvent extractions.

See Chapter 10 for more details about absorption spectrophotometry.

See Chapter 5 for more details about methods of standardization, including calibration curves.

See Chapter 12 for more details about ion-exchange.

tion is between 0.025–0.080 mg/L; 250 mL if the expected concentration is between 0.08–0.40 mg/L; and 100 mL if the expected concentration is between 0.4–2.0 mg/L. If the expected concentration is greater than 2 mg/L, a sample that contains between 40–200 μg is diluted to 100 mL with distilled water.

Chapter 4

Most of the problems in this chapter require the calculation of a data set's basic statistical characteristics, such as its mean, median, range, standard deviation, or variance. Although equations for these calculations are highlighted in the solution to the first problem, for the remaining problems, both here and elsewhere in this text, such values simply are provided. Be sure you have access to a scientific calculator, a spreadsheet program, such as Excel, or a statistical software program, such as R, and that you know how to use it to complete these most basic of statistical calculations.

1. The mean is obtained by adding together the mass of each quarter and dividing by the number of quarters; thus

    $$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$
    $$= \frac{5.683 + 5.549 + \cdots + 5.554 + 5.632}{12}$$
    $$= 5.583 \text{ g}$$

    To find the median, we first order the data from the smallest mass to the largest mass

    $$5.536 \quad 5.539 \quad 5.548 \quad 5.549 \quad 5.551 \quad 5.552$$
    $$5.552 \quad 5.554 \quad 5.560 \quad 5.632 \quad 5.683 \quad 5.684$$

    and then, because there is an even number of samples, take the average of the $n/2$ and the $n/2+1$ values; thus

    $$\widetilde{X} = \frac{X_6 + X_7}{2} = \frac{5.552 + 5.552}{2} = 5.552 \text{ g}$$

    The range is the difference between the largest mass and the smallest mass; thus

    $$w = X_{\text{largest}} - X_{\text{smallest}} = 5.684 - 5.536 = 0.148 \text{ g}$$

    The standard deviation for the data is

    $$s = \sqrt{\frac{\sum_{i}^{n} (X_i - \overline{X})^2}{n - 1}}$$
    $$= \sqrt{\frac{(5.683 - 5.583)^2 + \cdots + (5.632 - 5.583)^2}{12 - 1}}$$
    $$= 0.056 \text{ g}$$

    The variance is the square of the standard deviation; thus

    $$s^2 = (0.056)^2 = 3.1 \times 10^{-3}$$

As a reminder, if we have an odd number of data points, then the median is the middle data point in the rank-ordered data set, or, more generally, the value of the $(n+1)/2$ data point in the rank-ordered data set where n is the number of values in the data set.

The variance in this case has units of g^2, which is correct but not particularly informative in an intuitive sense; for this reason, we rarely attach a unit to the variance. See Rumsy, D. J. *Journal of Statistics Education* **2009**, *17(3)* for an interesting argument that the variance should be excluded for summary statistics.
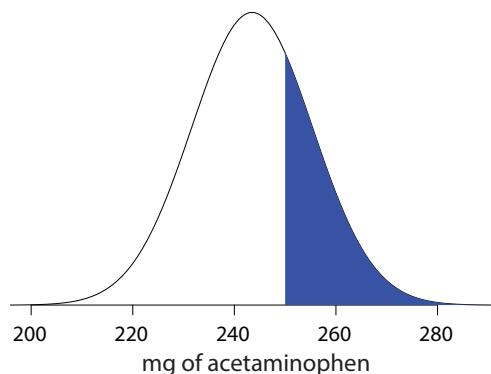
2. (a) The values are as follows:

    mean: 243.5 mg

    median: 243.4 mg

    range: 37.4 mg

    standard deviation: 11.9 mg

    variance: 141

    (b) We are interested in the area under a normal distribution curve that lies to the right of 250 mg, as shown in Figure SM4.1. Because this limit is greater than the mean, we need only calculate the deviation, z, and look up the corresponding probability in Appendix 3; thus,

    $$z = \frac{X - \mu}{\sigma} = \frac{250 - 243.5}{11.9} = 0.546$$

    From Appendix 3 we see that the probability is 0.2946 when z is 0.54 and 0.2912 when z is 0.55. Interpolating between these values gives the probability for a z of 0.546 as

    $$0.2946 - 0.6(0.2946 - 0.2912) = 0.2926$$

    Based on our experimental mean and standard deviation, we expect that 29.3% of the tablets will contain more than 250 mg of acetaminophen.

3. (a) The means and the standard deviations for each of the nominal dosages are as follows:

nominal dosage	mean	std. dev.
100-mg	95.56	2.16
60-mg	55.47	2.11
30-mg	26.85	1.64
10-mg	8.99	0.14

    (b) We are interested in the area under a normal distribution curve that lies to the right of each tablet's nominal dosage, as shown in Figure SM4.2 for tablets with a nominal dosage of 100-mg. Because the nominal dosage is greater than the mean, we need only calculate the deviation, z, for each tablet and look up the corresponding probability in Appendix 3. Using the 100-mg tablet as an example, the deviation is

    $$z = \frac{X - \mu}{\sigma} = \frac{100 - 95.56}{2.16} = 2.06$$

    for which the probability is 0.0197; thus, we expect that 1.97% of tablets drawn at random from this source will exceed the nominal dosage. The table below summarizes results for all four sources of tablets.

Figure SM4.1 Normal distribution curve for Problem 4.2 given a population with a mean of 243.5 mg and a standard deviation of 11.9 mg; the area in blue is the probability that a random sample has more than 250.0 mg of acetaminophen.
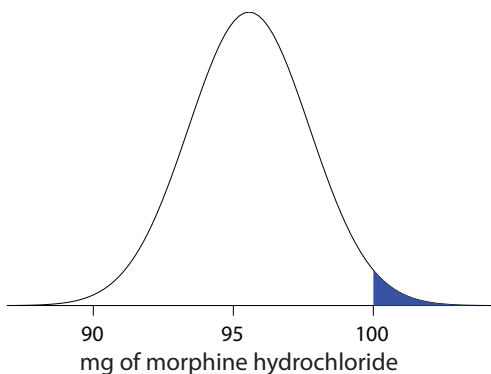

Figure SM4.2 Normal distribution curve for Problem 4.3 given a population with a mean of 95.56 mg and a standard deviation of 2.16 mg; the area in blue is the probability that a random sample has more than 100.0 mg of morphine hydrochloride.

nominal dosage	z	% exceeding nominal dosage
100-mg	2.06	1.97
60-mg	2.15	1.58
30-mg	1.92	2.74
10-mg	7.21	—

For tablets with a 10-mg nominal dosage, the value of z is sufficiently large that effectively no tablet is expected to exceed the nominal dosage.

4. The mean and the standard deviation for the eight spike recoveries are 99.5% and 6.3%, respectively. As shown in Figure SM4.3, to find the expected percentage of spike recoveries in the range 85%–115%, we find the percentage of recoveries that exceed the upper limit by calculating z and using Appendix 3 to find the corresponding probability

$$z = \frac{X - \mu}{\sigma} = \frac{115 - 99.5}{6.3} = 2.46 \text{ or } 0.695\%$$

and the percentage of recoveries that fall below the lower limit

$$z = \frac{X - \mu}{\sigma} = \frac{85 - 99.5}{6.3} = -2.30 \text{ or } 1.07\%$$

Subtracting these two values from 100% gives the expected probability of spike recoveries between 85%–115% as

$$100\% - 0.695\% - 1.07\% = 98.2\%$$

Figure SM4.3 Normal distribution curve for Problem 4.4 given a population with a mean of 99.5% and a standard deviation of 6.3%; the area in blue is the probability that a spike recovery is between 85% and 115%.

5. (a) Substituting known values for the mass, the gas constant, the temperature, the pressure, and the volume gives the compound's formula weight as

$$FW = \frac{(0.118 \text{ g}) (0.082056 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}) (298.2 \text{ K})}{(0.724 \text{ atm}) (0.250 \text{ L})} = 16.0 \text{ g/mol}$$

To estimate the uncertainty in the formula weight, we use a propagation of uncertainty. The relative uncertainty in the formula weight is

$$\frac{u_{FW}}{FW} = \sqrt{\begin{array}{c} \left(\frac{0.002}{0.118}\right)^2 + \left(\frac{0.000001}{0.082056}\right)^2 + \\ \left(\frac{0.1}{298.2}\right)^2 + \left(\frac{0.005}{0.724}\right)^2 + \left(\frac{0.005}{0.250}\right)^2 \end{array}} = 0.0271$$

which makes the absolute uncertainty in the formula weight

$$u_{FW} = 0.0271 \times 16.0 \text{ g/mol} = 0.43 \text{ g/mol}$$

The formula weight, therefore, is 16.0 ± 0.4 g/mol.

(b) To improve the uncertainty in the formula weight we need to identify the variables that have the greatest individual uncertainty. The relative uncertainties for the five measurements are
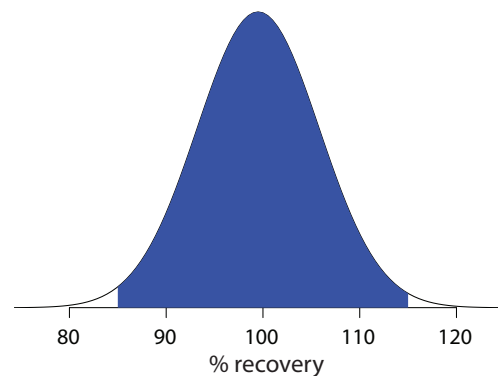
mass: $0.002/0.118 = 0.017$

gas constant: $0.000001/0.082056 = 1.22 \times 10^{-5}$

temperature: $0.1/298.2 = 3.4 \times 10^{-4}$

pressure: $0.005/0.724 = 0.007$

volume: $0.005/0.250 = 0.020$

Of these variables, the two with the largest relative uncertainty are the mass in grams and the volume in liters; these are the measurements where an improvement in uncertainty has the greatest impact on the formula weight's uncertainty.

6. (a) The concentration of Mn^{2+} in the final solution is

$$\frac{0.250 \text{ g}}{0.1000 \text{ L}} \times \frac{1000 \text{ mg}}{\text{g}} \times \frac{10.00 \text{ mL}}{500.0 \text{ mL}} = 50.0 \text{ mg/L}$$

To estimate the uncertainty in concentration, we complete a propagation of uncertainty. The uncertainties in the volumes are taken from Table 4.2; to find the uncertainty in the mass, however, we must account for the need to tare the balance. Taking the uncertainty in any single determination of mass as ± 1 mg, the absolute uncertainty in mass is

$$u_{\text{mass}} = \sqrt{((0.001)^2 + (0.001)^2} = 0.0014 \text{ g}$$

The relative uncertainty in the concentration of Mn^{2+}, therefore, is

$$\frac{u_C}{C} = \sqrt{\frac{\left(\frac{0.0014}{0.250}\right)^2 + \left(\frac{0.00008}{0.1000}\right)^2 +}{\left(\frac{0.02}{10.00}\right)^2 + \left(\frac{0.20}{500.0}\right)^2}} = 0.00601$$

which makes the relative uncertainty in the concentration

$$u_C = 0.00601 \times (50.0 \text{ ppm}) = 0.3 \text{ ppm}$$

The concentration, therefore, is 50.0 ± 0.3 ppm.

(b) No, we cannot improve the concentration's uncertainty by measuring the HNO_3 with a pipet instead of a graduated cylinder. As we can see from part (a), the volume of HNO_3 does not affect our calculation of either the concentration of Mn^{2+} or its uncertainty.

There is no particular need to tare the balance when we weigh by difference if the two measurements are made at approximately the same time; this is the usual situation when we acquire a sample by this method. If the two measurements are separated by a signifcant period of time, then we should tare the balance before each measurement and then include the uncertainty of both tares when we calculate the absolute uncertainty in mass.

7. The weight of the sample taken is the difference between the container's original weight and its final weight; thus, the mass is

$$\text{mass} = 23.5811 \text{ g} - 22.1559 \text{ g} = 1.4252 \text{ g}$$

and its absolute uncertainty is

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

The molarity of the solution is

$$\frac{1.4252 \text{ g}}{0.1000 \text{ L}} \times \frac{1 \text{ mol}}{121.34 \text{ g}} = 0.1175 \text{ M}$$

The relative uncertainty in this concentration is

$$\frac{u_C}{C} = \sqrt{\left(\frac{0.00014}{1.4252}\right)^2 + \left(\frac{0.01}{121.34}\right)^2 + \left(\frac{0.00008}{0.1000}\right)^2} = 0.00081$$

and the absolute uncertainty in the concentration is

$$u_C = 0.00081 \times (0.1175 \text{ M}) = 0.000095 \text{ M}$$

The concentration, therefore, is 0.1175 ± 0.0001 M.

8. The mean value for n measurements is

$$\overline{X} = \frac{\sum\limits_{i}^{n} X_i}{n}$$

$$= \frac{X_1 + X_2 + \cdots + X_{n-1} + X_n}{n}$$

$$= \frac{1}{n}\{X_1 + X_2 + \cdots + X_{n-1} + X_n\}$$

If we let the absolute uncertainty in the measurement of X_i equal σ, then a propagation of uncertainty for the sum of n measurements is

$$\sigma_{\overline{X}} = \frac{1}{n}\sqrt{(\sigma)_1^2 + (\sigma)_2^2 + \cdots + (\sigma)_{n-1}^2 + (\sigma)_n^2}$$

$$= \frac{1}{n}\sqrt{n(\sigma)^2} = \frac{\sqrt{n}}{n}\sigma = \frac{\sigma}{\sqrt{n}}$$

9. Because we are subtracting $\overline{X}_B$ from $\overline{X}_A$, a propagation of uncertainty of their respective uncertainties shows us that

$$u_{|\overline{X}_B - \overline{X}_A|} = \sqrt{\left(\frac{t_{\exp} s_A}{\sqrt{n_A}}\right)^2 + \left(\frac{t_{\exp} s_B}{\sqrt{n_B}}\right)^2}$$

$$= \sqrt{\frac{t_{\exp}^2 s_A^2}{n_A} + \frac{t_{\exp}^2 s_B^2}{n_B}}$$

$$= \sqrt{t_{\exp}^2 \left(\frac{s_A^2}{n_A} + \frac{s_A^2}{n_A}\right)}$$

$$= t_{\exp} \sqrt{\left(\frac{s_A^2}{n_A} + \frac{s_A^2}{n_A}\right)}$$

10. To have a relative uncertainty of less than 0.1% requires that we satisfy the following inequality

$$\frac{0.1 \text{ mg}}{x} \leq 0.001$$

where x is the minimum mass we need to take. Solving for x shows that we need to weigh out a sample of at least 100 mg.

11. It is tempting to assume that using the 50-mL pipet is the best option because it requires only two transfers to dispense 100.0 mL, providing

fewer opportunities for a determinate error; although this is true with respect to determinate errors, our concern here is with indeterminate errors. We can estimate the indeterminate error for each of the three methods using a propagation of uncertainty. When we use a pipet several times, the total volume dispensed is

$$V_{total} = \sum_i^n V_i$$

for the which the uncertainty is

$$u_{V_{total}} = \sqrt{(u_{V_1})^2 + (u_{V_2})^2 + \cdots + (u_{V_{n-1}})^2 + (u_{V_n})^2} = \sqrt{n(u_{V_i})^2}$$

The uncertainties for dispensing 100.0 mL using each pipet are:

$$\text{50-mL pipet: } u_{V_{total}} = \sqrt{2(0.05)^2} = 0.071 \text{ mL}$$

$$\text{25-mL pipet: } u_{V_{total}} = \sqrt{4(0.03)^2} = 0.060 \text{ mL}$$

$$\text{10-mL pipet: } u_{V_{total}} = \sqrt{10(0.02)^2} = 0.063 \text{ mL}$$

where the uncertainty for each pipet are from Table 4.2. Based on these calculations, if we wish to minimize uncertainty in the form of indeterminate errors, then the best option is to use a 25-mL pipet four times.

12. There are many ways to use the available volumetric glassware to accomplish this dilution. Shown here are the optimum choices for a one-step, a two-step, and a three-step dilution using the uncertainties from Table 4.2. For a one-step dilution we use a 5-mL volumetric pipet and a 1000-mL volumetric flask; thus

$$\frac{u_C}{C} = \sqrt{\left(\frac{0.01}{5.00}\right)^2 + \left(\frac{0.30}{1000.0}\right)^2} = 0.0020$$

For a two-step dilution we use a 50-mL volumetric pipet and a 1000-mL volumetric flask followed by a 50-mL volumetric pipet and a 500-mL volumetric flask; thus

$$\frac{u_C}{C} = \sqrt{\begin{array}{c}\left(\frac{0.05}{50.00}\right)^2 + \left(\frac{0.30}{1000.0}\right)^2 + \\ \left(\frac{0.05}{50.00}\right)^2 + \left(\frac{0.20}{500.0}\right)^2\end{array}} = 0.0015$$

Finally, for a three-step dilution we use 50-mL volumetric pipet and a 100-mL volumetric flask, a 50-mL volumetric flask and a 500-mL volumetric flask, and a 50-mL volumetric pipet and a 500-mL volumetric flask; thus

$$\frac{u_C}{C} = \sqrt{\begin{array}{c}\left(\frac{0.05}{50.00}\right)^2 + \left(\frac{0.08}{100.0}\right)^2 + \left(\frac{0.05}{50.00}\right)^2 + \\ \left(\frac{0.20}{500.0}\right)^2 + \left(\frac{0.05}{50.00}\right)^2 + \left(\frac{0.20}{500.0}\right)^2\end{array}} = 0.0020$$

The smallest uncertainty is obtained with the two-step dilution.

13. The mean is the average value. If each measurement, X_i, is changed by the same amount, ΔX, then the total change for n measurement is $n\Delta X$ and the average change is $n\Delta X/n$ or ΔX. The mean, therefore, changes by ΔX. When we calculate the standard deviation

$$s = \sqrt{\frac{(X_i - \overline{X})^2}{n - 1}}$$

the important term is the summation in the numerator, which consists of the difference between each measurement and the mean value

$$(X_i - \overline{X})^2$$

Because both X_i and $\overline{X}$ change by ΔX, the value of $X_i - \overline{X}$ becomes

$$X_i + \Delta X - (\overline{X} + \Delta X) = X_i - \overline{X}$$

which leaves unchanged the numerator of the equation for the standard deviation; thus, changing all measurements by ΔX has no effect on the standard deviation.

14. Answers to this question will vary with the object chosen. For a simple, regularly shaped object—a sphere or cube, for example—where you can measure the linear dimensions with a caliper, Method A should yield a smaller standard deviation and confidence interval than Method B. When using a mm ruler to measure the linear dimensions of a regularly shaped object, the two methods should yield similar results. For an object that is irregular in shape, Method B should yield a smaller standard deviation and confidence interval.

15. The isotopic abundance for ^{13}C is 1.11%; thus, for a molecule to average at least one atom of ^{13}C, the total number of carbon atoms must be at least

$$N = \frac{\mu}{p} = \frac{1}{0.0111} = 90.1$$

which we round up to 91 atoms. The probability of finding no atoms of ^{13}C in a molecule with 91 carbon atoms is given by the binomial distribution; thus

$$P(0,91) = \frac{91!}{0!(91 - 0)!}(0.0111)^0(1 - 0.0111)^{91-0} = 0.362$$

and 36.2% of such molecules will not contain an atom of ^{13}C.

16. (a) The probability that a molecule of cholesterol has one atom of ^{13}C is

$$P(1,27) = \frac{27!}{1!(27 - 0)!}(0.0111)^1(1 - 0.0111)^{27-1} = 0.224$$

or 22.4%. (b) From Example 4.10, we know that $P(0,27)$ is 0.740. Because the total probability must equal one, we know that

$$P(\geq 2, 27) = 1.000 - P(0, 27) - P(1, 27)$$
$$P(\geq 2, 27) = 1.00 - 0.740 - 0.224$$
$$P(\geq 2, 27) = 0.036$$

and 3.6% of cholesterol molecules will have two or more atoms of ^{13}C.

17. The mean and the standard deviation for the eight samples are, respectively, 16.883% w/w Cr and 0.0794% w/w Cr. The 95% confidence interval is

$$\mu = \overline{X} \pm \frac{ts}{\sqrt{n}} = 16.883 \pm \frac{(2.365)(0.0794)}{\sqrt{8}}$$
$$= 16.883 \pm 0.066\% \text{ w/w Cr}$$

Based on this one set of experiments, and in the absence of any determinate errors, there is a 95% probability that the actual %w/w Cr in the reference material is in the range 16.817–16.949% w/w Cr.

18. (a) The mean and the standard deviation for the nine samples are 36.1 ppt and 4.15 ppt, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\mu - \overline{X}|\sqrt{n}}{s} = \frac{|40.0 - 36.1|\sqrt{9}}{4.15} = 2.82$$

The critical value for $t(0.05,8)$ is 2.306. Because t_{exp} is greater than $t(0.05,8)$, we reject the null hypothesis and accept the alternative hypothesis, finding evidence, at $\alpha = 0.05$, that the difference between $\overline{X}$ and μ is too great to be explained by random errors in the measurements.

(b) Because concentration, C, and signal are proportional, we can use concentration in place of the signal when calculating detection limits. For σ_{mb} we use the standard deviation for the method blank of 0.16 ppt, and for σ_A we use the standard deviation of 4.15 ppt from part (a); thus

$$C_{DL} = C_{mb} + z\sigma_{mb} = 0.16 + (3.00)(1.20) = 3.76 \text{ ppt}$$

$$C_{LOI} = C_{mb} + z\sigma_{mb} + z\sigma_A$$
$$= 0.16 + (3.00)(1.20) + (3.00)(4.15) = 16.21 \text{ ppt}$$

$$C_{LOQ} = C_{mb} + 10\sigma_{mb} = 0.16 + (10.00)(1.20) = 12.16 \text{ ppt}$$

19. The mean and the standard deviation are, respectively, 0.639 and 0.00082. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\mu - \overline{X}|\sqrt{n}}{s} = \frac{|0.640 - 0.639|\sqrt{7}}{0.00082} = 3.23$$

The critical value for $t(0.01,6)$ is 3.707. Because t_{exp} is less than $t(0.01,6)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.01$, that there is a significant difference between $\overline{X}$ and μ.

20. The mean and the standard deviation are 76.64 decays/min and 2.09 decays/min, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\mu - \overline{X}|\sqrt{n}}{s} = \frac{|77.5 - 76.64|\sqrt{12}}{2.09} = 1.43$$

The critical value for $t(0.05,11)$ is 2.2035. Because t_{exp} is less than $t(0.05,11)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that there is a significant difference between $\overline{X}$ and μ.

21. The mean and the standard deviation are, respectively, 5730 ppm Fe and 91.3 ppm Fe. In this case we need to calculate μ, which is

$$\mu = \frac{(2.6540 \text{ g sample}) \times \dfrac{0.5351 \text{ g Fe}}{\text{g sample}} \times \dfrac{1 \times 10^6 \text{ μg}}{\text{g}}}{250.0 \text{ mL}}$$
$$= 5681 \text{ ppm Fe}$$

The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\mu - \overline{X}|\sqrt{n}}{s} = \frac{|5681 - 5730|\sqrt{4}}{91.3} = 1.07$$

The critical value for $t(0.05,3)$ is 3.182. Because t_{exp} is less than $t(0.05,3)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that there is a significant difference between $\overline{X}$ and μ.

22. This problem involves a comparison between two sets of unpaired data. For the digestion with HNO_3, the mean and the standard deviation are, respectively, 163.8 ppb Hg and 3.11 ppb Hg, and for the digestion with the mixture of HNO_3 and HCl, the mean and the standard deviation are, respectively, 148.3 ppb Hg and 7.53 ppb Hg.

The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X}_{HNO_3} = \overline{X}_{mix} \qquad H_A: \overline{X}_{HNO_3} \neq \overline{X}_{mix}$$

Before we can test these hypotheses, however, we first must determine if we can pool the standard deviations. To do this we use the following null hypothesis and alternative hypothesis

$$H_0: s_{\text{HNO}_3} = s_{\text{mix}} \qquad H_A: s_{\text{HNO}_3} \neq s_{\text{mix}}$$

The test statistic is F_{exp} for which

$$F_{\text{exp}} = \frac{s_{\text{mix}}^2}{s_{\text{HNO}_3}^2} = \frac{(7.53)^2}{(3.11)^2} = 5.86$$

The critical value for $F(0.05,5,4)$ is 9.364. Because F_{exp} is less than $F(0.05,5,4)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that there is a significant difference between the standard deviations. Pooling the standard deviations gives

$$s_{\text{pool}} = \sqrt{\frac{(4)(3.11)^2 + (5)(7.53)^2}{5 + 6 - 2}} = 5.98$$

The test statistic for the comparison of the means is t_{exp}, for which

$$t_{\text{exp}} = \frac{|\overline{X}_{\text{HNO}_3} - \overline{X}_{\text{mix}}|}{s_{\text{pool}}} \times \sqrt{\frac{n_{\text{HNO}_3} \times n_{\text{mix}}}{n_{\text{HNO}_3} + n_{\text{mix}}}}$$
$$= \frac{|163.8 - 148.3|}{5.98} \times \sqrt{\frac{5 \times 6}{5 + 6}} = 4.28$$

with nine degrees of freedom. The critical value for $t(0.05,9)$ is 2.262. Because t_{exp} is greater than $t(0.05,9)$, we reject the null hypothesis and accept the alternative hypothesis, finding evidence, at $\alpha = 0.05$, that the difference between the means is significant.

23. This problem involves a comparison between two sets of unpaired data. For the samples of atmospheric origin, the mean and the standard deviation are, respectively, 2.31011 g and 0.000143 g, and for the samples of chemical origin, the mean and the standard deviation are, respectively, 2.29947 g and 0.00138 g.

The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X}_{\text{atm}} = \overline{X}_{\text{chem}} \qquad H_A: \overline{X}_{\text{atm}} \neq \overline{X}_{\text{chem}}$$

Before we can test these hypotheses, however, we first must determine if we can pool the standard deviations. To do this we use the following null hypothesis and alternative hypothesis

$$H_0: s_{\text{atm}} = s_{\text{chem}} \qquad H_A: s_{\text{atm}} \neq s_{\text{chem}}$$

The test statistic is F_{exp} for which

$$F_{\text{exp}} = \frac{s_{\text{chem}}^2}{s_{\text{atm}}^2} = \frac{(0.00138)^2}{(0.000143)^2} = 97.2$$

The critical value for $F(0.05,7,6)$ is 5.695. Because F_{exp} is less than $F(0.05,5,6)$, we reject the null hypothesis and accept the alternative hypothesis that the standard deviations are different at $\alpha = 0.05$. Be-

cause we cannot pool the standard deviations, the test statistic, t_{exp}, for comparing the means is

$$t_{exp} = \frac{|\overline{X}_{atm} - \overline{X}_{chem}|}{\sqrt{\dfrac{s_{atm}^2}{n_{atm}} + \dfrac{s_{chem}^2}{n_{chem}}}}$$

$$= \frac{|2.31011 - 2.29947|}{\sqrt{\dfrac{(0.000143)^2}{7} + \dfrac{(0.00138)^2}{8}}} = 21.68$$

The number of degrees of freedom is

$$\nu = \frac{\left(\dfrac{(0.000143)^2}{7} + \dfrac{(0.00138)^2}{8}\right)^2}{\dfrac{\left(\dfrac{(0.000143)^2}{7}\right)^2}{7+1} + \dfrac{\left(\dfrac{(0.00138)^2}{8}\right)^2}{8+1}} - 2 = 7.21 \approx 7$$

The critical value for $t(0.05,7)$ is 2.365. Because t_{exp} is greater than $t(0.05,7)$, we reject the null hypothesis and accept the alternative hypothesis, finding evidence, at $\alpha = 0.05$, that the difference between the means is significant. Rayleigh observed that the density of N_2 isolated from the atmosphere was significantly larger than that for N_2 derived from chemical sources, which led him to hypothesize the presence of an unaccounted for gas in the atmosphere.

24. This problem involves a comparison between two sets of unpaired data. For the standard method, the mean and the standard deviation are, respectively, 22.86 $\mu L/m^3$ and 1.28 $\mu L/m^3$, and for the new method, the mean and the standard deviation are, respectively, 22.51 $\mu L/m^3$ and 1.92 $\mu L/m^3$.

The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X}_{std} = \overline{X}_{new} \qquad H_A: \overline{X}_{std} \neq \overline{X}_{new}$$

Before we can test these hypotheses, however, we first must determine if we can pool the standard deviations. To do this we use the following null hypothesis and alternative hypothesis

$$H_0: s_{std} = s_{new} \qquad H_A: s_{std} \neq s_{new}$$

The test statistic is F_{exp} for which

$$F_{exp} = \frac{s_{new}^2}{s_{std}^2} = \frac{(1.92)^2}{(1.28)^2} = 2.25$$

The critical value for $F(0.05,6,6)$ is 5.820. Because F_{exp} is less than $F(0.05,6,6)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that there is a significant difference between the standard deviations. Pooling the standard deviations gives

$$s_{pool} = \sqrt{\frac{(6)(1.28)^2 + (6)(1.92)^2}{7 + 7 - 2}} = 1.63$$

The test statistic for the comparison of the means is t_{exp}, for which

$$t_{exp} = \frac{|\overline{X}_{std} - \overline{X}_{new}|}{s_{pool}} \times \sqrt{\frac{n_{std} \times n_{new}}{n_{std} + n_{new}}}$$

$$= \frac{|22.86 - 22.51|}{1.63} \times \sqrt{\frac{7 \times 7}{7 + 7}} = 0.40$$

with 12 degrees of freedom. The critical value for $t(0.05,12)$ is 2.179. Because t_{exp} is less than $t(0.05,9)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that there is a significant difference between new method and the standard method.

25. This problem is a comparison between two sets of paired data,. The differences, which we define as (measured – accepted), are

$$0.0001 \quad 0.0013 \quad -0.0003 \quad 0.0015 \quad -0.0006$$

The mean and the standard deviation for the differences are 0.00040 and 0.00095, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{d} = 0 \qquad H_A: \overline{d} \neq 0$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\overline{d}|\sqrt{n}}{s} = \frac{|0.00040|\sqrt{5}}{0.00095} = 0.942$$

The critical value for $t(0.05,4)$ is 2.776. Because t_{exp} is less than $t(0.05,4)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that the spectrometer is inaccurate.

26. This problem is a comparison between two sets of paired data. The differences, which we define as (ascorbic acid – sodium bisulfate), are

$$15 \quad -31 \quad 1 \quad 20 \quad 4 \quad -52 \quad -22 \quad -62 \quad -50$$

The mean and the standard deviation for the differences are -19.7 and 30.9, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{d} = 0 \qquad H_A: \overline{d} \neq 0$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\overline{d}|\sqrt{n}}{s} = \frac{|-19.7|\sqrt{9}}{30.9} = 1.91$$

The critical value for $t(0.10,8)$ is 1.860. Because t_{exp} is greater than $t(0.10,8)$, we reject the null hypothesis and accept the alternative hypothesis, finding evidence, at $\alpha = 0.10$, that the two preservatives do not have equivalent holding times.

27. This problem is a comparison between two sets of paired data. The differences, which we define as (actual – found), are

$$-1.8 \quad -1.7 \quad 0.2 \quad -0.5 \quad -3.6 \quad -1.7 \quad 1.1 \quad -1.7 \quad 0.3$$

The mean and the standard deviation for the differences are –1.04 and 1.44, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{d} = 0 \qquad H_A: \overline{d} \neq 0$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\overline{d}|\sqrt{n}}{s} = \frac{|-1.04|\sqrt{9}}{1.44} = 2.17$$

The critical value for $t(0.05,8)$ is 2.306. Because t_{exp} is less than $t(0.10,8)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that the analysis for kaolinite is inaccurate.

28. This problem is a comparison between two sets of paired data. The differences, which we define as (electrode – spectrophotometric), are

$$0.6 \quad -5.8 \quad 0.2 \quad 0.1 \quad -0.5 \quad -0.6$$

$$0.1 \quad -0.5 \quad -0.7 \quad -0.3 \quad 0.3 \quad 0.1$$

The mean and the standard deviation for the differences are –0.583 and 1.693, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{d} = 0 \qquad H_A: \overline{d} \neq 0$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\overline{d}|\sqrt{n}}{s} = \frac{|-0.583|\sqrt{12}}{1.693} = 1.19$$

The critical value for $t(0.05,11)$ is 2.2035. Because t_{exp} is less than $t(0.05,11)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that the two methods yield different results.

29. This problem is a comparison between two sets of paired data. The differences, which we define as (proposed – standard), are

$$0.19 \quad 0.91 \quad 1.39 \quad 1.02 \quad -2.38 \quad -2.40 \quad 0.03 \quad 0.82$$

The mean and the standard deviation for the differences are –0.05 and 1.51, respectively. The null hypothesis and the alternative hypothesis are

$$H_0: \overline{d} = 0 \qquad H_A: \overline{d} \neq 0$$

The test statistic is t_{exp}, for which

$$t_{exp} = \frac{|\overline{d}|\sqrt{n}}{s} = \frac{|-0.05|\sqrt{8}}{1.51} = 0.09$$

The critical value for $t(0.05,7)$ is 2.365. Because t_{exp} is less than $t(0.05,11)$, we retain the null hypothesis, finding no evidence, at $\alpha = 0.05$, that the two methods yield different results. This is not a very satisfying result, however, because many of the individual differ-

ences are quite large. In this case, additional work might help better characterize the improved method relative to the standard method.

30. The simplest way to organize this data is to make a table, such as the one shown here

sample	smallest value	next-to-smallest value	next-to-largest value	largest value
1	21.3	21.5	23.0	23.1
2	12.9	13.5	13.9	14.2
3	15.9	16.0	17.4	17.5

The only likely candidate for an outlier is the smallest value of 12.9 for sample 2. Using Dixon's Q-test, the test statistic, Q_{exp}, is

$$Q_{exp} = \frac{|X_{out} - X_{nearest}|}{X_{largest} - X_{smallest}} = \frac{13.5 - 12.9}{14.2 - 12.9} = 0.462$$

which is smaller than the critical value for $Q(0.05,10)$ of 0.466; thus, there is no evidence using Dixon's Q-test at $\alpha = 0.05$ to suggest that 12.9 is outlier.

To use Grubb's test we need the mean and the standard deviation for sample 2, which are 13.67 and 0.356, respectively. The test statistic, G_{exp}, is

$$G_{exp} = \frac{|X_{out} - \overline{X}|}{s} = \frac{|12.9 - 13.67|}{0.356} = 2.16$$

which is smaller than the critical value for $G(0.05,10)$ of 2.290; thus, there is no evidence using Grubb's test at $\alpha = 0.05$ that 12.9 is an outlier.

To use Chauvenet's criterion we calculate the deviation, z, for the suspected outlier, assuming a normal distribution and using the sample's mean and standard deviation

$$z = \frac{|X_{out} - \overline{X}|}{s} = \frac{|12.9 - 13.67|}{0.356} = 2.16$$

which, from Appendix 3, corresponds to a probability of 0.0154. The critical value to which we compare this is $(2n)^{-1}$, or $(2 \times 10)^{-1} = 0.05$. Because the experimental probability of 0.0154 is smaller than the theoretical probability of 0.05 for 10 samples, we have evidence using Chauvenet's criterion that 12.9 is an outlier.

At this point, you may be asking yourself what to make of these seemingly contradictory results, in which two tests suggest that 12.9 is not an outlier and one test suggests that it is an outlier. Here it is helpful to keep in mind three things. First, Dixon's Q-test and Grubb's test require us to pick a particular confidence level, α, and make a decision based on that confidence level. When using Chauvenet's

criterion, however, we do not assume a particular confidence level; instead, we simply evaluate the probability that the outlier belongs to a normal distribution described by the sample's mean and standard deviation relative to a predicted probability defined by the size of the sample. Second, although Q_{exp} and G_{exp} are not large enough to identify 12.9 as an outlier at $\alpha = 0.05$, their respective values are not far removed from their respective critical values (0.462 vs. 0.466 for Dixon's Q-test and 2.16 vs. 2.290 for Grubb's test). Both tests, for example, identify 12.9 as an outlier at $\alpha = 0.10$. Third, and finally, for the reasons outlined in the text, you should be cautious when rejecting a possible outlier based on a statistical test only. All three of these tests, however, suggest that we should at least take a closer look at the measurement that yielded 12.9 as a result.

31. (a) The mean is 1.940, the median is 1.942 (the average of the 31st and the 32nd rank ordered values rounded to four significant figures), and the standard deviation is 0.047.

(b) Figure SM4.4 shows a histogram for the 60 results using bins of size 0.02. The resulting distribution is a reasonably good approximation to a normal distribution, although it appears to have a slight skew toward smaller Cu/S ratios.

(c) The range $\overline{X} \pm 1s$ extends from a Cu/S ratio of 1.893 to 1.987. Of the 62 experimental results, 44 or 71% fall within this range. This agreement with the expected value of 68.26% for a normal distribution is reasonably good.

(d) For a deviation of

$$z = \frac{2.000 - 1.940}{0.047} = 1.28$$

the probability from Appendix 3 that a Cu/S ratio is greater than 2 is 10.03%. Of the 62 experimental results, three or 4.8% fall within this range. This is a little lower than expected for a normal distribution, but consistent with the observation from part (b) that the data are skewed slightly toward smaller Cu/S ratios.

(e) The null hypothesis and the alternative hypothesis are

$$H_0: \overline{X} = 2.000 \qquad H_A: \overline{X} < 2.000$$

Note that the alternative hypothesis here is one-tailed as we are interested only in whether the mean Cu/S ratio is significantly less than 2. The test statistic, t_{exp}, is

$$t_{exp} = \frac{|1.940 - 2.000|\sqrt{62}}{0.047} = 10.0$$

As t_{exp} is greater than the one-tailed critical value for $t(0.05, 61)$, which is between 1.65 and 1.75, we reject the null hypothesis and
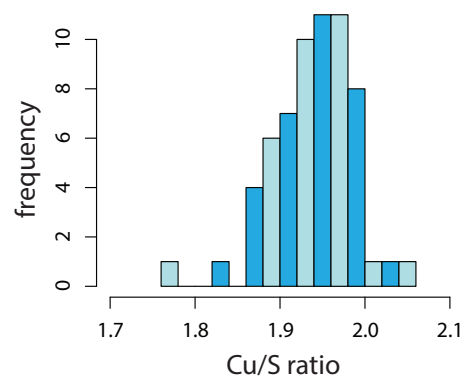
Figure SM4.4 Histogram for the data in problem 31. Each bar in has a width of 0.02. For example, the bar on the far left includes all Cu/S ratios from 1.76 to 1.78, which includes the single result of 1.764.

accept the alternative hypothesis, finding evidence that the Cu/S ratio is significantly less than its expected stoichiometric ratio of 2.

32. Although answers for this problem will vary, here are some details you should address in your report. The descriptive statistics for all three data sets are summarized in the following table.

statistic	sample X	sample Y	sample Z
mean	24.56	27.76	23.75
median	24.55	28.00	23.52
range	1.26	4.39	5.99
std dev	0.339	1.19	1.32
variance	0.115	1.43	1.73

The most interesting observation from this summary is that the spread of values for sample X—as given by the range, the standard deviation, and the variance—is much smaller than that for sample Y and for sample Z.

Outliers are one possible explanation for the difference in spread among these three samples. Because the number of individual results for each sample is greater than the largest value of n for the critical values included in Appendix 6 for Dixon's Q-test and in Appendix 7 for Grubb's test, we will use Chauvenet's criterion; the results are summarized in the following table.

statistic	sample X	sample Y	sample Z
possible outlier	23.92	24.41	28.79
z	1.89	2.63	3.83
probability	0.0294	0.0043	0.0000713

For 18 samples, the critical probability is $(2\times18)^{-1}$ or 0.0277; thus, we have evidence that there is an outlier in sample Y and in sample Z, but not in sample X. Removing these outliers and recalculating the descriptive statistics gives the results in the following table.

statistic	sample X	sample Y	sample Z
mean	24.56	27.74	23.45
median	24.55	28.00	23.48
range	1.26	3.64	1.37
std dev	0.339	0.929	0.402
variance	0.115	0.863	0.161

The spread for sample Y still seems large relative to sample X, but the spread for sample Z now seems similar to sample X. An F-test of the variances using the following null hypothesis and alternative hypothesis

$$H_0: s_1 = s_2 \qquad H_A: s_1 \neq s_2$$

gives an F_{exp} of 5.340 when comparing sample Y to sample Z, and of 1.406 when comparing sample Z to sample X. Comparing these values to the critical value for $F(0.05,17,17)$, which is between 2.230 and 2.308, suggests that our general conclusions are reasonable.

The mean values for the three samples appear different from each other. A t-test using the following null hypothesis and alternative hypothesis

$$H_0: \overline{X}_1 = \overline{X}_2 \qquad H_A: \overline{X}_1 \neq \overline{X}_2$$

gives a t_{exp} of 13.30 when comparing sample Y to sample X, which is much greater than the critical value for $t(0.05,20)$ of 2.086. The value of t_{exp} when comparing sample Z to sample X is 8.810, which is much greater than the critical value for $t(0.05,33)$, which is between 2.042 and 2.086.

This process of completing multiple significance tests is not without problems, for reasons we will discuss in Chapter 14 when we consider analysis of variance.

Chapter 5

Many of the problems in this chapter require a regression analysis. Although equations for these calculations are highlighted in the solution to the first such problem, for the remaining problems, both here and elsewhere in this text, the results of a regression analysis simply are provided. Be sure you have access to a scientific calculator, a spreadsheet program, such as Excel, or a statistical software program, such as R, and that you know how to use it to complete a regression analysis.

1. For each step in a dilution, the concentration of the new solution, C_{new}, is

$$C_{new} = \frac{C_{orig} V_{orig}}{V_{new}}$$

where C_{orig} is the concentration of the original solution, V_{orig} is the volume of the original solution taken, and V_{new} is the volume to which the original solution is diluted. A propagation of uncertainty for C_{new} shows that its relative uncertainty is

<aside>See Chapter 4C to review the propagation of uncertainty.</aside>

$$\frac{u_{C_{new}}}{C_{new}} = \sqrt{\left(\frac{u_{C_{orig}}}{C_{orig}}\right)^2 + \left(\frac{u_{V_{orig}}}{V_{orig}}\right)^2 + \left(\frac{u_{V_{new}}}{V_{new}}\right)^2}$$

For example, if we dilute 10.00 mL of the 0.1000 M stock solution to 100.0 mL, C_{new} is 1.000×10^{-2} M and the relative uncertainty in C_{new} is

$$\frac{u_{C_{new}}}{C_{new}} = \sqrt{\left(\frac{0.0002}{0.1000}\right)^2 + \left(\frac{0.02}{10.00}\right)^2 + \left(\frac{0.08}{100.0}\right)^2} = 2.94 \times 10^{-3}$$

The absolute uncertainty in C_{new}, therefore, is

$$u_{C_{new}} = (1.000 \times 10^{-2}\text{ M}) \times (2.94 \times 10^{-3}) = 2.94 \times 10^{-5}\text{ M}$$

The relative and the absolute uncertainties for each solution's concentration are gathered together in the tables that follow (all concentrations are given in mol/L and all volumes are given in mL). The uncertainties in the volumetric glassware are from Table 4.2 and Table 4.3. For a V_{orig} of 0.100 mL and of 0.0100 mL, the uncertainties are those for a 10–100 µL digital pipet.

For a serial dilution, each step uses a 10.00 mL volumetric pipet and a 100.0 mL volumetric flask; thus

C_{new}	C_{orig}	V_{orig}	V_{new}	$u_{V_{orig}}$	$u_{V_{new}}$
1.000×10^{-2}	0.1000	10.00	100.0	0.02	0.08
1.000×10^{-3}	1.000×10^{-2}	10.00	100.0	0.02	0.08
1.000×10^{-4}	1.000×10^{-3}	10.00	100.0	0.02	0.08
1.000×10^{-5}	1.000×10^{-4}	10.00	100.0	0.02	0.08

C_{new}	C_{orig}	$\dfrac{u_{C_{new}}}{C_{new}}$	$u_{C_{new}}$
1.000×10^{-2}	0.1000	2.94×10^{-3}	2.94×10^{-5}
1.000×10^{-3}	1.000×10^{-2}	3.64×10^{-3}	3.64×10^{-6}
1.000×10^{-4}	1.000×10^{-3}	4.23×10^{-3}	4.23×10^{-7}
1.000×10^{-5}	1.000×10^{-4}	4.75×10^{-3}	4.75×10^{-8}

For the set of one-step dilutions using the original stock solution, each solution requires a different volumetric pipet; thus

C_{new}	C_{orig}	V_{orig}	V_{new}	$u_{V_{orig}}$	$u_{V_{new}}$
1.000×10^{-2}	0.1000	10.00	100.0	0.02	0.08
1.000×10^{-3}	0.1000	1.000	100.0	0.006	0.08
1.000×10^{-4}	0.1000	0.100	100.0	8.00×10^{-4}	0.08
1.000×10^{-5}	0.1000	0.0100	100.0	3.00×10^{-4}	0.08

C_{new}	C_{orig}	$\dfrac{u_{C_{new}}}{C_{new}}$	$u_{C_{new}}$
1.000×10^{-2}	0.1000	2.94×10^{-3}	2.94×10^{-5}
1.000×10^{-3}	0.1000	6.37×10^{-3}	6.37×10^{-6}
1.000×10^{-4}	0.1000	8.28×10^{-3}	8.28×10^{-7}
1.000×10^{-5}	0.1000	3.01×10^{-2}	3.01×10^{-7}

Note that for each C_{new}, the absolute uncertainty when using a serial dilution always is equal to or better than the absolute uncertainty when using a single dilution of the original stock solution. More specifically, for a C_{new} of 1.000×10^{-3} M and of 1.000×10^{-4} M, the improvement in the absolute uncertainty is approximately a factor of 2, and for a C_{new} of 1.000×10^{-5} M, the improvement in the absolute uncertainty is approximately a factor of 6. This is a distinct advantage of a serial dilution. On the other hand, for a serial dilution a determinate error in the preparation of the 1.000×10^{-2} M solution carries over as a determinate error in each successive solution, which is a distinct disadvantage.

2. We begin by determining the value for k_A in the equation

$$S_{total} = k_A C_A + S_{reag}$$

where S_{total} is the average of the three signals for the standard of concentration C_A, and S_{reag} is the signal for the reagent blank. Making appropriate substitutions

$$0.1603 = k_A(10.0\ \text{ppm}) + 0.002$$

and solving for k_A gives its value as 0.01583 ppm^{-1}. Substituting in the signal for the sample

$$0.118 = (0.01583\ \text{ppm}^{-1})\,C_A + 0.002$$

and solving for C_A gives the analyte's concentration as 7.33 ppm.

3. This standard addition follows the format of equation 5.9

$$\frac{S_{samp}}{C_A \dfrac{V_o}{V_f}} = \frac{S_{spike}}{C_A \dfrac{V_o}{V_f} + C_{std}\dfrac{V_{std}}{V_f}}$$

in which both the sample and the standard addition are diluted to the same final volume. Making appropriate substitutions

$$\frac{0.235}{C_A \times \dfrac{10.00\ \text{mL}}{25.00\ \text{mL}}} = \frac{0.502}{C_A \times \dfrac{10.00\ \text{mL}}{25.00\ \text{mL}} + (1.00\ \text{ppm}) \times \dfrac{10.00\ \text{mL}}{25.00\ \text{mL}}}$$

$$0.0940C_A + 0.0940\ \text{ppm} = 0.2008C_A$$

and solving gives the analyte's concentration, C_A, as 0.800 ppm. The concentration of analyte in the original solid sample is

> Here we assume that a part per million is equivalent to mg/L.

$$\frac{(0.880\ \text{mg/L})\,(0.250\ \text{L})\left(\dfrac{1\,\text{g}}{1000\ \text{mg}}\right)}{10.00\ \text{g sample}} \times 100 = 2.20 \times 10^{-3}\ \%\ \text{w/w}$$

4. This standard addition follows the format of equation 5.11

$$\frac{S_{samp}}{C_A} = \frac{S_{spike}}{C_A \dfrac{V_o}{V_o + V_{std}} + C_{std}\dfrac{V_{std}}{V_o + V_{std}}}$$

in which the standard addition is made directly to the solution that contains the analyte. Making appropriate substitutions

$$\frac{11.5}{C_A} = \frac{23.1}{C_A \dfrac{50.00\ \text{mL}}{50.00\ \text{mL} + 1.00\ \text{mL}} + \dfrac{(10.0\ \text{ppm})\,(1.00\ \text{mL})}{50.00\ \text{mL} + 1.00\ \text{mL}}}$$

$$23.1C_A = 11.27C_A + 2.255\ \text{ppm}$$

and solving gives the analyte's concentration, C_A, as 0.191 ppm.

5. To derive a standard additions calibration curve using equation 5.10

$$S_{spike} = k_A\left(C_A \frac{V_o}{V_o + V_{std}} + C_{std}\frac{V_{std}}{V_o + V_{std}}\right)$$

we multiply through both sides of the equation by $V_o + V_{std}$

$$S_{spike}(V_o + V_{std}) = k_A C_A V_o + k_A C_{std} V_{std}$$

As shown in Figure SM5.1, the slope is equal to k_A and the y-intercept is equal to $k_A C_A V_o$. The x-intercept occurs when $S_{spike}(V_o + V_{std})$ equals zero; thus

$$0 = k_A C_A V_o + k_A C_{std} V_{std}$$

Figure SM5.1 Standard additions calibration curve based on equation 5.10.

and the x-intercept is equal to $-C_A V_o$. We must plot the calibration curve this way because if we plot S_{spike} on the y-axis versus $C_{std} \times \{V_{std}/(V_o + V_{std})\}$ on the x-axis, then the term we identify as y-intercept

$$\frac{k_A C_A V_o}{V_o + V_{std}}$$

is not a constant because it includes a variable, V_{std}, whose value changes with each standard addition.

6. Because the concentration of the internal standard is maintained at a constant level for both the sample and the standard, we can fold the internal standard's concentration into the proportionality constant K in equation 5.12; thus, using S_A, S_{IS}, and C_A for the standard

$$\frac{S_A}{S_{IS}} = \frac{0.155}{0.233} = \frac{k_A C_A}{k_{IS} C_{IS}} = KC_A = K(10.00 \text{ mg/L})$$

gives K as 0.06652 L/mg. Substituting in S_A, S_{IS}, and K for the sample

$$\frac{0.155}{0.233} = (0.06652 \text{ L/mg}) C_A$$

gives the concentration of analyte in the sample as 20.8 mg/L.

7. For each pair of calibration curves, we seek to find the calibration curve that yields the smallest uncertainty as expressed in the standard deviation about the regression, s_r, the standard deviation in the slope, s_{b_1}, or the standard deviation in the y-intercept, s_{b_0}.

(a) The calibration curve on the right is the better choice because it uses more standards. All else being equal, the larger the value of n, the smaller the value for s_r in equation 5.19, and for s_{b_0} in equation 5.21.

(b) The calibration curve on the left is the better choice because the standards are more evenly spaced, which minimizes the term $\sum x_i^2$ in equation 5.21 for s_{b_0}.

(c) The calibration curve on the left is the better choice because the standards span a wider range of concentrations, which minimizes the term $\sum (x_i - \overline{X})^2$ in equation 5.20 and in equation 5.21 for s_{b_1} and s_{b_0}, respectively.

As a reminder, for this problem we will work through the details of an unweighted linear regression calculation using the equations from the text. For the remaining problems, it is assumed you have access to a calculator, a spreadsheet, or a statistical program that can handle most or all of the relevant calculations for an unweighted linear regression.

8. To determine the slope and the y-intercept for the calibration curve at a pH of 4.6 we first need to calculate the summation terms that appear in equation 5.17 and in equation 5.18; these are:

$$\sum x_i = 308.4 \quad \sum y_i = 131.0$$
$$\sum x_i y_i = 8397.5 \quad \sum x_i^2 = 19339.6$$

Substituting these values into the equation 5.17

$$b_1 = \frac{(6 \times 8397.5) - (308.4 \times 131.0)}{(6 \times 19339.6) - (308.4)^2} = 0.477$$

gives the slope as 0.477 nA/nM, and substituting into equation 5.18

$$b_0 = \frac{131.0 - (0.477 \times 308.4)}{6} = -2.69$$

gives the y-intercept as –2.69 nA. The equation for the calibration curve is

$$S_{total} = 0.477 \text{nA/nM} \times C_{Cd} - 2.69 \text{ nA}$$

Figure SM5.2 shows the calibration data and the calibration curve.

To find the confidence intervals for the slope and for the y-intercept, we use equation 5.19 to calculate the standard deviation about the regression, s_r, and use equation 5.20 and equation 5.21 to calculate the standard deviation in the slope, s_{b_1}, and the standard deviation in the y-intercept, s_{b_0}, respectively. To calculate s_r we first calculate the predicted values for the signal, $\widehat{y}_i$, using the known concentrations of Cd^{2+} and the regression equation, and the squared residual errors, $(y_i - \widehat{y}_i)^2$; the table below summarizes these results

x_i	y_i	$\widehat{y}_i$	$(y_i - \widehat{y}_i)^2$
15.4	4.8	4.66	0.0203
30.4	11.4	11.81	0.7115
44.9	18.2	18.73	0.2382
59.0	26.6	25.46	1.3012
72.7	32.3	32.00	0.0926
86.0	37.7	38.34	0.4110

Adding together the last column, which equals 2.2798, gives the numerator for equation 5.19; thus, the standard deviation about the regression is

$$s_r = \sqrt{\frac{2.2798}{6 - 2}} = 0.7550$$

To calculate the standard deviations in the slope and in the y-intercept, we use equation 5.20 and equation 5.21, respectively, using the standard deviation about the regression and the summation terms outlined earlier; thus

$$s_{b_1} = \sqrt{\frac{6 \times (0.7550)^2}{(6 \times 19339.6) - (308.4)^2}} = 0.02278$$

$$s_{b_0} = \sqrt{\frac{(0.7550)^2 \times 19339.6}{(6 \times 19339.6) - (308.4)^2}} = 0.7258$$

With four degrees of freedom, the confidence intervals for the slope and the y-intercept are

$$\beta_1 = b_1 \pm t s_{b_1} = 0.477 \pm (2.776)(0.0128)$$
$$= 0.477 \pm 0.036 \text{ nA/nM}$$
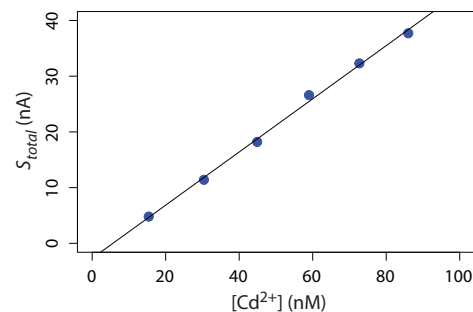
Figure SM5.2 Calibration curve at pH 4.6 for the data in Problem 5.8.
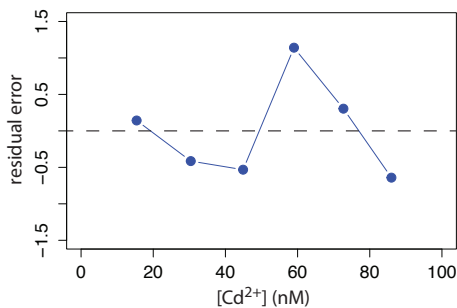
Figure SM5.3 Plot of the residual errors for the calibration standards in Problem 5.8 at a pH of 4.6.
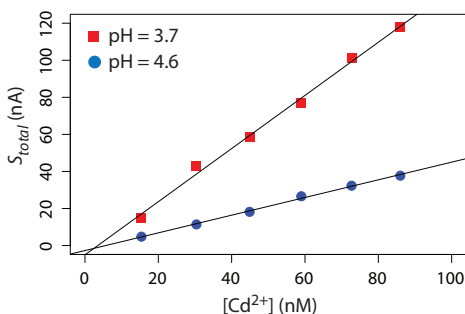
Figure SM5.4 Calibration curves for the data in Problem 5.8 at a **pH of 3.7** and at a **pH of 4.6**.

$$\beta_1 = b_0 \pm ts_{b_0} = -2.69 \pm (2.776)(0.7258)$$
$$= -2.69 \pm 2.01 \text{ nA}$$

(b) The table below shows the residual errors for each concentration of Cd^{2+}. A plot of the residual errors (Figure SM5.3) shows no discernible trend that might cause us to question the validity of the calibration equation.

x_i	y_i	$\widehat{y}_i$	$y_i - \widehat{y}_i$
15.4	4.8	4.66	0.14
30.4	11.4	11.81	–0.41
44.9	18.2	18.73	–0.53
59.0	26.6	25.46	1.14
72.7	32.3	32.00	0.30
86.0	37.7	38.34	–0.64

(c) A regression analysis for the data at a pH of 3.7 gives the calibration curve's equation as

$$S_{total} = 1.43 \text{ nA/nM} \times C_{Cd} - 5.02 \text{ nA}$$

The more sensitive the method, the steeper the slope of the calibration curve, which, as shown in Figure SM5.4, is the case for the calibration curve at pH 3.7. The relative sensitivities for the two pHs is the ratio of their respective slopes

$$\frac{k_{pH\,3.7}}{k_{pH\,4.6}} = \frac{1.43}{0.477} = 3.00$$

The sensitivity at a pH of 3.7, therefore, is three times more sensitive than that at a pH of 4.6.

(d) Using the calibration curve at a pH of 3.7, the concentration of Cd^{2+} in the sample is

$$[Cd^{2+}] = \frac{S_{total} - b_0}{b_1} = \frac{66.3 \text{ nA} - (-5.02 \text{ nA})}{1.43 \text{ nA/nM}} = 49.9 \text{ nM}$$

To calculate the 95% confidence interval, we first use equation 5.25

$$s_{C_{Cd}} = \frac{s_r}{b_1} \sqrt{\frac{1}{m} + \frac{1}{n} + \frac{(\overline{S}_{samp} - \overline{S}_{std})^2}{(b_1)^2 \sum_{i=1}^{n}(C_{std_i} - \overline{C}_{std})^2}}$$

to determine the standard deviation in the concentration where the number of samples, m, is one, the number of standards, n, is six, the standard deviation about the regression, s_r, is 2.826, the slope, b_1, is 1.43, the average signal for the one sample, $\overline{S}_{samp}$, is 66.3, and the average signal for the six standards, $\overline{S}_{std}$, is 68.7. At first glance, the term $\sum(C_{std_i} - \overline{C}_{std})^2$, where C_{std_i} is the concentration of the ith standard and $\overline{C}_{std}$ is the average concentration for the n standards, seems

cumbersome to calculate. We can simplify the calculation, however, by recognizing that $\sum (C_{std_i} - \overline{C}_{std})^2$ is the numerator in the equation that gives the standard deviation for the concentrations of the standards, s_{Cd}. Because s_{Cd} is easy to determine using a calculator, a spreadsheet, or a statistical software program, it is easy to calculate $\sum (C_{std_i} - \overline{C}_{std})^2$; thus

$$s_{Cd} = \sqrt{\frac{\sum (C_{std_i} - \overline{C}_{std})^2}{n-1}}$$

$$\sum_{i=1}^{n} (C_{std_i} - \overline{C}_{std})^2 = (n-1)(s_{Cd})^2 = (6-1)(26.41)^2 = 3487$$

Substituting all terms back into equation 5.25 gives the standard deviation in the concentration as

$$s_{C_{Cd}} = \frac{2.826}{1.43}\sqrt{\frac{1}{1} + \frac{1}{6} + \frac{(66.3 - 68.7)^2}{(1.43)^2(3487)}} = 2.14$$

The 95% confidence interval for the sample's concentration, therefore, is

$$\mu_{Cd} = 49.9 \pm (2.776)(2.14) = 49.9 \pm 5.9 \text{ nM}$$

9.   The standard addition for this problem follows equation 5.10, which, as we saw in Problem 5.5, is best treated by plotting $S_{spike}(V_o + V_{std})$ on the y-axis vs. $C_s V_s$ on the x-axis, the values for which are

V_{std} (mL)	S_{spike} (arb. units)	$S_{spike}(V_o + V_{std})$	$C_{std}V_{std}$
0.00	0.119	0.595	0.0
0.10	0.231	1.178	60.0
0.20	0.339	1.763	120.0
0.30	0.442	2.343	180.0

Figure SM5.5 shows the resulting calibration curve for which the calibration equation is

$$S_{spike}(V_o + V_{std}) = 0.5955 + 0.009713 \times C_{std} V_{std}$$

To find the analyte's concentration, C_A, we use the absolute value of the x-intercept, $-C_A V_o$, which is equivalent to the y-intercept divided by the slope; thus

$$C_A V_o = C_A(5.00 \text{ mL}) = \frac{b_0}{k_A} = \frac{0.5955}{0.009713} = 61.31$$

which gives C_A as 12.3 ppb.

To find the 95% confidence interval for C_A, we use a modified form of equation 5.25 to calculate the standard deviation in the x-intercept

$$s_{C_A V_o} = \frac{s_r}{b_1}\sqrt{\frac{1}{n} + \frac{\{S_{spike}(V_o + V_{std})\}^2}{(b_1)^2 \sum_{i=1}^{n}(C_{std_i} V_{std_i} - \overline{C_{std} V_{std}})^2}}$$

where the number of standards, n, is four, the standard deviation about the regression, s_r, is 0.00155, the slope, b_1, is 0.009713, the
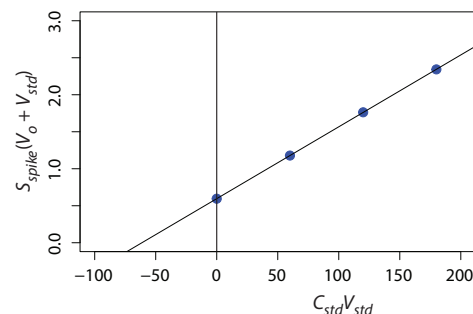
Figure SM5.5 Standard additions calibration curve for Problem 5.9.

average signal for the four standards, $\overline{S_{spike}(V_o + V_{std})}$, is 1.47, and the term $\sum(C_{std_i} V_{std_i} - \overline{C_{std} V_{std}})^2$ is 1.80×10^4. Substituting back into this equation gives the standard deviation of the x-intercept as

$$s_{C_A V_o} = \frac{0.00155}{0.009713} \sqrt{\frac{1}{4} + \frac{\{1.47\}^2}{(0.009713)^2 (1.8 \times 10^4)}} = 0.197$$

Dividing $s_{C_A V_o}$ by V_o gives the standard deviation in the concentration, s_{C_A}, as

$$s_{C_A} = \frac{s_{C_A V_o}}{V_o} = \frac{0.197}{5.00} = 0.0393$$

The 95% confidence interval for the sample's concentration, therefore, is

$$\mu = 12.3 \pm (4.303)(0.0393) = 12.3 \pm 0.2 \text{ ppb}$$

10. (a) For an internal standardization, the calibration curve places the signal ratio, S_A/S_{IS}, on the y-axis and the concentration ratio, C_A/C_{IS}, on the x-axis. Figure SM5.6 shows the resulting calibration curve, which is characterized by the following values

   slope (b_1): 0.5576

   y-intercept (b_0): 0.3037

   standard deviation for slope (s_{b_1}): 0.0314

   standard deviation for y-intercept (s_{b_0}): 0.0781

Based on these values, the 95% confidence intervals for the slope and the y-intercept are, respectively

$$\beta_0 = b_0 \pm ts_{b_0} = 0.3037 \pm (3.182)(0.0781) = 0.3037 \pm 0.2484$$

$$\beta_1 = b_1 \pm ts_{b_1} = 0.5576 \pm (3.182)(0.0314) = 0.5576 \pm 0.1001$$

(b) The authors concluded that the calibration model is inappropriate because the 95% confidence interval for the y-intercept does not include the expected value of 0.00. A close observation of Figure SM5.6 shows that the calibration curve has a subtle, but distinct curvature, which suggests that a straight-line is not a suitable model for this data.

11. Figure SM5.7 shows a plot of the measured values on the y-axis and the expected values on the x-axis, along with the regression line, which is characterized by the following values:

   slope (b_1): 0.9996

   y-intercept (b_0): 0.000761

   standard deviation for slope (s_{b_1}): 0.00116

   standard deviation for y-intercept (s_{b_0}): 0.00112

For the y-intercept, t_{exp} is

Figure SM5.6 Internal standards calibration curve for the data in Problem 5.10.
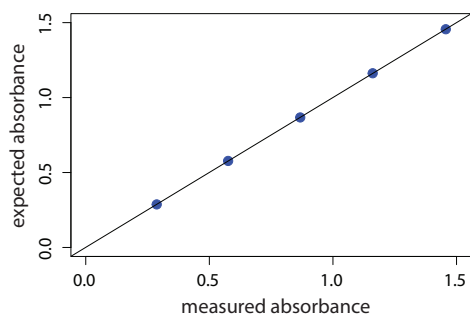
Figure SM5.7 Plot of the measured absorbance values for a series of spectrophotometric standards versus their expected absorbance values. The original data is from Problem 4.25.

$$t_{exp} = \frac{|\beta_0 - b_0|}{s_{b_0}} = \frac{|0.00 - 0.00761|}{0.00112} = 0.679$$

and t_{exp} for the slope is

$$t_{exp} = \frac{|\beta_1 - b_1|}{s_{b_1}} = \frac{|1.00 - 0.9996|}{0.00116} = 0.345$$

For both the y-intercept and the slope, t_{exp} is less than the critical value of $t(0.05,3)$, which is 3.182; thus, we retain the null hypothesis and have no evidence at $\alpha = 0.05$ that the y-intercept or the slope differ significantly from their expected values of zero, and, therefore, no evidence at $\alpha = 0.05$ that there is a difference between the measured absorbance values and the expected absorbance values.

12. (a) Knowing that all three data sets have identical regression statistics suggests that the three data sets are similar to each other. A close look at the values of y suggests that all three data sets show a general increase in the value of y as the value of x becomes larger, although the trend seems noisy.

(b) The results of a regression analysis are gathered here

parameter	Data Set 1	Data Set 2	Data Set 3
b_0	3.0001	3.0010	3.0025
b_1	0.5001	0.5000	0.4997
s_{b_0}	1.1247	1.1250	1.1245
s_{b_1}	0.1179	0.1180	0.1179
s_r	1.237	1.237	1.236

and are in agreement with the values reported in part (a). Figure SM5.8 shows the residual plots for all three data sets. For the first data set, the residual errors are scattered at random around a residual error of zero and show no particular trend, suggesting that the regression model provides a reasonable explanation for the data. For data set 2 and for data set 3, the clear pattern to the residual errors indicates that neither regression models is appropriate.

(c) Figure SM5.9 shows each data set with its regression line. For data set 1, the regression line provides a good fit to what is rather noisy data. For the second data set, we see that the relationship between x and y is not a straight-line and that a quadratic model likely is more appropriate. With the exception of an apparent outlier, data set 3 is a straight-line; removing the outlier is likely to improve the regression analysis.

(d) The apparent outlier is the third point in the data set ($x = 13.00$, $y = 12.74$). Figure SM5.10 shows the resulting regression line, for which

slope (b_1): 0.345
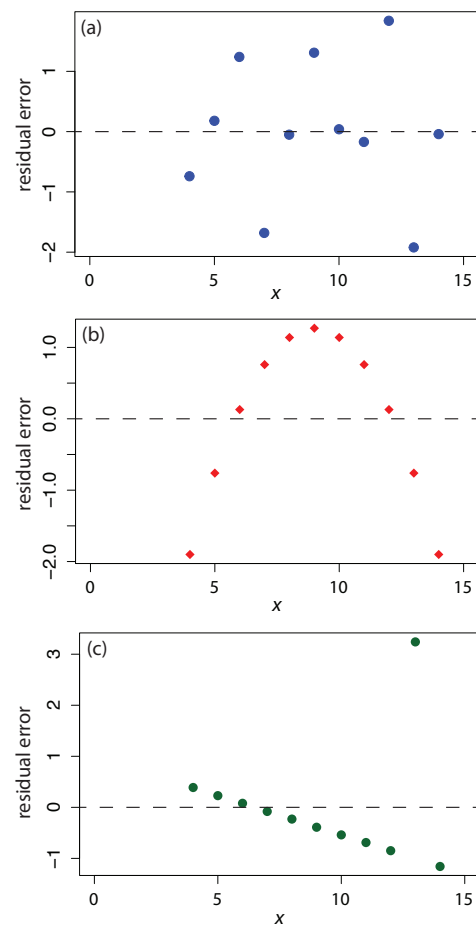
Figure SM5.8 Residual plots for (a) **data set 1**; (b) **data set 2**; and (c) **data set 3**. The dashed line in each plot shows the expected trend for the residual errors when the regression model provides a good fit to the data.
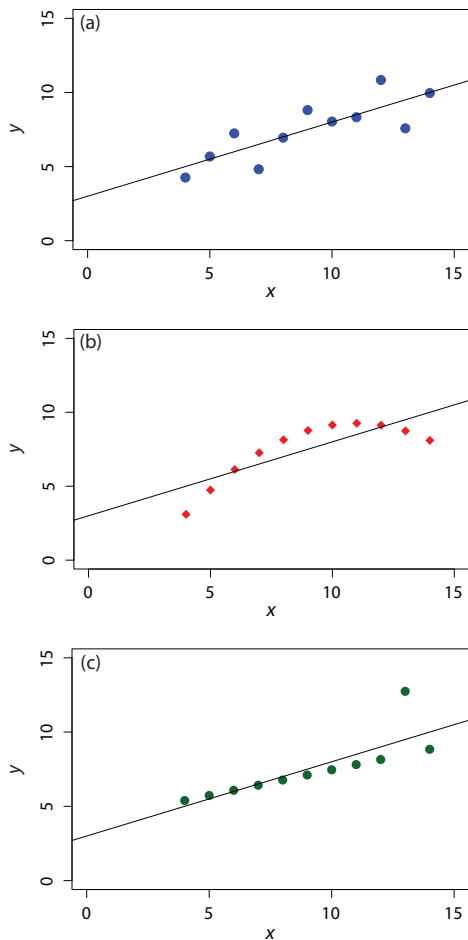
Figure SM5.9 Regression plots for the data from (a) **data set 1**; (b) **data set 2**; and (c) **data set 3**.
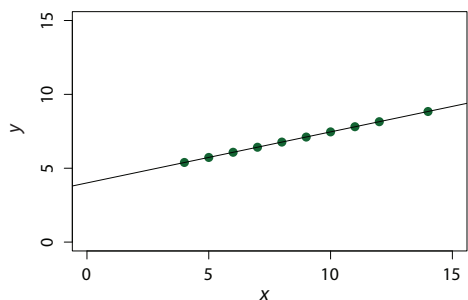
Figure SM5.10 Regression plot for data set 3 after removing the apparent outlier.

y-intercept (b_0): 4.01

standard deviation for slope (s_{b_1}): 0.00321

standard deviation for y-intercept (s_{b_0}): 0.00292

standard deviation about the regression (s_r): 0.00308

Note that s_r, s_{b_0}, and s_{b_1} are much smaller after we remove the apparent outlier, which is consistent with the better fit of the regression line to the data.

(e) The analysis of this data set drives home the importance of examining your data in a graphical form. As suggested earlier in the answer to part (a), it is difficult to see the underlying pattern in a data set when we look at numbers only.

13. To complete a weighted linear regression we first must determine the weighting factors for each concentration of thallium; thus

x_i	y_i (avg)	s_{y_i}	$(s_{y_i})^{-2}$	w_i
0.000	2.626	0.1137	77.3533	3.3397
0.387	8.160	0.2969	11.3443	0.4898
1.851	29.114	0.5566	3.2279	0.1394
5.734	85.714	1.1768	0.7221	0.0312

where y_i (avg) is the average of the seven replicate measurements for each of the i standard additions, and s_{y_i} is the standard deviation for these replicate measurements; note that the increase in s_{y_i} with larger values of x_i indicates that the indeterminate errors affecting the signal are not independent of the concentration of thallium, which is why a weighted linear regression is used here. The weights in the last column are calculated using equation 5.28 and, as expected, the sum of the weights is equal to the number of standards.

To calculate the y-intercept and the slope, we use equation 5.26 and equation 5.27, respectively, using the table below to organize the various summations

x_i	y_i (avg)	$w_i x_i$	$w_i y_i$	$w_i x_i^2$	$w_i x_i y_i$
0.000	2.626	0.0000	8.7701	0.0000	0.0000
0.387	8.160	0.1896	3.9968	0.0734	1.5467
1.851	29.114	0.2580	4.0585	0.4776	7.5123
5.734	85.714	0.1789	2.6743	1.0258	15.3343
totals		0.6265	19.4997	1.5768	24.3933

$$b_1 = \frac{n\sum_{i=1}^{n} w_i x_i y_i - \sum_{i=1}^{n} w_i x_i \sum_{i=1}^{n} w_i y_i}{n\sum_{i=1}^{n} w_i x_i^2 - \left(\sum_{i=1}^{n} w_i x_i\right)^2}$$

$$= \frac{(4)(24.3933) - (0.6265)(19.4997)}{(4)(1.5768) - (0.6265)^2} = 14.43$$

$$b_0 = \frac{\sum_{i=1}^{n} w_i y_i - b_1 \sum_{i=1}^{n} w_i x_i}{n}$$

$$= \frac{19.4997 - (14.431)(0.6265)}{4} = 2.61$$

The calibration curve, therefore, is

$$S_{total} = 2.61\,\mu A + (14.43\,\mu A/ppm) \times C_{Tl}$$

Figure SM5.11 shows the calibration data and the weighted linear regression line.
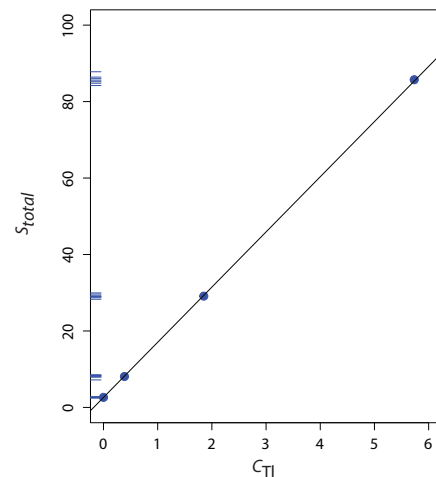
Figure SM5.11 Calibration data and calibration curve for the data in Problem 5.13. The individual points show the average signal for each standard and the calibration curve is from a weighted linear regression. The **blue** tick marks along the y-axis show the replicate signals for each standard; note that the spacing of these marks reflect the increased magnitude of the signal's indeterminate error for higher concentrations of thallium.

Chapter 6

1. (a) The equilibrium constant expression is

$$K = \frac{[NH_4^+]}{[NH_3][H_3O^+]}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of two reactions, each with a standard equilibrium constant; thus
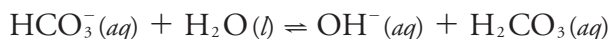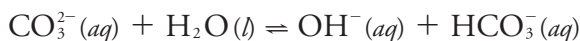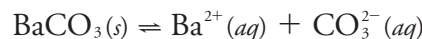
$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$
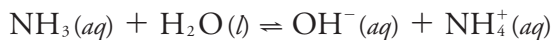
$$K = K_{b,NH_3} \times (K_w)^{-1} = \frac{K_w}{K_{a,NH_4^+}} \times \frac{1}{K_w} = \frac{1}{K_{a,NH_4^+}}$$

$$K = \frac{1}{5.70 \times 10^{-10}} = 1.75 \times 10^9$$

By "standard equilibrium constant," we mean one of the following: an acid dissociation constant, a base dissociation constant, a solubility product, a stepwise or an overall formation constant, or a solvent dissociation constant.

(b) The equilibrium constant expression is

$$K = \frac{[I^-]^2}{[S^{2-}]}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of two reactions, each with a standard equilibrium constant; thus

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

$$Pb^{2+}(aq) + S^{2-}(aq) \rightleftharpoons PbS(s)$$
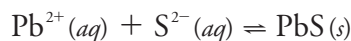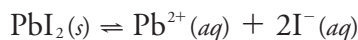
$$K = K_{sp,PbI_2} \times (K_{sp,PbS})^{-1}$$

$$K = (7.9 \times 10^{-9}) \times \frac{1}{3 \times 10^{-28}} = 3 \times 10^{19}$$

(c) The equilibrium constant expression is

$$K = \frac{[Cd(CN)_4^{2-}][Y^{4-}]}{[CdY^{2-}][CN^-]^4}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of two reactions, each with a standard equilibrium constant; thus

$$CdY^{2-}(aq) \rightleftharpoons Cd^{2+}(aq) + Y^{4-}(aq)$$

$$Cd^{2+}(aq) + 4CN^-(aq) \rightleftharpoons Cd(CN)_4^{2-}(aq)$$
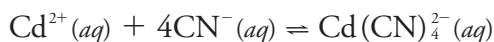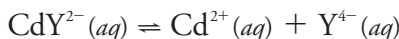
$$K = (K_{f,CdY^{2-}})^{-1} \times \beta_{4,Cd(CN)_4^{2-}}$$

$$= \frac{1}{2.88 \times 10^{16}} \times (8.32 \times 10^{17}) = 28.9$$

where β_4 is equal to $K_1 \times K_2 \times K_3 \times K_4$.

From Appendix 12, we have $\log K_1 = 6.01$, $\log K_2 = 5.11$, $\log K_3 = 4.53$, and $\log K_4 = 2.27$. Adding together these four values gives $\log \beta_4$ as 17.92 and β_4 as 8.32×10^{17}.

(d) The equilibrium constant expression is

$$K = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of two reactions, each with a standard equilibrium constant; thus

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$$
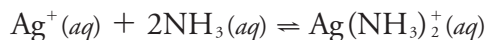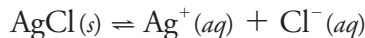
$$K = K_{sp,AgCl} \times \beta_{2,Ag(NH_3)_2^+}$$

$$K = (1.8 \times 10^{-10}) \times (1.66 \times 10^7) = 3.0 \times 10^{-3}$$

(e) The equilibrium constant expression is

$$K = \frac{[Ba^{2+}][H_2CO_3]}{[H_3O^+]^2}$$

To find the equilibrium constant's value, we note that the overall reaction is the sum of five reactions, each with a standard equilibrium constant; thus

$$BaCO_3(s) \rightleftharpoons Ba^{2+}(aq) + CO_3^{2-}(aq)$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$K = K_{sp,BaCO_3} \times K_{b,CO_3^{2-}} \times K_{b,HCO_3^-} \times (K_w)^{-2}$$

$$K = K_{sp,BaCO_3} \times \frac{K_w}{K_{a,HCO_3^-}} \times \frac{K_w}{K_{a,H_2CO_3}} \times \frac{1}{(K_w)^2}$$

$$K = (5.0 \times 10^{-9}) \times \frac{1}{4.69 \times 10^{-11}} \times \frac{1}{4.45 \times 10^{-7}} = 2.4 \times 10^8$$

2. Figure SM6.1 shows the ladder diagram for H_3PO_4 and for HF. From the ladder diagram, we predict that a reaction between H_3PO_4 and F^- is favorable because their respective areas of predominance do not overlap. On the other hand, a reaction between $H_2PO_4^-$ and F^-, which must take place if the final product is to include HPO_4^{2-}, is unfavorable because the areas of predominance for $H_2PO_4^-$ and F^-, overlap.

To find the equilibrium constant for the first reaction, we note that it is the sum of three reactions, each with a standard equilibrium constant; thus

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$$
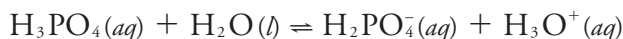
From Appendix 12, we have $\log K_1 = 3.31$ and $\log K_2 = 3.91$. Adding together these four values gives $\log\beta_2$ as 7.22 and β_2 as 1.66×10^7.
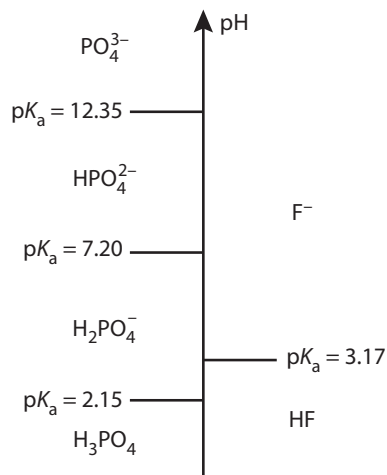
Figure SM6.1 Ladder diagram showing the areas of predominance for H_3PO_4 on the left and the areas of predominance for HF on the right.

$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$
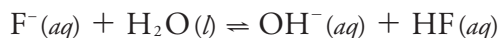
$$K = K_{a,H_3PO_4} \times K_{b,F^-} \times (K_w)^{-1} = K_{a,H_3PO_4} \times \frac{K_w}{K_{a,HF}} \times \frac{1}{K_w}$$

$$K = \frac{7.11 \times 10^{-3}}{6.8 \times 10^{-4}} = 10.5$$

Because K is greater than 1, we know that the reaction is favorable.

To find the equilibrium constant for the second reaction, we note that it is the sum of six reactions, each with a standard equilibrium constant; thus

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$

$$F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$
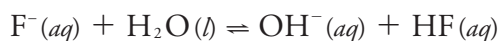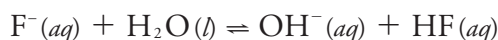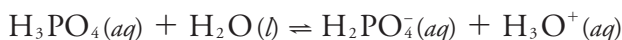
$$K = K_{a,H_3PO_4} \times K_{a,H_2PO_4^-} \times (K_{b,F^-})^2 \times (K_w)^{-2}$$

$$K = K_{a,H_3PO_4} \times K_{a,H_2PO_4^-} \times \left(\frac{K_w}{K_{a,HF}}\right)^2 \times \left(\frac{1}{K_w}\right)^2$$

$$K = (7.11 \times 10^{-3}) \times (6.32 \times 10^{-8}) \times \left(\frac{1}{6.8 \times 10^{-4}}\right)^2 = 9.7 \times 10^{-4}$$

Because K is less than 1, we know that the reaction is unfavorable.

3. To calculate the potential we use the Nernst equation; thus

$$E = (E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Sn^{4+}/Sn^{2+}}) - \frac{0.05916}{2}\log\frac{[Sn^{4+}][Fe^{2+}]^2}{[Sn^{2+}][Fe^{3+}]^2}$$

$$= (0.771 - 0.154) - \frac{0.05916}{2}\log\frac{(0.020)(0.030)^2}{(0.015)(0.050)^2}$$

$$= +0.626 \text{ V}$$

4. We can balance these reactions in a variety of ways; here we will identify the balanced half-reactions from Appendix 13 and add them together after adjusting the stoichiometric coefficients so that all electrons released in the oxidation reaction are consumed in the reduction reaction.

(a) The two half-reactions are

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$
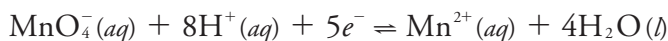
which combine to give an overall reaction of

Within the context of this problem, we do not need to balance the reactions; instead, we simply need to identify the two half-reactions and subtract their standard state reduction potentials to arrive at the reaction's standard state potential. Nevertheless, it is useful to be able to write the balanced overall reaction from the half-reactions as this information is needed if, as in Problem 3, we seek the reaction's potential under non-standard state conditions.
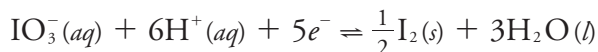
$$2MnO_4^{2-}(aq) + 5H_2SO_3(aq) \rightleftharpoons$$
$$2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^+(aq) + 3H_2O(l)$$
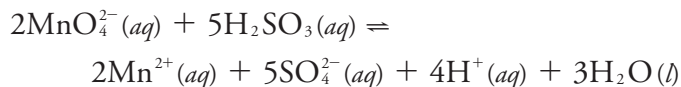
Using the Nernst equation, the standard state potential is

$$E^\circ = (E^\circ_{MnO_4^-/Mn^{2+}} - E^\circ_{SO_4^{2-}/H_2SO_3}) = 1.51 - 0.172$$
$$= 1.338 \text{ V} \approx 1.34 \text{ V}$$

and an equilibrium constant of

$$K = 10^{nE^\circ/0.05916} = 10^{(10)(1.338)/0.05916} = 1.47 \times 10^{226}$$
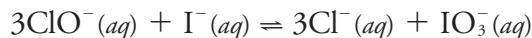
(b) The two half-reactions are
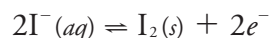
$$IO_3^-(aq) + 6H^+(aq) + 5e^- \rightleftharpoons \frac{1}{2}I_2(s) + 3H_2O(l)$$

$$2I^-(aq) \rightleftharpoons I_2(s) + 2e^-$$

which combine to give an overall reaction of

$$IO_3^-(aq) + 5I^-(aq) + 6H^+(aq) \rightleftharpoons 3I_2(s) + 3H_2O(l)$$

Using the Nernst equation, the standard state potential is

$$E^\circ = (E^\circ_{IO_3^-/I_2} - E^\circ_{I_2/I^-}) = 1.195 - 0.5355$$
$$= 0.6595 \text{ V} \approx 0.660 \text{ V}$$

and an equilibrium constant of

$$K = 10^{nE^\circ/0.05916} = 10^{(5)(0.6595)/0.05916} = 5.48 \times 10^{55}$$

(c) The two half-reactions are
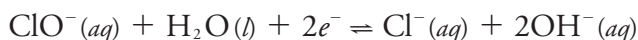
$$ClO^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq)$$

$$I^-(aq) + 6OH^-(aq) \rightleftharpoons IO_3^-(aq) + 3H_2O(l) + 6e^-$$

which combine to give an overall reaction of

$$3ClO^-(aq) + I^-(aq) \rightleftharpoons 3Cl^-(aq) + IO_3^-(aq)$$

Using the Nernst equation, the standard state potential is

$$E^\circ = (E^\circ_{ClO^-/Cl^-} - E^\circ_{IO_3^-/I^-}) = 0.890 - 0.257 = 0.633 \text{ V}$$

and an equilibrium constant of

$$K = 10^{nE^\circ/0.05916} = 10^{(6)(0.633)/0.05916} = 1.58 \times 10^{64}$$

5. (a) Because SO_4^{2-} is a weak base, decreasing the solution's pH, which makes the solution more acidic, converts some of the SO_4^{2-} to HSO_4^-. Decreasing the concentration of SO_4^{2-} shifts the solubility reaction to the right, increasing the solubility of $BaSO_4$.

(b) Adding $BaCl_2$, which is a soluble salt, increases the concentration of Ba^{2+} in solution, pushing the solubility reaction to the left and decreasing the solubility of $BaSO_4$.

(c) Increasing the solution's volume by adding water decreases the concentration of both Ba^{2+} and of SO_4^{2-}, which, in turn, pushes the solubility reaction to the right, increasing the solubility of $BaSO_4$.

6. (a) A solution of NaCl contains the following species: Na^+, Cl^-, H_3O^+, and OH^-. The charge balance equation is

$$[H_3O^+] + [Na^+] = [Cl^-] + [OH^-]$$

and the mass balance equations are

$$0.10\ M = [Na^+]$$
$$0.10\ M = [Cl^-]$$

(b) A solution of HCl contains the following species: Cl^-, H_3O^+, and OH^-. The charge balance equation is

$$[H_3O^+] = [Cl^-] + [OH^-]$$

and the mass balance equation is

$$0.10\ M = [Cl^-]$$

A solution of HCl will contain some un-dissociated HCl(*aq*); however, because HCl is a strong acid, the concentration of HCl(*aq*) is so small that we can safely ignore it when writing the mass balance equation for chlorine.

(c) A solution of HF contains the following species: HF, F^-, H_3O^+, and OH^-. The charge balance equation is

$$[H_3O^+] = [F^-] + [OH^-]$$

and the mass balance equation is

$$0.10\ M = [HF] + [F^-]$$

(d) A solution of NaH_2PO_4 contains the following species: Na^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3O^+, and OH^-. The charge balance equation is

$$[Na^+] + [H_3O^+] = [OH^-] + [H_2PO_4^-] +$$
$$2 \times [HPO_4^{2-}] + 3 \times [PO_4^{3-}]$$

and the mass balance equations are

$$0.10\ M = [Na^+]$$
$$0.10\ M = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

(e) A saturated solution of $MgCO_3$ contains the following species: Mg^{2+}, CO_3^{2-}, HCO_3^-, H_2CO_3, H_3O^+, and OH^-. The charge balance equation is

$$2 \times [Mg^{2+}] + [H_3O^+] = [OH^-] + [HCO_3^-] + 2 \times [CO_3^{2-}]$$

and the mass balance equation is

$$[Mg^{2+}] = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

For a saturated solution of $MgCO_3$, we know that the concentration of Mg^{2+} must equal the combined concentration of carbonate in all three of its forms.

(f) A solution of $Ag(CN)_2^-$ prepared using $AgNO_3$ and KCN contains the following ions: Ag^+, NO_3^-, K^+, CN^-, $Ag(CN)_2^-$, HCN, H_3O^+, and OH^-. The charge balance equation is

$$[Ag^+] + [K^+] + [H_3O^+] =$$
$$[OH^-] + [NO_3^-] + [CN^-] + [Ag(CN)_2^-]$$

and the mass balance equations are

$$[NO_3^-] = [Ag^+] + [Ag(CN)_2^-]$$

$$[K^+] = [CN^-] + [HCN] + 2 \times [Ag(CN)_2^-]$$

(g) A solution of HCl and $NaNO_2$ contains the following ions: H_3O^+, OH^-, Cl^-, Na^+, NO_2^-, and HNO_2. The charge balance equation is

$$[Na^+] + [H_3O^+] = [OH^-] + [NO_2^-] + [Cl^-]$$

and the mass balance equations are

$$0.10 \text{ M} = [Cl^-]$$

$$0.050 \text{ M} = [Na^+]$$

$$0.050 \text{ M} = [NO_2^-] + [HNO_2]$$

7. (a) Perchloric acid, $HClO_4$, is a strong acid, a solution of which contains the following species: H_3O^+, OH^-, and ClO_4^-. The composition of the solution is defined by a charge balance equation and a mass balance equation for ClO_4^-

$$[H_3O^+] = [OH^-] + [ClO_4^-]$$

$$[ClO_4^-] = 0.050 \text{ M}$$

and by the K_w expression for water.

$$[H_3O^+][OH^-] = K_w$$

Because $HClO_4$ is a strong acid and its concentration of 0.050 M is relatively large, we can assume that

$$[OH^-] << [ClO_4^-]$$

and that

$$[H_3O^+] = [ClO_4^-] = 0.050 \text{ M}$$

The pH, therefore is, 1.30. To check our assumption, we note that a pH of 1.30 corresponds to a pOH of 12.70 and to a $[OH^-]$ of 2.0×10^{-13} M. As this is less than 5% of 0.050 M, our assumption that

$$[OH^-] << [ClO_4^-]$$

is reasonable.

(b) Hydrochloric acid, HCl, is a strong acid, a solution of which contains the following species: H_3O^+, OH^-, and Cl^-. The composition of the solution is defined by a charge balance equation and a mass balance equation for Cl^-

$$[H_3O^+] = [OH^-] + [Cl^-]$$

$$[Cl^-] = 1.00 \times 10^{-7} \text{ M}$$

and by the K_w expression for water.

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Although HCl is a strong acid, its concentration of 1.00×10^{-7} M is relatively small such that we likely cannot assume that

$$[OH^-] \ll [Cl^-]$$

To find the pH, therefore, we substitute the mass balance equation for Cl^- into the charge balance equation and rearrange to solve for the concentration of OH^-

$$[OH^-] = [H_3O^+] - 1.00 \times 10^{-7}$$

and then substitute this into the K_w expression for the dissociation of water

$$[H_3O^+]\{[H_3O^+] - 1.00 \times 10^{-7}\} = 1.00 \times 10^{-14}$$

$$[H_3O^+]^2 + (1.00 \times 10^{-7})[H_3O^+] + 1.00 \times 10^{-14} = 0$$

Solving the quadratic equation gives $[H_3O^+]$ as 1.62×10^{-7} and the pH as 6.79.

(c) Hypochlorous acid, HOCl, is a weak acid, a solution of which contains the following species: H_3O^+, OH^-, HOCl, and ClO^-. The composition of the solution is defined by a charge balance equation and a mass balance equation for HOCl

$$[H_3O^+] = [OH^-] + [OCl^-]$$

$$[HOCl] + [ClO^-] = 0.025 \text{ M}$$

and by the K_a and K_w expressions for HOCl and water, respectively

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = 3.0 \times 10^{-8}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because the solution is acidic, let's assume that

$$[OH^-] \ll [H_3O^+]$$

which reduces the charge balance equation to

$$[H_3O^+] = [ClO^-] = x$$

Next, we substitute this equation for $[ClO^-]$ into the mass balance equation and solve for [HOCl]

$$[HOCl] = 0.025 - x$$

Here, and elsewhere in this textbook, we assume that you have access to a calculator or other tool that can solve the quadratic equation. Be sure that you examine both roots to the equation and that you choose the root that makes chemical sense.

Having defined the concentrations of all three species in terms of a single variable, we substitute them back into the K_a expression for HOCl

$$K_a = \frac{[H_3O^+][OCl^-]}{[HOCl]} = \frac{x^2}{0.025 - x} = 3.0 \times 10^{-8}$$

which we can solve using the quadratic equation. Alternatively, we can simplify further by recognizing that because HOCl is a weak acid, x likely is significantly smaller than 0.025 and $0.025 - x \approx 0.025$

$$\frac{x^2}{0.025} = 3.0 \times 10^{-8}$$

which gives x as 2.74×10^{-5} and the pH as 4.56. Checking our assumptions, we note that both are reasonable: 2.74×10^{-5} is less than 5% of 0.025 and $[OH^-]$, which is 3.6×10^{-10} is less than 5% of $[H_3O^+$, which is 2.74×10^{-5}.

(d) Formic acid, HCOOH, is a weak acid, a solution of which contains the following species: H_3O^+, OH^-, HCOOH, and $HCOO^-$. The composition of the solution is defined by a charge balance equation and a mass balance equation for HCOOH

$$[H_3O^+] = [OH^-] + [HCOO^-]$$

$$[HCOOH] + [HCOO^-] = 0.010 \text{ M}$$

and the K_a and K_w expressions for HCOOH and water, respectively

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = 1.80 \times 10^{-4}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because the solution is acidic, let's assume that

$$[OH^-] \ll [H_3O^+]$$

which reduces the charge balance equation to

$$[H_3O^+] = [HCOO^-] = x$$

Next, we substitute this equation for $[HCOO^-]$ into the mass balance equation and solve for [HCOOH]

$$[HCOOH] = 0.010 - x$$

Having defined the concentrations of all three species in terms of a single variable, we substitute them back into the K_a expression for HCOOH

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{x^2}{0.010 - x} = 1.80 \times 10^{-4}$$

and solve for x. In Problem 8b we simplified this equation further by assuming that x is significantly smaller than the initial concentration

of the weak acid; this likely is not the case here because HCOOH is a stronger weak acid than HOCl and, therefore, more likely to dissociate. Solving for x using the quadratic equation gives its value as 1.25×10^{-3} and the pH as 2.90. Checking our one assumption, we note that it is reasonable: the $[OH^-]$, which is 8.00×10^{-12}, is less than 5% of $[H_3O^+]$, which is 1.25×10^{-3}.

(e) Barium hydroxide, $Ba(OH)_2$, is a strong base, a solution of which contains the following species: H_3O^+, OH^-, and Ba^{2+}. The composition of the solution is defined by a charge balance equation and a mass balance equation for Ba^{2+}

$$2 \times [Ba^{2+}] + [H_3O^+] = [OH^-]$$

$$[Ba^{2+}] = 0.050 \text{ M}$$

and by the K_w expression for water.

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because $Ba(OH)_2$ is a strong base and its concentration of 0.050 M is relatively large, we can assume that

$$[H_3O^+] \ll [OH^-]$$

and that

$$[OH^-] = 2 \times [Ba^{2+}] = 2 \times (0.050 \text{ M}) = 0.10 \text{ M}$$

The pOH, therefore is, 1.00 and the pH is 13.00. To check our assumption, we note that a pH of 13.00 corresponds to a $[H_3O^+]$ of 1.0×10^{-13} M. As this is less than 5% of 0.10 M, our assumption that

$$[H_3O^+] \ll [OH^-]$$

is reasonable.

(f) Pyridine, C_5H_5N, is a weak base, a solution of which contains the following species: H_3O^+, OH^-, C_5H_5N, and $C_5H_5NH^+$. The composition of the solution is defined by a charge balance equation and a mass balance equation for C_5H_5N

$$[H_3O^+] + [C_5H_5NH^+] = [OH^-]$$

$$[C_5H_5N] + [C_5H_5NH^+] = 0.010 \text{ M}$$

and the K_b and K_w expressions for C_5H_5N and water, respectively

$$K_b = \frac{[OH^-][C_5H_5NH^+]}{[C_5H_5N]} = 1.69 \times 10^{-9}$$

$$[H_3O^+][OH^-] = K_w = 1.00 \times 10^{-14}$$

Because the solution is basic, let's assume that

$$[H_3O^+] << [OH^-]$$

which reduces the charge balance equation to

$$[C_5H_5N^+] = [OH^-] = x$$

Next, we substitute this equation for $[C_5H_5NH^+]$ into the mass balance equation and solve for $[C_5H_5N]$

$$[C_5H_5N] = 0.010 - x$$

Having defined the concentrations of all three species in terms of a single variable, we substitute them back into the K_b expression for C_5H_5NH

$$K_b = \frac{[OH^-][C_5H_5NH^+]}{[C_5H_5N]} = \frac{x^2}{0.010 - x} = 1.69 \times 10^{-9}$$

which we can solve using the quadratic equation. Alternatively, we can simplify further by recognizing that because C_5H_5N is a weak base, x likely is significantly smaller than 0.010 and $0.010 - x \approx 0.010$

$$\frac{x^2}{0.010} = 1.69 \times 10^{-9}$$

which gives x as 4.11×10^{-6}, the pOH as 5.39, and the pH as 8.61. Checking our assumptions, we note that both are reasonable: 4.11×10^{-6} is less than 5% of 0.010 and $[H_3O^+]$, which is 2.43×10^{-9} is less than 5% of $[OH^-]$, which is 4.11×10^{-6}.

8. (a) Figure SM6.2 shows a ladder diagram for maleic acid. A solution of 0.10 M H_2A will contain more H_2A than HA^-, and have a pH of less than 1.910. Maleic acid is a relatively strong weak acid (K_{a1} is 0.0123) and is likely to dissociate to an appreciable extent; thus, a reasonable estimate is that the solution's pH falls in the acidic portion of maleic acid's buffer region, perhaps between 1.4 and 1.6.

A solution of 0.10 M NaHA will contain more HA^- than H_2A or A^{2-}, and have a pH between 1.910 and 6.332. A reasonable estimate is that the pH is near the middle of the predominance region for HL^-, or approximately 4.1.

A solution of 0.10 M Na_2A will contain more A^{2-} than H_2A or HA^-, and, because A^{2-} is a weak base, will have a pH greater than 7. Although more difficult to estimate, a pH between 9 and 10 is a reasonable guess.

(b) Figure SM6.3 shows a ladder diagram for malonic acid. A solution of 0.10 M H_2A will contain more H_2A than HA^-, and have a pH of less than 2.847. Malonic acid is a relatively strong weak acid (K_{a1} is 1.42×10^{-3}) and is likely to dissociate to an appreciable extent, but less than for maleic acid; thus, a reasonable estimate is that the solution's
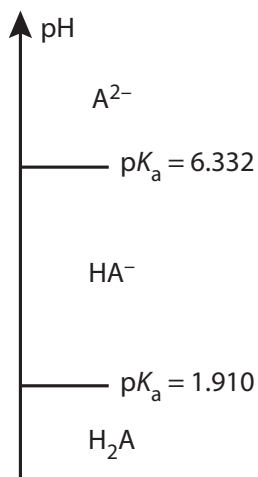

Figure SM6.2 Ladder diagram for maleic acid showing the pH values for which H_2A, HA^-, and A^{2-} are the predominate species.
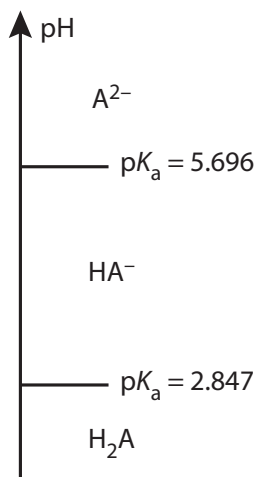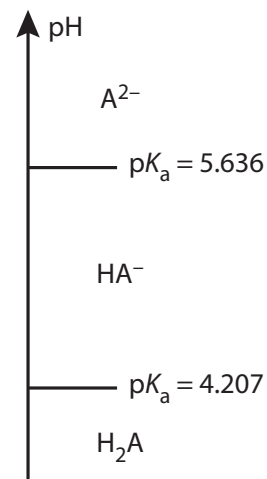

Figure SM6.3 Ladder diagram for malonic acid showing the pH values for which H_2A, HA^-, and A^{2-} are the predominate species.

pH falls close to the bottom of the acidic portion of malonic acid's buffer region, perhaps between 1.8 and 2.0.

A solution of 0.10 M NaHA will contain more HA^- than H_2A or A^{2-}, and have a pH between 2.847 and 5.696. A reasonable estimate is that the pH is near the middle of the predominance region for HA^-, or approximately 4.3.

A solution of 0.10 M Na_2A will contain more A^{2-} than H_2A or HA^-, and, because A^{2-} is a weak base, will have a pH greater than 7. Although more difficult to estimate, a pH between 9 and 10 is a reasonable guess.

(c) Figure SM6.4 shows a ladder diagram for succinic acid. A solution of 0.10 M H_2A will contain more H_2A than HA^-, and have a pH of less than 4.207. Maleic acid is not a relatively strong weak acid (K_{a1} is 6.21×10^{-5}); thus, a reasonable estimate is that the solution's pH falls below maleic acid's buffer region, perhaps between 2.5 and 3.0.

A solution of 0.10 M NaHA will contain more HA^- than H_2A or A^{2-}, and have a pH between 4.207 and 5.636. A reasonable estimate is that the pH is near the middle of the predominance region for HA^-, or approximately 4.9.

A solution of 0.10 M Na_2A will contain more A^{2-} than H_2A or HA^-, and, because A^{2-} is a weak base, will have a pH greater than 7. Although more difficult to estimate, a pH between 9 and 10 is a reasonable guess.

Figure SM6.4 Ladder diagram for succinic acid showing the pH values for which H_2A, HA^-, and A^{2-} are the predominate species.

9. (a) Malonic acid, H_2A, is a diprotic weak acid, a solution of which contains the following species: H_3O^+, OH^-, H_2A, HA^-, and A^{2-}. From its ladder diagram (see Figure SM6.3), we assume that

$$[A^{2-}] << [HA^-]$$

which means we can treat a solution of H_2L as if it is a monoprotic weak acid. Assuming that

$$[OH^-] << [H_3O^+]$$

then we know that

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} = \frac{x^2}{0.10 - x} = 1.42 \times 10^{-3}$$

which we solve using the quadratic equation, finding that x is 0.0112 and that the pH is 1.95, which is within our estimated range of 1.8–2.0 from Problem 8. Checking our assumptions, we note that the concentration of OH^-, which is 8.93×10^{-13}, is less than 5% of $[H_3O^+]$; thus, this assumption is reasonable. To evaluate the assumption that we can ignore A^{2-}, we use K_{a2} to determine its concentration

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = \frac{(0.0112)[A^{2-}]}{(0.0112)} = [A^{2-}] = 2.01 \times 10^{-6}$$

finding that it is less than 5% of [HA⁻]; thus, this assumption is reasonable as well.

(b) A solution of monohydrogen malonate, NaHA, contains the following species: H_3O^+, OH^-, H_2A, and HA^-, and A^{2-}. From its ladder diagram (see Figure SM6.3), we assume that

$$[H_2A] \ll [HA^-] \quad \text{and} \quad [A^{2-}] \ll [HA^-]$$

Under these conditions, the $[H_3O^+]$ is given by the equation

$$[H_3O^+] = \sqrt{\frac{K_{a1} K_{a2} C_{NaHA} + K_{a1} K_w}{C_{NaHA} + K_{a1}}}$$

Substituting in values for K_{a1}, K_{a2}, K_w, and C_{NaHA} gives $[H_3O^+]$ as 5.30×10^{-5}, or a pH of 4.28, which is very close to our estimate of 4.3 from Problem 8. To evaluate the assumption that we can ignore H_2A, we use K_{a1} to calculate its concentration

$$[H_2A] = \frac{[H_3O^+][HA^-]}{K_{a1}} = \frac{(5.30 \times 10^{-5})(0.10)}{1.42 \times 10^{-3}} = 3.73 \times 10^{-3}$$

finding that it is less than 5% of $[HA^-] \approx C_{NaHA} = 0.10$ M. To evaluate the assumption that we can ignore A^{2-}, we use K_{a2} to determine its concentration

$$[A^{2-}] = \frac{K_{a2}[HA^-]}{[H_3O^+]} = \frac{(2.01 \times 10^{-6})(0.10)}{5.30 \times 10^{-5}} = 3.79 \times 10^{-3}$$

finding that it, too, is less than 5% of $[HA^-] \approx C_{NaHA} = 0.10$ M.

(c) Sodium malonate, Na_2A, is a diprotic weak base, a solution of which contains the following species: H_3O^+, OH^-, Na^+, H_2A, HA^-, and A^{2-}. From its ladder diagram (see Figure SM6.3), we assume that

$$[H_2A] \ll [HA^-]$$

which means we can treat a solution of A^{2-} as if it is a monoprotic weak base. Assuming that

$$[H_3O^+] \ll [OH^-]$$

then we know that

$$K_{b1} = \frac{[OH^-][HA^-]}{[A^{2-}]} = \frac{x^2}{0.10 - x} = 4.98 \times 10^{-9}$$

which we solve using the quadratic equation, finding that x is 2.23×10^{-5}, that the pOH is 4.65, and that the pH is 9.35, which is within our estimated range of 9–10 from Problem 8. Checking our assumptions, we note that the concentration of H_3O^+, which is 4.48×10^{-10}, is less than 5% of $[OH^-]$; thus, this assumption is reasonable. To evaluate the assumption that we can ignore H_2A, we use K_{b2} to determine its concentration

$$[H_2A] = \frac{K_{b2}[HA^-]}{[OH^-]} =$$

$$\frac{(7.04 \times 10^{-12})(2.23 \times 10^{-5})}{(2.23 \times 10^{-5})} = 7.04 \times 10^{-12}$$

finding that it is less than 5% of $[HA^-]$; thus, this assumption is reasonable as well.

10. For a simple solubility reaction without any complications from acid–base chemistry or from complexation chemistry, the composition of the system at equilibrium is determined by the solubility reaction

$$Hg_2Br_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Br^-(aq)$$
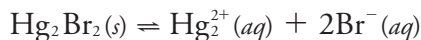
its corresponding solubility product

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = 5.6 \times 10^{-23}$$

and the stoichiometry of the solubility reaction.

(a) For a simple saturated solution of Hg_2Br_2, the following table defines the equilibrium concentrations of Hg_2^{2+} and Br^- in terms of their concentrations in the solution prior to adding Hg_2Br_2 and the change in their concentrations due to the solubility reaction.

$Hg_2Br_2(s)$	$\rightleftharpoons$	$Hg_2^{2+}(aq)$	$+$	$2Br^-(aq)$
intial	—	0		0
change	—	$+x$		$+2x$
equilibrium	—	x		$2x$

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = (x)(2x)^2 = 4x^3 = 5.6 \times 10^{-23}$$

and solving gives x as 2.4×10^{-8}. The molar solubility of Hg_2Br_2 is the concentration of Hg_2^{2+}, which is x or 2.4×10^{-8} M.

(b) For a saturated solution of Hg_2Br_2 in 0.025 M $Hg_2(NO_3)_2$, the following table defines the equilibrium concentrations of Hg_2^{2+} and Br^- in terms of their concentrations in the solution prior to adding Hg_2Br_2, and the change in their concentrations due to the solubility reaction.

$Hg_2Br_2(s)$	$\rightleftharpoons$	$Hg_2^{2+}(aq)$	$+$	$2Br^-(aq)$
I	—	0.025		0
C	—	$+x$		$+2x$
E	—	$0.025 + x$		$2x$

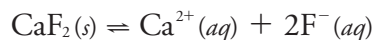Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = (0.025 + x)(2x)^2 = 5.6 \times 10^{-23}$$

leaves us with a cubic equation that is difficult to solve. We can simplify the problem if we assume that x is small relative to 0.025 M, an

Although perhaps not obvious, the approach we are taking here is equivalent to the systematic approach to solving equilibrium problems described in Section 6G.3 that combines a charge balance equation and/or a mass balance equation with equilibrium constant expressions. For part (a), a charge balance equation requires that

$$2 \times [Hg_2^{2+}] = [Cl^-]$$

If we define the concentration of Hg_2^{2+} as x, then the concentration of Cl^- is $2x$, which is the stoichiometric relationship shown in the table and leads to the same equation

$$K_{sp} = 4x^3 = 5.6 \times 10^{-23}$$

Note that we ignore the presence of H_3O^+ and OH^- when writing this charge balance equation because the solution has a neutral pH and the concentrations of H_3O^+ and OH^- are identical.

The same argument holds true for parts (b) and (c), although you may need to do a little work to convince yourself of this.

To save space, we use "I" to label the row of initial concentrations, "C" to label the row showing changes in concentration, and "E" to label the row of equilibrium concentrations. For obvious reasons, these tables sometimes are called ICE tables.

assumption that seems reasonable given that the molar solubility of Hg_2Br_2 in water is just 2.4×10^{-8} M; thus

$$K_{sp} = (0.025 + x)(2x)^2 \approx (0.025)(2x)^2 = 5.6 \times 10^{-23}$$

Solving gives x as 2.4×10^{-11}, a result that clearly is significantly less than 0.025. The molar solubility of Hg_2Br_2 is the concentration of Hg_2^{2+} from the Hg_2Br_2, which is x or 2.4×10^{-11} M.

(c) For a saturated solution of Hg_2Br_2 in 0.050 M NaBr, the following table defines the equilibrium concentrations of Hg_2^{2+} and Br^- in terms of their concentrations in the solution prior to adding Hg_2Br_2 and the change in their concentrations due to the solubility reaction.

$Hg_2Br_2(s)$	$\rightleftharpoons$	$Hg_2^{2+}(aq)$	$+$	$2Br^-(aq)$
I	—	0		0.050
C	—	$+x$		$+2x$
E	—	x		$0.050 + 2x$

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Hg_2^{2+}][Br^-]^2 = (x)(0.050 + 2x)^2 = 5.6 \times 10^{-23}$$

leaves us with a cubic equation that is difficult to solve. We can simplify the problem if we assume that $2x$ is small relative to 0.050 M, an assumption that seems reasonable given that the molar solubility of Hg_2Br_2 in water is just 2.4×10^{-8} M; thus

$$K_{sp} = (x)(0.050 + 2x)^2 \approx (x)(0.050)^2 = 5.6 \times 10^{-23}$$

Solving gives x as 2.2×10^{-20}, a result that clearly makes $2x$ significantly less than 0.050. The molar solubility of Hg_2Br_2 is the concentration of Hg_2^{2+}, which is x or 2.2×10^{-20} M.

11. Because F^- is a weak base, the molar solubility of CaF_2 depends on the solution's pH and whether fluorine is present as F^- or as HF. The ladder diagram for HF, which is included in Figure SM6.1, shows that F^- is the only significant form of fluorine at a pH of 7.00, which means the solubility of CaF_2 is determined by the reaction

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

for which the equilibrium constant expression is

$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$

The following table defines the equilibrium concentrations of Ca^{2+} and F^- in terms of their concentrations in the solution prior to adding CaF_2, and the change in their concentrations due to the solubility reaction.

$$\begin{array}{c|ccc}
 & \text{CaF}_2\,(s) & \rightleftharpoons & \text{Ca}^{2+}\,(aq) & + & 2\text{F}^-\,(aq) \\
\hline
\text{I} & - & & 0 & & 0 \\
\text{C} & - & & +x & & +2x \\
\text{E} & - & & x & & 2x
\end{array}$$

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

and solving gives x as 2.1×10^{-4}. The molar solubility of CaF_2 at a pH of 7.00 is the concentration of Ca^{2+}, which is x or 2.1×10^{-4} M. Our solution here assumes that we can ignore the presence of HF; as a check on this assumption, we note that

$$[\text{HF}] = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{K_{a,\text{HF}}} = \frac{(1.0 \times 10^{-7})(2.1 \times 10^{-4})}{6.8 \times 10^{-4}} = 3.1 \times 10^{-8}$$

a concentration that is negligible when compared to the concentration of F^-.

At a pH of 2.00, the only significant form of fluorine is HF, which means we must write the solubility reaction for CaF_2 in terms of HF instead of F^-; thus
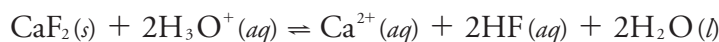
$$\text{CaF}_2\,(s) + 2\text{H}_3\text{O}^+\,(aq) \rightleftharpoons \text{Ca}^{2+}\,(aq) + 2\text{HF}\,(aq) + 2\text{H}_2\text{O}\,(l)$$

To determine the equilibrium constant for this reaction, we note that it is the sum of five reactions, each with a standard equilibrium constant; thus

$$\text{CaF}_2\,(s) \rightleftharpoons \text{Ca}^{2+}\,(aq) + 2\text{F}^-\,(aq)$$

$$\text{F}^-\,(aq) + \text{H}_2\text{O}\,(l) \rightleftharpoons \text{HF}\,(aq) + \text{OH}^-\,(aq)$$

$$\text{F}^-\,(aq) + \text{H}_2\text{O}\,(l) \rightleftharpoons \text{HF}\,(aq) + \text{OH}^-\,(aq)$$

$$\text{H}_3\text{O}^+\,(aq) + \text{OH}^-\,(aq) \rightleftharpoons 2\text{H}_2\text{O}\,(l)$$

$$\text{H}_3\text{O}^+\,(aq) + \text{OH}^-\,(aq) \rightleftharpoons 2\text{H}_2\text{O}\,(l)$$
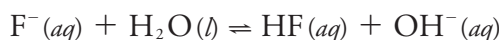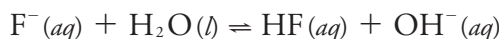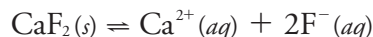
$$\begin{aligned}
K &= K_{sp,\text{CaF}_2} \times (K_{b,\text{F}^-})^2 \times (K_w)^{-2} \\
&= K_{sp,\text{CaF}_2} \times \left(\frac{K_w}{K_{a,\text{HF}}}\right)^2 \times \left(\frac{1}{K_w}\right)^2 \\
&= \frac{K_{sp,\text{CaF}_2}}{(K_{a,\text{HF}})^2} = \frac{3.9 \times 10^{-11}}{(6.8 \times 10^{-4})^2} = 8.4 \times 10^{-5}
\end{aligned}$$

The following table defines the equilibrium concentrations of Ca^{2+}, HF, and H_3O^+ in terms of their concentrations in the solution prior to adding CaF_2, and the change in their concentrations due to the solubility reaction; for H_3O^+, note that its concentration does not change because the solution is buffered.

Note that the molar solubility of CaF_2 is independent of pH for any pH level greater than approximately $pK_{a,\text{HF}} + 1 \approx 4.2$. This is because at these pH levels the solubility reaction does not include any acid-base chemistry.

We also can write this reaction as

$$\text{CaF}_2\,(s) + 2\text{H}_2\text{O}\,(l) \rightleftharpoons$$
$$\text{Ca}^{2+}\,(aq) + 2\text{F}^-\,(aq) + 2\text{OH}^-\,(aq)$$
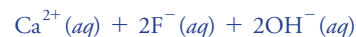
and then make appropriate changes to the equations that follow. The final answer is the same.

		$CaF_2(s)$	+	$2H_3O^+$	$\rightleftharpoons$	Ca^{2+}	+	$2HF$	+	$2H_2O(l)$
I	—			0.010		0		0		—
C	—			—		$+x$		$+2x$		—
E	—			0.010		x		$2x$		—

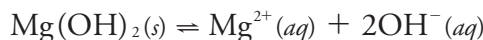Substituting the equilibrium concentrations into the reaction's equilibrium constant expression

$$K = \frac{[Ca^{2+}][HF]^2}{[H_3O^+]^2} = \frac{(x)(2x)^2}{(0.010)^2} = \frac{4x^3}{(0.010)^2} = 8.4 \times 10^{-5}$$

and solving gives x as 1.3×10^{-3}. The molar solubility of CaF_2 at a pH of 2.00 is the concentration of Ca^{2+}, which is x or 1.3×10^{-3} M. Our solution here assumes that we can ignore the presence of F^-; as a check on this assumption, we note that

$$[F^-] = \frac{K_{a,HF}[HF]}{[H_3O^+]} = \frac{(6.8 \times 10^{-4})(1.3 \times 10^{-3})}{0.01} = 8.8 \times 10^{-5}$$

a concentration that is negligible when compared to the concentration of HF.

12. The solubility of $Mg(OH)_2$ is determined by the following reaction

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

for which the equilibrium constant expression is

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 7.1 \times 10^{-12}$$

The following table defines the equilibrium concentrations of Mg^{2+} and OH^- in terms of their concentrations in the solution prior to adding CaF_2 and the change in their concentrations due to the solubility reaction; note that the concentration of OH^- is fixed by the buffer.

		$Mg(OH)_2(s)$	$\rightleftharpoons$	$Mg^{2+}(aq)$	+	$2OH^-(aq)$
I	—			0		1.0×10^{-7}
C	—			$+x$		—
E	—			x		1.0×10^{-7}

Substituting the equilibrium concentrations into the K_{sp} expression

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(1.0 \times 10^{-7})^2 = 7.1 \times 10^{-12}$$

and solving gives x as 710. The molar solubility of $Mg(OH)_2$ at a pH of 7.00 is the concentration of Mg^{2+}, which is x or 710 M; clearly, $Mg(OH)_2$ is very soluble in a pH 7.00 buffer.

If the solution is not buffered, then we have

	$Mg(OH)_2(s)$	$\rightleftharpoons$	$Mg^{2+}(aq)$	$+$	$2OH^-(aq)$
I	—		0		1.0×10^{-7}
C	—		$+x$		$+2x$
E	—		x		$(1.0 \times 10^{-7}) + 2x$

and substituting into the equilibrium constant expression

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)\{(1.0 \times 10^{-7}) + 2x)\}^2 = 7.1 \times 10^{-12}$$

leaves us with an equation that is not easy to solve exactly. To simplify the problem, lets assume that x is sufficiently large that

$$(1.0 \times 10^{-7}) + 2x \approx 2x$$

Substituting back

$$K_{sp} = [Mg^{2+}][OH^-]^2 = (x)(2x)^2 = 4x^3 = 7.1 \times 10^{-12}$$

and solving gives x as 1.2×10^{-4}. Checking our one assumption, we note that it is reasonable: 1.0×10^{-7} is less than 5% of $2x$. The molar solubility of $Mg(OH)_2$ is the concentration of Mg^{2+}, which is x or 1.2×10^{-4} M; clearly, $Mg(OH)_2$ is much less soluble in the unbuffered solution.

13. Because PO_4^{3-} is a weak base, the molar solubility of Ag_3PO_4 depends on the solution's pH and the specific form of phosphate present. The ladder diagram for H_3PO_4, which is included in Figure SM6.1, shows that HPO_4^{2-} is the only significant form of phosphate at a pH of 9.00, which means the solubility of Ag_3PO_4 is determined by the reaction
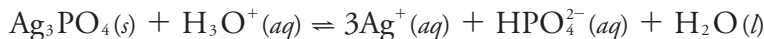
$$Ag_3PO_4(s) + H_3O^+(aq) \rightleftharpoons 3Ag^+(aq) + HPO_4^{2-}(aq) + H_2O(l)$$

To determine the equilibrium constant for this reaction, we note that it is the sum of three reactions, each with a standard equilibrium constant; thus

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$$

$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HPO_4^{2-}(aq)$$

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$
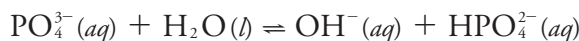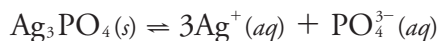
$$K = K_{sp,Ag_3PO_4} \times K_{b,PO_4^{3-}} \times (K_w)^{-1} = K_{sp,Ag_3PO_4} \times \frac{K_w}{K_{a,HPO_4^{2-}}} \times \frac{1}{K_w}$$

$$= \frac{K_{sp,Ag_3PO_4}}{K_{a,HPO_4^{2-}}} = \frac{2.8 \times 10^{-18}}{4.5 \times 10^{-13}} = 6.2 \times 10^{-6}$$

The following table defines the equilibrium concentrations of Ag^+, HPO_4^{2-}, and H_3O^+ in terms of their concentrations in the solution prior to adding Ag_3PO_4, and the change in their concentrations due to the solubility reaction; for H_3O^+, note that its concentration does not change because the solution is buffered.

	$Ag_3PO_4(s)$	+	H_3O^+	$\rightleftharpoons$	$3Ag^+$	+	HPO_4^{2-}	+	$H_2O(l)$
I	—		1.0×10^{-9}		0		0		—
C	—		—		$+3x$		$+x$		—
E	—		1.0×10^{-9}		$3x$		x		—

Substituting the equilibrium concentrations into the reaction's equilibrium constant expression

$$K = \frac{[Ag^+]^3[HPO_4^{2-}]}{[H_3O^+]} = \frac{(3x)^3(x)}{1.0 \times 10^{-9}} = \frac{27x^4}{1.0 \times 10^{-9}} = 6.2 \times 10^{-6}$$

and solving gives x as 1.2×10^{-4}. The molar solubility of Ag_3PO_4 at a pH of 2.00 is the concentration of HPO_4^{2-}, which is x or 1.2×10^{-4} M. Our solution here assumes that we can ignore the presence of other phosphate species; as a check on this assumption, we note that

$$[PO_4^{3-}] = \frac{K_{a,HPO_4^{2-}}[HPO_4^{2-}]}{[H_3O^+]} =$$

$$\frac{(4.5 \times 10^{-13})(1.2 \times 10^{-4})}{1.0 \times 10^{-9}} = 5.4 \times 10^{-8}$$

and that

$$[H_2PO_4^-] = \frac{[HPO_4^{2-}][H_3O^+]}{K_{a,H_2PO_4^-}} =$$

$$\frac{(1.2 \times 10^{-4})(1.0 \times 10^{-9})}{6.32 \times 10^{-8}} = 1.9 \times 10^{-6}$$

Both concentrations are less than 5% of the concentration of HPO_4^{2-}, so our assumptions are reasonable. Note that we do not need to check the assumption that the concentration of H_3PO_4 is negligible as it must be smaller than the concentration of $H_2PO_4^-$.

14. The equilibrium constants for the three reactions are

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

$$K_1 = \frac{[AgCl(aq)]}{[Ag^+][Cl^-]} = 5.01 \times 10^3$$

$$K_2 = \frac{[AgCl_2^-]}{[AgCl(aq)][Cl^-]} = 83.2$$

The concentration of $AgCl(aq)$ is easy to determine because the denominator of K_1 is simply K_{sp}; thus

$$[AgCl(aq)] = K_1K_{sp} = (5.01 \times 10^3)(1.8 \times 10^{-10}) = 9.0 \times 10^{-7} \text{ M}$$

To determine the concentration of the remaining species, we note that a charge balance equation requires that

$$[Ag^+] = [Cl^-] + [AgCl_2^-]$$

You may wonder why our approach to this problem does not involve setting up an ICE table. We can use an ICE table to organize our work if there is one and only one reaction that describes the equilibrium system. This is the case, for example, in Problem 10 where the solubility reaction for Hg_2Br_2 is the only reaction in solution, and the case in Problem 11 because only one reaction contributes significantly to the equilibrium condition. For more complicated systems, such as Problem 14 and several that follow, we must work with multiple equations, often solving them simultaneously.

Given that the concentration of AgCl(aq) is 9.0×10^{-7}, it seems reasonable to assume that the concentration of $AgCl_2^-$ is less than this and that we can simplify the charge balance equation to

$$[Ag^+] = [Cl^-] = x$$

Substituting into the K_{sp} equation

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.8 \times 10^{-10}$$

and solving gives x as 1.3×10^{-5}; thus, both the $[Ag^+]$ and the $[Cl^-]$ are 1.3×10^{-5} M. To check our assumption, we note that

$$[AgCl_2^-] = K_2[AgCl(aq)][Cl^-]$$
$$= (83.2)(9.0 \times 10^{-7})(1.3 \times 10^{-5}) = 9.7 \times 10^{-10}$$

the concentration of $AgCl_2^-$ is 9.7×10^{-10} M; thus, our assumption that we can ignore the concentration of $AgCl_2^-$ is reasonable.

15. (a) A solution of 0.050 M NaCl is 0.050 M in Na^+ and 0.050 M in Cl^-; thus

$$\mu = \frac{1}{2}\{(0.050)(+1)^2 + (0.050)(-1)^2\} = 0.050 \text{ M}$$

(b) A solution of 0.025 M $CuCl_2$ is 0.025 M in Cu^{2+} and 0.050 M in Cl^-; thus

$$\mu = \frac{1}{2}\{(0.025)(+2)^2 + (0.050)(-1)^2\} = 0.075 \text{ M}$$

(c) A solution of 0.10 M Na_2SO_4 is 0.20 M in Na^+ and 0.10 M in SO_4^{2-}; thus

$$\mu = \frac{1}{2}\{(0.20)(+1)^2 + (0.10)(-2)^2\} = 0.30 \text{ M}$$

16. (a) From Problem 10a, we know that the molar solubility of Hg_2Br_2 is sufficiently small that the solution's ionic strength is not altered significantly by the limited number of Hg_2^{2+} and Br^- ions in solution. The molar solubility remains 2.4×10^{-8} M.

(b) From Problem 10b we know that the molar solubility of Hg_2Br_2 is sufficiently small that the solution's ionic strength is not altered significantly by the limited number of Br^- ions or Hg_2^{2+} ions arising from the solubility reaction; however, we cannot ignore the contribution of $Hg_2(NO_3)_2$ to the solution's ionic strength, which is

$$\mu = \frac{1}{2}\{(0.025)(+2)^2 + (0.050)(-1)^2\} = 0.075 \text{ M}$$

Given the ionic strength, we next find the activity coefficients for Hg_2^{2+} and for Br^-; thus

$$-\log \gamma_{Hg_2^{2+}} = \frac{(0.51)(+2)^2\sqrt{0.075}}{1 + (3.3)(0.40)\sqrt{0.075}} = 0.410$$
$$\gamma_{Hg_2^{2+}} = 0.389$$

As we must form AgCl(*aq*) before we can form $AgCl_2^-$, the concentration of $AgCl_2^-$ will be less than [AgCl(*aq*)] unless there is a large excess of Cl^-.

Note that we did not include H_3O^+ and OH^- when calculating the ionic strength of these solutions because their concentrations are sufficiently small that they will not affect the ionic strength within the limit of our significant figures.

The same reasoning explains why we did not consider the acid-base chemistry of SO_4^{2-} in part (c) as the concentrations of H_3O^+, OH^-, and HSO_4^- are sufficiently small that we can safely ignore them.

$$-\log\gamma_{Br^-} = \frac{(0.51)(-1)^2\sqrt{0.075}}{1+(3.3)(0.30)\sqrt{0.075}} = 0.110$$

$$\gamma_{Br^-} = 0.776$$

where values of alpha are from Table 6.2. The ionic strength-adjusted K_{sp} for the solubility of Hg_2Br_2 is

$$K_{sp} = [Hg_2^{2+}][Br^-]^2\gamma_{Hg_2^{2+}}\gamma_{Br^-}^2 = 5.6 \times 10^{-23}$$

From here, we proceed as in Problem 10b; thus

$$K_{sp} = (0.025+x)(2x)^2(0.389)(0.776)^2 = 5.6 \times 10^{-23}$$

$$\approx (0.025)(2x)^2(0.389)(0.776)^2 = 5.6 \times 10^{-23}$$

finding that x is 4.9×10^{-11} and that the molar solubility of Hg_2Br_2 of 4.9×10^{-11} M is greater than the value of 2.4×10^{-11} M that we calculated when we ignored the affect on solubility of ionic strength.

(c) From Problem 10c we know that the molar solubility of Hg_2Br_2 is sufficiently small that the solution's ionic strength is not altered significantly by the limited number of Br^- ions or Hg_2^{2+} ions arising from the solubility reaction; however, we cannot ignore the contribution of NaBr to the solution's ionic strength, which is

$$\mu = \frac{1}{2}\{(0.050)(+1)^2+(0.050)(-1)^2\} = 0.050 \text{ M}$$

Given the ionic strength, we next find the activity coefficients for Hg_2^{2+} and for Br^-; thus

$$-\log\gamma_{Hg_2^{2+}} = \frac{(0.51)(+2)^2\sqrt{0.050}}{1+(3.3)(0.40)\sqrt{0.050}} = 0.352$$

$$\gamma_{Hg_2^{2+}} = 0.444$$

$$-\log\gamma_{Br^-} = \frac{(0.51)(-1)^2\sqrt{0.050}}{1+(3.3)(0.30)\sqrt{0.050}} = 0.0934$$

$$\gamma_{Br^-} = 0.807$$

where values of alpha are from Table 6.2. The ionic strength-adjusted K_{sp} for the solubility of Hg_2Br_2 is

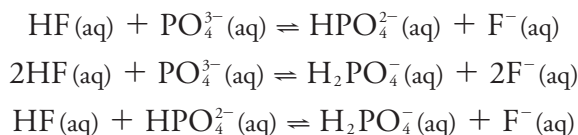$$K_{sp} = [Hg_2^{2+}][Br^-]^2\gamma_{Hg_2^{2+}}\gamma_{Br^-}^2 = 5.6 \times 10^{-23}$$

From here, we proceed as in Problem 10c; thus

$$K_{sp} = (x)(0.050+2x)^2(0.444)(0.807)^2 = 5.6 \times 10^{-23}$$

$$K_{sp} \approx (x)(0.050)^2(0.444)(0.807)^2 = 5.6 \times 10^{-23}$$

finding that x is 7.7×10^{-20} and that the molar solubility of Hg_2Br_2 of 7.7×10^{-20} M is greater than the value of 2.2×10^{-20} M that we calculated when we ignored the affect on solubility of ionic strength.
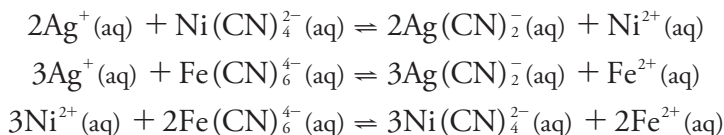
17. Because phosphate is a weak base, the solubility of $Ca_3(PO_4)_2$ will increase at lower pH levels as the predominate phosphate species transitions from PO_4^{3-} to HPO_4^{2-} to $H_2PO_4^-$ to H_3PO_4. A ladder diagram for phosphate is included in Figure SM6.1 and shows that PO_4^{3-} is the predominate species for pH levels greater than 12.35; thus, to minimize the solubility of $Ca_3(PO_4)_2$ we need to maintain the pH above 12.35.

18. (a) Figure SM6.1 shows a ladder diagram for HF and H_3PO_4. Based on this ladder diagram, we expect that the weak acid HF will react with the weak bases PO_4^{3-} and HPO_4^{2-} as their areas of predominance do not overlap with HF; thus

$$HF\,(aq) + PO_4^{3-}\,(aq) \rightleftharpoons HPO_4^{2-}\,(aq) + F^-\,(aq)$$

$$2HF\,(aq) + PO_4^{3-}\,(aq) \rightleftharpoons H_2PO_4^-\,(aq) + 2F^-\,(aq)$$

$$HF\,(aq) + HPO_4^{2-}\,(aq) \rightleftharpoons H_2PO_4^-\,(aq) + F^-\,(aq)$$

We also expect that the weak base F^- will react with the weak acid H_3PO_4; thus

$$F^-\,(aq) + H_3PO_4\,(aq) \rightleftharpoons H_2PO_4^{2-}\,(aq) + HF\,(aq)$$
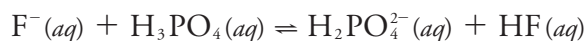
(b) Figure SM6.5 shows a ladder diagram for the cyano complexes of Ag^+, Ni^{2+}, and Fe^{2+}. Based on this ladder diagram, we expect that Ag^+ will displace Ni^{2+} from the $Ni(CN)_4^{2-}$ complex, that Ag^+ will displace Fe^{2+} from the $Fe(CN)_6^{4-}$ complex, and that Ni^{2+} will displace Fe^{2+} from the $Fe(CN)_6^{4-}$; thus

$$2Ag^+\,(aq) + Ni(CN)_4^{2-}\,(aq) \rightleftharpoons 2Ag(CN)_2^-\,(aq) + Ni^{2+}\,(aq)$$

$$3Ag^+\,(aq) + Fe(CN)_6^{4-}\,(aq) \rightleftharpoons 3Ag(CN)_2^-\,(aq) + Fe^{2+}\,(aq)$$

$$3Ni^{2+}\,(aq) + 2Fe(CN)_6^{4-}\,(aq) \rightleftharpoons 3Ni(CN)_4^{2-}\,(aq) + 2Fe^{2+}\,(aq)$$

(c) Figure SM6.6 shows a ladder diagram for the $Cr_2O_7^{2-}/Cr^{3+}$ and the Fe^{3+}/Fe^{2+} redox half-reactions. Based on this ladder diagram, we expect that Fe^{2+} will reduce $Cr_2O_7^{2-}$ to Cr^{3+}; thus

$$Cr_2O_7^{2-}\,(aq) + 6Fe^{2+}\,(aq) + 14H^+\,(aq) \rightleftharpoons$$
$$2Cr^{3+}\,(aq) + 6Fe^{3+}\,(aq) + 7H_2O\,(l)$$
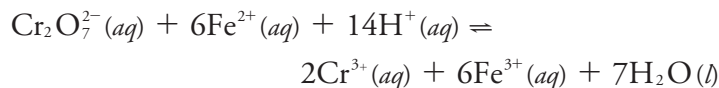
19. The pH of a buffer that contains a weak acid, HA, and its conjugate weak base, A^-, is given by equation 6.60

$$pH = pK_a + \log\frac{C_{A^-}}{C_{HA}}$$

which holds if the concentrations of OH^- and of H_3O^+ are significantly smaller than the concentrations of HA, C_{HA}, and of A^-, C_{A^-}.

(a) The pH of the buffer is

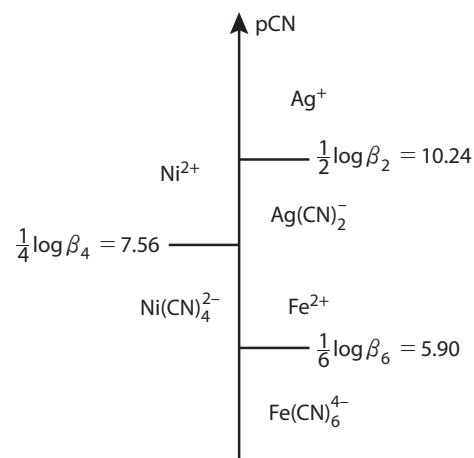$$pH = 3.745 + \log\frac{0.015}{0.025} = 3.52$$

Figure SM6.5 Ladder diagram for Problem 18b showing the areas of predominance for Ag^+, Ni^{2+}, and Fe^{3+} and their cyano complexes.
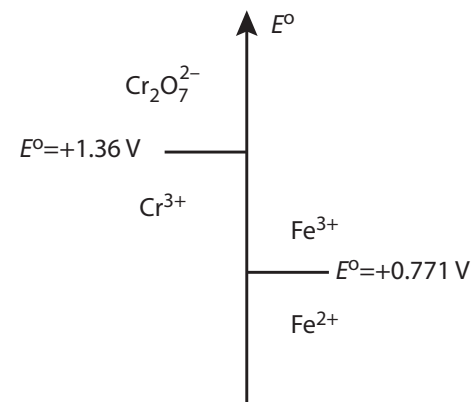

Figure SM6.6 Ladder diagram for Problem 18c showing the $Cr_2O_7^{2-}/Cr^{3+}$ and the Fe^{3+}/Fe^{2+} redox half-reactions.

With a pH of 3.52, the $[H_3O^+]$ is 3.0×10^{-4} and the $[OH^-]$ is 3.3×10^{-11}); thus, the assumptions inherent in equation 6.60 hold.

(b) A mixture consisting of an excess of a weak base, NH_3, and a limiting amount of a strong acid, HCl, will react to convert some of the NH_3 to its conjugate weak acid form, NH_4^+; thus

$$NH_3\,(aq) + HCl\,(aq) \longrightarrow NH_4^+\,(aq) + Cl^-\,(aq)$$

The moles of NH_4^+ formed are

$$\text{mol } NH_4^+ = M_{HCl}\,V_{HCl} = (1.0\text{ M})(0.00350\text{ L}) = 3.50 \times 10^{-3}$$

which leaves the moles of NH_3 as

$$\begin{aligned}
\text{mol } NH_3 &= M_{NH_3}\,V_{NH_3} - M_{HCl}\,V_{HCl} \\
&= (0.12\ M)(0.05000\ L) - (1.0\ M)(0.00350\ L) \\
&= 2.50 \times 10^{-3}
\end{aligned}$$

The total volume is 53.50 mL, which gives the concentrations of NH_4^+ and of NH_3 as

$$[NH_4^+] = \frac{3.50 \times 10^{-3}\text{ mol}}{0.0535\text{ L}} = 0.0654\text{ M}$$

$$[NH_3] = \frac{2.50 \times 10^{-3}\text{ mol}}{0.0535\text{ L}} = 0.0467\text{ M}$$

and a pH of

$$pH = 9.244 + \log\frac{0.0467}{0.0654} = 9.10$$

With a pH of 9.10, the $[H_3O^+]$ is 8.0×10^{-10} and the $[OH^-]$ is 1.3×10^{-5}); thus, the assumptions inherent in equation 6.60 hold.

(c) To calculate the pH we first determine the concentration of the weak acid, HCO_3^-, and the weak base, CO_3^{2-}

$$[HCO_3^-] = \frac{5.00\text{ g NaHCO}_3 \times \dfrac{1\text{ mol HCO}_3^-}{84.007\text{ g NaHCO}_3}}{0.100\text{ L}} = 0.595\text{ M}$$

$$[CO_3^{2-}] = \frac{5.00\text{ g Na}_2CO_3 \times \dfrac{1\text{ mol CO}_3^{2-}}{105.99\text{ g Na}_2CO_3}}{0.100\text{ L}} = 0.472\text{ M}$$

and then the pH

$$pH = 10.329 + \log\frac{0.472}{0.595} = 10.23$$

With a pH of 10.23, the $[H_3O^+]$ is 5.9×10^{-11} and the $[OH^-]$ is 1.7×10^{-4}); thus, the assumptions inherent in equation 6.60 hold.

20. Adding 5.0×10^{-4} mol of HCl converts 5.0×10^{-4} mol of the buffer's conjugate weak base, A^-, to its conjugate weak acid, HA. To simplify the calculations, we note that we can replace the concentrations of HA and of A^- in equation 6.60 with their respective moles as both

HA and A^- are in the same solution and, therefore, share the same volume.

(a) The pH after adding 5.0×10^{-4} mol of HCl is

$$pH = 3.745 + \log \frac{(0.015)(0.100) - 5.00 \times 10^{-4}}{(0.025)(0.100) + 5.00 \times 10^{-4}} = 3.27$$

As expected, adding HCl makes the solution more acidic, with the pH decreasing from 3.52 to 3.27.

With a pH of 3.27, the $[H_3O^+]$ is 5.4×10^{-4} and the $[OH^-]$ is 1.9×10^{-11}); thus, the assumptions inherent in equation 6.60 hold.

(b) The pH after adding 5.0×10^{-4} mol of HCl is

$$pH = 9.244 + \log \frac{(0.0467)(0.0535) - 5.00 \times 10^{-4}}{(0.0654)(0.0535) + 5.00 \times 10^{-4}} = 8.94$$

As expected, adding HCl makes the solution more acidic, with the pH decreasing from 9.01 to 8.94.

With a pH of 8.94, the $[H_3O^+]$ is 1.1×10^{-9} and the $[OH^-]$ is 9.1×10^{-6}); thus, the assumptions inherent in equation 6.60 hold.

(c) The pH after adding 5.0×10^{-4} mol of HCl is

$$pH = 10.329 + \log \frac{(0.472)(0.100) - 5.00 \times 10^{-4}}{(0.595)(0.100) + 5.00 \times 10^{-4}} = 10.22$$

As expected, adding HCl makes the solution more acidic, with the pH decreasing from 10.23 to 10.22; the change in pH is smaller here because the concentration of the buffering agents is larger.

With a pH of 10.22, the $[H_3O^+]$ is 6.0×10^{-11} and the $[OH^-]$ is 1.7×10^{-4}); thus, the assumptions inherent in equation 6.60 hold.

21. Adding 5.0×10^{-4} mol of NaOH converts 5.0×10^{-4} mol of the buffer's conjugate weak base, HA, to its conjugate weak acid, A^-. To simplify the calculations, we note that we can replace the concentrations of HA and of A^- in equation 6.60 with their respective moles as both HA and A^- are in the same solution and, therefore, share the same volume.

(a) The pH after adding 5.0×10^{-4} mol of NaOH is

$$pH = 3.745 + \log \frac{(0.015)(0.100) + 5.00 \times 10^{-4}}{(0.025)(0.100) - 5.00 \times 10^{-4}} = 3.74$$

As expected, adding NaOH makes the solution more basic, with the pH increasing from 3.52 to 3.74.

With a pH of 3.74, the $[H_3O^+]$ is 1.8×10^{-4} and the $[OH^-]$ is 5.5×10^{-11}); thus, the assumptions inherent in equation 6.60 hold.

(b) The pH after adding 5.0×10^{-4} mol of NaOH is

$$pH = 9.244 + \log \frac{(0.0467)(0.0535) + 5.00 \times 10^{-4}}{(0.0654)(0.0535) - 5.00 \times 10^{-4}} = 9.24$$

As expected, adding NaOH makes the solution more basic, with the pH increasing from 9.01 to 9.24.

With a pH of 9.24, the $[H_3O^+]$ is 5.8×10^{-10} and the $[OH^-]$ is 1.7×10^{-5}); thus, the assumptions inherent in equation 6.60 hold.

(c) The pH after adding 5.0×10^{-4} mol of NaOH is

$$pH = 10.329 + \log \frac{(0.472)(0.100) + 5.00 \times 10^{-4}}{(0.595)(0.100) - 5.00 \times 10^{-4}} = 10.24$$

As expected, adding NaOH makes the solution more basic, with the pH increasing from 10.23 to 10.22; the change in pH is smaller here because the concentration of the buffering agents is larger.

With a pH of 10.24, the $[H_3O^+]$ is 5.8×10^{-11} and the $[OH^-]$ is 1.7×10^{-4}); thus, the assumptions inherent in equation 6.60 hold.

22. (a) The equilibrium constant for the reaction is

$$K_1 = \frac{[ML]}{[M][L]}$$

Taking the log of both sides of this equation gives

$$\log K_1 = \log \frac{[ML]}{[L]} - \log[M] = \log \frac{[ML]}{[L]} + pM$$

which, upon rearranging, gives the desired equation

$$pM = \log K_1 - \log \frac{[ML]}{[L]}$$

For the case where K_1 is 1.5×10^8 we have

$$pM = \log(1.5 \times 10^8) - \log \frac{[ML]}{[L]} = 8.18 - \log \frac{[ML]}{[L]}$$

(b) Because the reaction between M and L is very favorable, we expect that all of M, which is the limiting reagent, is converted to ML, consuming an equivalent amount of L. Once equilibrium is reached, 0.010 mol of L remain and 0.010 mol of ML are formed, which gives

$$pM = 8.18 - \log \frac{0.010}{0.010} = 8.18$$

(c) Adding an additional 0.002 mol M converts an additional 0.002 mol of L to ML; thus, we now have 0.012 mol ML and 0.008 mol L, and pM is

$$pM = 8.18 - \log \frac{0.012}{0.008} = 8.00$$

23. The potential of a redox buffer is given by the Nernst equation

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Because Fe^{2+} and Fe^{3+} are in the same solution, we can replace their concentrations in the Nernst equation with moles; thus

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{\text{mol } Fe^{2+}}{\text{mol } Fe^{3+}} =$$

$$0.771 - 0.05916 \log \frac{0.015}{0.010} = 0.761 \text{ V}$$

After converting 0.002 mol Fe^{2+} to Fe^{3+}, the solution contains 0.013 mol Fe^{2+} and 0.012 mol Fe^{3+}; the potential, therefore, is

$$E = 0.771 - 0.05916 \log \frac{0.013}{0.012} = 0.769 \text{ V}$$

24. A general approach to each problem is provided here, but more specific details of setting up an Excel spreadsheet or writing a function in R are left to you; see Section 6J for more details.

(a) To find the solubility of CaF_2 we first write down all relevant equilibrium reactions; these are

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
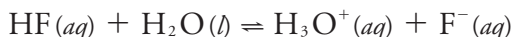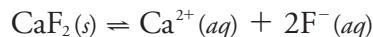
There are five species whose concentrations define this system (Ca^{2+}, F^-, HF, H_3O^+, and OH^-), which means we need five equations that relate the concentrations of these species to each other; these are the three equilibrium constant expressions

$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.8 \times 10^{-4}$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

a charge balance equation

$$2[Ca^{2+}] + [H_3O^+] = [OH^-] + [F^-]$$

and a mass balance equation

$$2 \times [Ca^{2+}] = [HF] + [F^-]$$

Be sure you understand why the concentration of Ca^{2+} is multiplied by 2.

To solve this system of five equations, we make a guess for $[Ca^{2+}]$, and then use K_{sp} to calculate $[F^-]$, the mass balance equation to calculate [HF], K_a to calculate $[H_3O^+]$, and K_w to calculate $[OH^-]$. We evaluate each guess by rewriting the charge balance equation as an error function

$$error = 2 \times [Ca^{2+}] + [H_3O^+] - [OH^-] - [F^-]$$

searching for a $[Ca^{2+}]$ that gives an error sufficiently close to zero. Successive iterations over a narrower range of concentrations for Ca^{2+} will lead you to a equilibrium molar solubility of 2.1×10^{-4} M.

(b) To find the solubility of AgCl we first write down all relevant equilibrium reactions; these are

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

$$Ag^+\,(aq) + Cl^-\,(aq) \rightleftharpoons AgCl\,(aq)$$

$$AgCl\,(aq) + Cl^-\,(aq) \rightleftharpoons AgCl_2^-\,(aq)$$

$$AgCl_2^-\,(aq) + Cl^-\,(aq) \rightleftharpoons AgCl_3^-\,(aq)$$

$$AgCl_3^-\,(aq) + Cl^-\,(aq) \rightleftharpoons AgCl_4^-\,(aq)$$
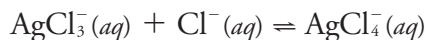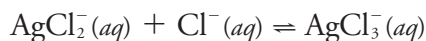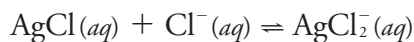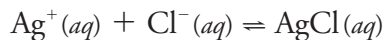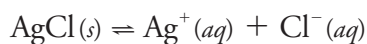
There are six species whose concentrations define this system (Ag^+, Cl^-, AgCl(aq), $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$), which means we need six equations that relate the concentrations of these species to each other; these are the five equilibrium constant expressions

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

$$K_1 = \frac{[AgCl\,(aq)]}{[Ag^+][Cl^-]} = 5.01 \times 10^3$$

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

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

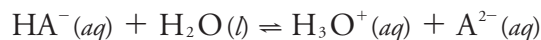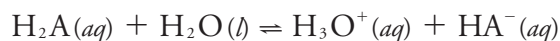$$K_4 = \frac{[\text{AgCl}_4^{3-}]}{[\text{AgCl}_3^{2-}][\text{Cl}^-]} = 0.501$$

You can substitute a mass balance equation for the charge balance equation, but the latter is easier to write in this case.

and a charge balance equation

$$[\text{Ag}^+] = [\text{Cl}^-] + [\text{AgCl}_2^-] + 2 \times [\text{AgCl}_3^{2-}] + 3 \times [\text{AgCl}_4^{3-}]$$

To solve this system of five equations, we make a guess for $[\text{Ag}^+]$, and then use K_{sp} to calculate $[\text{Cl}^-]$, K_1 to calculate $[\text{AgCl}(aq)]$, K_2 to calculate $[\text{AgCl}_2^-]$, K_3 to calculate $[\text{AgCl}_3^{2-}]$, and K_4 to calculate $[\text{AgCl}_4^{3-}]$. We evaluate each guess by rewriting the charge balance equation as an error function

$$\text{error} = [\text{Ag}^+] - [\text{Cl}^-] - [\text{AgCl}_2^-] - 2 \times [\text{AgCl}_3^{2-}] - 3 \times [\text{AgCl}_4^{3-}]$$

searching for a $[\text{Ag}^+]$ that gives an error sufficiently close to zero. Successive iterations over a narrower range of concentrations for Ag^+ will lead you to a equilibrium molar solubility of 1.3×10^{-5} M.

(c) To find the pH of 0.10 M fumaric acid we first write down all relevant equilibrium reactions; letting H_2A represent fumaric acid, these are

$$H_2A(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HA^-(aq)$$

$$HA^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^{2-}(aq)$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

There are five species whose concentrations define this system (H_2A, HA^-, A^{2-}, H_3O^+, and OH^-), which means we need five equations that relate the concentrations of these species to each other; these are the three equilibrium constant expressions

$$K_{a1} = \frac{[H_3O^+][HA^-]}{[H_2A]} = 8.85 \times 10^{-4}$$

$$K_{a2} = \frac{[H_3O^+][A^{2-}]}{[HA^-]} = 3.21 \times 10^{-5}$$

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

a charge balance equation

$$[H_3O^+] = [OH^-] + [HA^-] + 2 \times [A^{2-}]$$

and a mass balance equation

$$0.10\ \text{M} = [H_2A] + [HA^-] + [A^{2-}]$$

To solve this system of five equations, we make a guess for the pH, calculate $[H_3O^+]$ and use K_w to calculate $[OH^-]$. Because each of the remaining equations include at least two of the remaining species, we must combine one or more of these equations to isolate a single species. There are several ways to accomplish this, one of which is to use K_{a1} to express $[HA^-]$ in terms of $[H_2A]$, and to use K_{a1} and K_{a2} to express $[A^{2-}]$ in terms of $[H_2A]$

$$[HA^-] = \frac{K_{a1}[H_2A]}{[H_3O^+]}$$

$$[A^{2-}] = \frac{K_{a2}[HA^-]}{[H_3O^+]} = \frac{K_{a1}K_{a2}[H_2A]}{[H_3O^+]^2}$$

and then substitute both into the mass balance equation

$$0.10\,M = [H_2A] + \frac{K_{a1}[H_2A]}{[H_3O^+]} + \frac{K_{a1}K_{a2}[H_2A]}{[H_3O^+]^2}$$

$$= [H_2A] \times \left\{ 1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1}K_{a2}}{[H_3O^+]^2} \right\}$$

which we use to calculate $[H_2A]$. Finally, we calculate $[HA^-]$ using K_{a1} and $[A^{2-}]$ using K_{a2}. We evaluate each guess by rewriting the charge balance equation as an error function

$$\text{error} = [H_3O^+] - [OH^-] - [HA^-] - 2 \times [A^{2-}]$$

searching for a pH that gives an error sufficiently close to zero. Successive iterations over a narrower range of pH values will lead you to a equilibrium pH of 2.05.

25. The four equations that describe the composition of an equilibrium solution of HF are the K_a and K_w equilibrium constant expressions

$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

$$K_w = [H_3O^+][OH^-]$$

a charge balance equation

$$[H_3O^+] = [OH^-] + [F^-]$$

and a mass balance equation

$$C_{HF} = [HF] + [F^-]$$

To combine the equations, we first use the mass balance equation to express [HF] in terms of C_{HF} and $[F^-]$

$$[HF] = C_{HF} - [F^-]$$

and then substitute this into the K_a expression

$$K_a = \frac{[H_3O^+][F^-]}{C_{HF} - [F^-]}$$

which we then solve for $[F^-]$

$$K_a C_{HF} - K_a[F^-] = [H_3O^+][F^-]$$

$$K_a C_{HF} = [H_3O^+][F^-] + K_a[F^-]$$

$$[F^-]\{[H_3O^+] + K_a\} = K_a C_{HF}$$

$$[F^-] = \frac{K_a C_{HFa}}{[H_3O^+] + K_a}$$

Next, we solve K_w for $[OH^-]$

$$[OH^-] = \frac{K_w}{[H_3O^+]}$$

and then substitute this and the equation for $[F^-]$ into the charge balance equation

$$[H_3O^+] = \frac{K_w}{[H_3O^+]} + \frac{K_a C_{HF}}{[H_3O^+] + K_a}$$

Rearranging this equation

$$[H_3O^+] - \frac{K_w}{[H_3O^+]} - \frac{K_a C_{HFa}}{[H_3O^+] + K_a} = 0$$

multiplying through by $[H_3O^+]$

$$[H_3O^+]^2 - K_w - \frac{K_a C_{HF}[H_3O^+]}{[H_3O^+] + K_a} = 0$$

multiplying through by $[H_3O^+] + K_a$

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - K_w[H_3O^+] - $$
$$K_a K_w - K_a C_{HF}[H_3O^+] = 0$$

and gathering terms leaves us with the final equation

$$[H_3O^+]^3 + K_a[H_3O^+]^2 - (K_a C_{HF} + K_w)[H_3O^+] - K_a K_w = 0$$

Chapter 7

1. (a) The overall variance, which is the sum of the variance due to obtaining the sample and the variance due to the method

$$s^2_{overall} = s^2_{sampling} + s^2_{method}$$

is the variance in the results for the four replicate analyses of the sample, or 0.9144. The variance due to the method is the variance in the results for the four replicate analyses of the standard, or 0.0330. The variance due to sampling, therefore, is

$$s^2_{sampling} = s^2_{overall} - s^2_{method} = 0.9144 - 0.0330 = 0.8814$$

(b) The percentage of the overall variance due to sampling is

$$\frac{s^2_{sampling}}{s^2_{overall}} \times 100 = \frac{0.8814}{0.9144} \times 100 = 96.4\%$$

(c) To decrease the variance due to sampling we need to increase the number of particles in each sample. We can accomplish this by taking a larger sample for analysis, by decreasing the average particle size through additional pulverizing of the sample, or both.

2. Our random number table is a list of five digit numbers. As our barrels are numbered 1–100, we will use an entry's last two digits to identify a barrel to sample, with *xyz*01 representing the first barrel and *xyz*00 representing the hundredth barrel. The twelfth entry in the random number table is 91791; thus our first sample is from Barrel 91. Continuing with every third entry in the random number table, the samples are drawn from barrels

91 54 85 38 49 62 77 66 95 52

3. The Nyquist sampling theorem states that we must collect at least two samples per period. To monitor a daily cycle we need to collect a sample at least once every 12 hr, although collecting a sample every 6-8 hr is better. To monitor a yearly cycle we need to collect a sample at least once every six months, although every 3-4 months is better.

4. A plot of pH as a function of time, which appears in Figure SM7.1, shows a periodic cycle with a period of approximately 8 hr. At a minimum, we should collect a sample every 4 hr, although collecting a sample very 2-3 hr is better.

5. (a) Several of the possible sampling plans are reasonable options; others are less reasonable. A random sampling plan, for example, is a poor choice because it does not take advantage of the expected periodic fluctuations in atmospheric ozone levels due to changes in traffic patterns. The best choice is systematic/judgmental. The systematic portion of the sampling plan allows us to acquire fewer samples by taking into account the daily fluctuations in traffic patterns. The
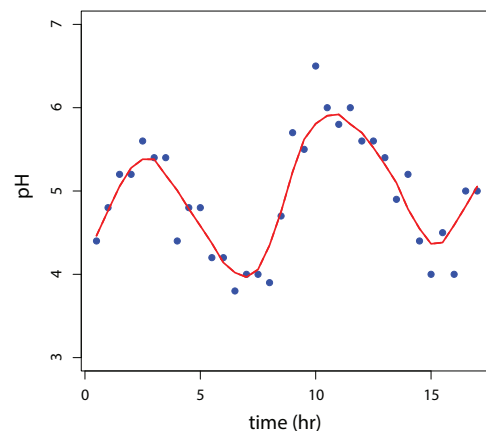

Figure SM7.1 The change in pH as a function of time for an industrial waste stream. The **blue** points are the data included with Problem 7.4 and the **red** line is a lowess fit, which uses a locally weighted polynomial linear regression to model the data; locally weighted means that the predicted value of *y* for each value of *x* is based on a subset of the data consisting of points adjacent to *x*.

judgmental portion of the sampling plan allows us to focus sampling on key locations, such as busy intersections, and to use areas with low levels of traffic, such as city parks, to provide background readings.

(b) For this study we will collect grab samples as we are interested in the concentration of ozone at a specific location and at a specific time.

(c) If our interest is in an average daily concentration of ozone, then we are better served by collecting a single composite sample at each location as this decreases the number of individual samples that we need to analyze.

6. (a) A homogeneous population is uniform in time and space. A heterogeneous population is not uniform and shows some variation in time, in space, or in both time and space.

(b) No. To show that a sample is homogeneous or heterogeneous, we must have information about the variability between samples, which requires that we analyze more than one sample.

7. Equation 7.4 provides a relationship between the relative sampling variance, $(s_{samp})^2_{rel}$, the probability, p, of obtaining a particular type of particle, and the number, n, of particles sampled.

$$n = \frac{1-p}{p} \times \frac{1}{(s_{samp})^2_{rel}}$$

Equation 7.5 is defined in terms of R^2, where R is the percent relative standard deviation

$$R^2 = (s_{samp})^2_{rel} \times (10^2)^2 = (s_{samp})^2_{rel} \times 10^4$$

Solving this equation for $(s_{samp})^2_{rel}$

$$(s_{samp})^2_{rel} = \frac{R^2}{10^4}$$

and substituting back into equation 7.4, and rearranging gives

$$nR^2 = \frac{1-p}{p} \times 10^4$$

The mass, m, of a single particle is the product of its density, d, and its volume, V, which, for a sphere is $\frac{4}{3}\pi r^3$ where r is the radius; thus, the mass of n particles is

$$m = \frac{4}{3}nd\pi r^3$$

Solving for n, substituting back, and rearranging gives

$$mR^2 = \frac{4}{3}d\pi r^3 \times \frac{1-p}{p} \times 10^4$$

For any given sample, each of the three terms on the right side of this equation is a constant, which leaves us with equation 7.5

$$mR^2 = K_s$$

where K_s is the sampling constant.

8. (a) From equation 7.5, the expected percent relative standard deviation for sampling, R, of a homogeneous material is

$$R = \sqrt{\frac{K_s}{m}} = \sqrt{\frac{35 \text{ g}}{1.0 \text{ g}}} = 5.9\%$$

(b) To find the number of samples, n_{samp}, we use equation 7.7

$$n_{samp} = \frac{t^2 s_{samp}^2}{e^2}$$

where s_{samp} is equivalent to R, and e is the desired sampling error of 5%. We begin using $t(0.05,\infty)$ for an infinite number of degrees of freedom; thus

$$n_{samp} = \frac{(1.960)^2 (5.9)^2}{(5.0)^2} = 5.3 \approx 5$$

This answer is not correct because we used $t(0.05,\infty)$ of 1.960 instead of the value for $5 - 1 = 4$ degrees of freedom. Using $t(0.05,4)$ of 2.776 and recalculating gives

$$n_{samp} = \frac{(2.776)^2 (5.9)^2}{(5.0)^2} = 10.7 \approx 11$$

This answer is not correct because we used $t(0.05,4)$ of 2.776 instead of the value for $11 - 1 = 10$ degrees of freedom. Using $t(0.05,10)$ of 2.228 and recalculating gives

$$n_{samp} = \frac{(2.228)^2 (5.9)^2}{(5.0)^2} = 6.9 \approx 7$$

This answer is not correct because we used $t(0.05,10)$ of 2.228 instead of the value for $7 - 1 = 6$ degrees of freedom. Using $t(0.05,6)$ of 2.447 and recalculating gives

$$n_{samp} = \frac{(2.447)^2 (5.9)^2}{(5.0)^2} = 8.3 \approx 8$$

This answer is not correct because we used $t(0.05,6)$ of 2.447 instead of the value for $8 - 1 = 7$ degrees of freedom. Using $t(0.05,7)$ of 2.365 and recalculating gives

$$n_{samp} = \frac{(2.365)^2 (5.9)^2}{(5.0)^2} = 7.8 \approx 8$$

This time there is agreement between the value of t and the degrees of freedom for n_{samp}; thus, we need to collect eight samples to achieve the desired maximum sample error of $\pm 5\%$.

9. The mean and the standard deviation for the 12 samples are 0.264 %w/w K_2O and 0.0423 %w/w K_2O, respectively. The percent relative standard deviation, R, is
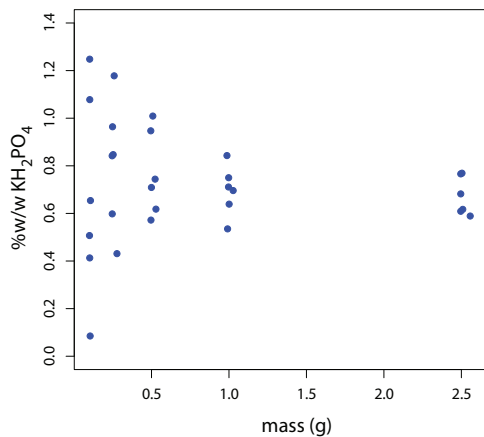
Figure SM7.2 The data for Problem 7.10 is shown here as a plot of %w/w K_2O as a function of the mass of sample taken. Note that the variability in the individual results decreases as the mass of sample taken increases.
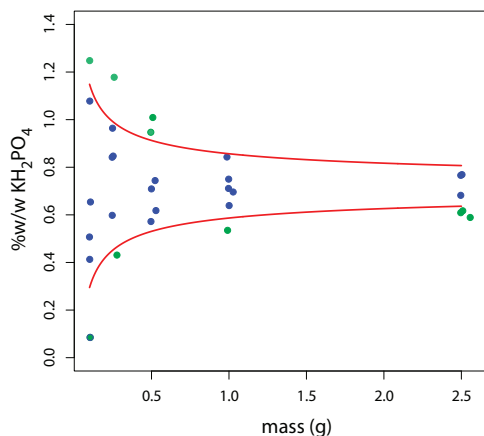

Figure SM7.3 The individual samples from Problem 7.10 are shown here as a series of **blue** and **green** points. The **red** curves show the range of expected results based on indeterminate sampling error defined here as $(\overline{X})_{global} \pm 1s$ where $(\overline{X})_{global}$ is the global mean of 0.722% w/w KH_2PO_4 for all 30 samples and s is the standard deviation for sampling based on a sampling constant of 350. The 20 **blue** points fall within this range and the 10 **green** points lie outside this range.

$$R = \frac{s}{\overline{X}} = \frac{0.0423}{0.264} \times 100 = 16.0$$

For a nominal mass of 0.10 g, this gives a sampling constant, K_s, of

$$K_s = mR^2 = (0.10 \text{ g})(16.0)^2 = 25.6 \text{ g}$$

To lower the relative standard deviation to 2%, we need to increase each sample's nominal mass to

$$m = \frac{K_s}{R^2} = \frac{25.6 \text{ g}}{2.0^2} = 6.4 \text{ g}$$

10. (a) Figure SM7.2 shows the plot of %w/w K_2O as a function of the mass of sample taken. Although the gross sample presumably is homogeneous, the spread in results for individual samples collected at different nominal masses show that indeterminate errors in the sampling process have a greater affect on the variability in individual results for samples of smaller nominal mass.

(b) The following table organizes results by nominal mass; the experimental percent relative standard deviations, R_{exp}, are calculated using the mean and the standard deviation for each nominal mass, and the theoretical percent relative standard deviations, R_{theo}, are calculate using the mean for each nominal mass and the sampling constant.

nominal mass (g)	mean mass (g)	$C_{KH_2PO_4}$ (%w/w)	s (g)	R_{exp}	R_{theo}
0.10	0.1020	0.664	0.432	65.1	58.6
0.25	0.2548	0.810	0.265	32.7	37.1
0.50	0.5086	0.766	0.176	23.0	26.2
1.00	1.0002	0.696	0.104	14.9	18.7
2.50	2.5097	0.672	0.080	11.9	11.8

The results here are consistent with our observation from part (a) as the percent relative standard deviation, R_{exp}, is much larger for samples of smaller nominal mass.

(c) The global mean, $(\overline{X})_{global}$, is 0.722%w/w KH_2PO_4. To calculate the theoretical standard deviation, s, for any mass, m, we use equation 7.5, where K_s is 350, and the definition of the percent relative standard deviation

$$R = \frac{s}{\overline{X}} \times 100$$

For example, taking m = 0.1000 g, we have

$$s = \sqrt{\frac{(350)(0.722)^2}{(0.1000)(10^4)}} = 0.427$$

Figure SM7.3 shows the same data as in Figure SM7.2 with two lines representing $(\overline{X})_{global} \pm 1s$ superimposed on the data. Of the 30 data

points, 20 or 67% lie between the two curves. If the sampling error is normally distributed, we expect that approximately 68% of the samples will fall within $\pm 1s$ of the global mean. It appears, therefore, that the sample is homogeneous and that the variability between samples of different size is explained by indeterminate sampling error.

11. Answers to this problem, of course, will vary. Here is some data I collected using a 47.9 g bag of plain M&Ms, with each result reporting the number of red M&Ms in a sample of five M&Ms:

$$
\begin{array}{cccccccccc}
0 & 0 & 3 & 2 & 0 & 0 & 2 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 & 1 & 2 & 2 & 1 & 2 & 1
\end{array}
$$

The mean and the standard deviation for this set of 20 results is 1.0 and 0.92, respectively, which correspond to percentages of 20% and of 18.4%, respectively.

After gathering this data, I counted the number of each color of M&Ms in the bag, obtaining the following results:

blue: 17   red: 9   yellow: 9

orange: 9   brown: 5   green: 6

for a total of 55 M&Ms. The percentage of red M&Ms in the bag is 16.4%, or a probability, p, of 0.164

Assuming binomial sampling statistics, if we draw five M&Ms from a population for which the probability of drawing a red M&M is 0.164, then we expect the average sample to contain

$$
n_{red} = np_{red} = 5 \times 0.164 = 0.82
$$

red M&Ms with a standard deviation of

$$
s_{red} = \sqrt{np_{red}(1 - p_{red})} = \sqrt{5 \times 0.164 \times 0.836} = 0.83
$$

red M&Ms, both of which are similar to the experimental values of 1.0 red M&Ms and 0.92 red M&Ms, respectively. Expressing these as percentages, the predicted mean and standard deviation are 16.4% and 16.6%, respectively, which compare favorably to the experimental values of 20% and 18.4%, respectively.

12. For all three scenarios, we use equation 7.8

$$
e = t\sqrt{\frac{s_{samp}^2}{n_{samp}} + \frac{s_{meth}^2}{n_{samp}n_{rep}}}
$$

where s_{samp}^2 is the sampling variance and s_{meth}^2 is variance in the analysis; thus, for (a) we have

$$
e = 2.306\sqrt{\frac{0.050}{9} + \frac{0.0025}{9 \times 1}} = 0.176
$$

and for (b) we have

Scenarios (a) and (b) each have a total of 9 analyses; thus, we use $t(0.05,8)$ as there are eight degrees of freedom. For scenario (c) there are 10 analyses and we use $t(0.05,9)$.

$$e = 2.306\sqrt{\frac{0.050}{1} + \frac{0.0025}{1 \times 9}} = 0.517$$

and for (c) we have

$$e = 2.260\sqrt{\frac{0.050}{5} + \frac{0.0025}{5 \times 2}} = 0.229$$

13. Because the error for scenario (b) exceeds the limit of 0.30, we need consider only scenario (a) and scenario (c). If the cost of obtaining a sample is $1 and the cost of analyzing the sample is $10, then scenario (a) is the more cost effective

    scenario (a): cost = 9×$1 + 9×$10 = $99

    scenario (c): cost = 5×$1 + 10×$10 = $105

    If the cost of obtaining a sample is $10 and the cost of analyzing the sample is $1, then scenario (c) is the more cost effective

    scenario (a): cost = 9×$10 + 9×$1 = $99

    scenario (c): cost = 5×$10 + 10×$1 = $60

14. The best way to evaluate these methods is to use a paired t-test. First, for each of the eight samples, we determine the mean for the microwave method, $(\overline{X})_{MW}$, and the mean for the standard method, $(\overline{X})_{std}$, and then the difference, d, between the means for each method; the results for all eight samples are tabulate below:

sample	$(\overline{X})_{MW}$	$(\overline{X})_{std}$	d
1	7.32	5.48	1.84
2	15.80	12.97	2.83
3	4.60	5.29	–0.69
4	9.04	6.77	2.27
5	7.16	6.00	1.16
6	6.80	5.84	0.96
7	9.90	14.30	–4.40
8	28.67	18.83	9.84

The mean difference for the eight samples, $\overline{d}$, is 1.73 and the standard deviation, s_d, is 3.99. For a paired t-test we use the following null hypothesis and alternative hypothesis

$$H_0: \overline{d} = 0 \quad H_A: \overline{d} \neq 0$$

Calculating t_{exp}

$$t_{exp} = \frac{\overline{d}\sqrt{n}}{s_d} = \frac{(1.70)\sqrt{8}}{3.99} = 1.21$$

we find that it is less than the critical value of 2.365 for $t(0.05,7)$; thus, there is no evidence to suggest that the difference between the methods is significant at $\alpha = 0.05$.

15. In anoxic sediments with relatively high concentrations of sulfide, S^{2-}, the speciation of Cu^{2+} is controlled by the formation of stable copper-sulfide phases, even at the very acidic pH levels obtained when using a strong acid, such as HNO_3, as a preservative. Adding H_2O_2 before adding HNO_3 oxidizes S^{2-} to SO_4^{2-}, which minimizes this problem.

16. (a) If the recovery for the interferent, R_I, is 1, then equation 7.19 for the error reduces to

$$E = R_A - 1 = 0.0630$$

and the apparent recovery for the analyte, R_A, is 1.063 or 106.3%.

(b) If the recovery for the analyte, R_A, is 1, then equation 7.19 for the error reduces to

$$E = \frac{K_{A,I}(C_I)_o}{(C_A)_o} \times R_I = \frac{(0.816)(1)}{5} \times R_I = 0.0630$$

and the apparent recovery for the interferent, R_I, is 0.386 or 38.6%.

17. (a) The recoveries for copper and for iron are

$$R_{Co} = \frac{275.9 \text{ mg}}{278.3 \text{ mg}} = 0.9914 \approx 0.991$$

$$R_{Fe} = \frac{3.6 \text{ mg}}{184.9 \text{ mg}} = 0.01947 \approx 0.019$$

(b) The separation factor, $S_{Fe,Co}$, in which iron is the interferent and cobalt is the analyte, is

$$S_{Fe,Co} = \frac{R_{Fe}}{R_{Co}} = \frac{0.01947}{0.9914} = 0.0196 \approx 0.020$$

(c) The selectivity of the method for the analyte, Co, relative to the interferent, Fe, is

$$K_{Co,Fe} = \frac{k_{Fe}}{k_{Co}} = \frac{0.699}{0.786} = 0.889$$

(d) If we make no attempt to separate the analyte and the interferent, then R_{Co} and R_{Fe} have values of 1; thus, the expected error in the analysis for Co is

$$E = (R_{Co} - 1) + \frac{K_{Co,Fe}(C_{Fe})_o}{(C_{Co})_o} \times R_{Fe} =$$

$$(1 - 1) + \frac{(0.889)(1)}{10.2} \times 1 = 0.0872$$

or an error of +8.72%.

(e) If we complete the separation, then the expected error in the analysis for Co is

$$E = (R_{Co} - 1) + \frac{K_{Co,Fe}(C_{Fe})_o}{(C_{Co})_o} \times R_{Fe} =$$

$$(0.991 - 1) + \frac{(0.889)(1)}{10.2} \times (0.019) = -0.0073$$

or an error of -0.73%.

(f) The error in this case is defined by

$$E = (R_{Co} - 1) + \frac{K_{Co,Fe}(C_{Fe})_o}{(C_{Co})_o} \times R_{Fe} =$$

$$(1 - 1) + \frac{(0.889)(1)}{10.2} \times R_{Fe} = 0.0005$$

Solving for R_{Fe} gives its value as 0.0057; thus, we cannot recover more than 0.57% of the Fe to achieve the desired error.

18. To determine the recoveries for Ca and for Mg, we begin with the following pair of equations

$$E = (R_{Ca} - 1) + \frac{(0.843)(0.5)}{1} \times R_{Mg} = -0.037$$

$$E = (R_{Ca} - 1) + \frac{(0.843)(2.0)}{1} \times R_{Mg} = +0.055$$

Subtracting the first equation from the second equation

$$1.2645 R_{Mg} = 0.092$$

and solving for R_{Mg} gives its value as 0.073; substituting back into either equation and solving for R_{Ca} gives its value as 0.932.

19. The relevant reactions are

$$Al^{3+}(aq) + Y^{4-}(aq) \rightleftharpoons AlY^{-}(aq)$$

$$Al^{3+}(aq) + 6F^{-}(aq) \rightleftharpoons AlF_6^{3-}(aq)$$

From Appendix 12, we have $\log K_1 = 6.11$, $\log K_2 = 5.01$, $\log K_3 = 3.88$, $\log K_4 = 3.00$, $\log K_5 = 1.4$, and $\log K_6 = 0.4$ for the complexes between Al^{3+} and F^-. Adding together these six values gives $\log \beta_6$ as 19.8 and β_6 as 6.3×10^{19}.
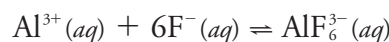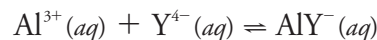
for which K_1 for AlY^- is 2.0×10^{16} and β_6 for AlF_6^{3-} is 6.3×10^{19}. Fluoride is an effective masking agent because it binds more strongly with Al^{3+} than does EDTA and, therefore, cannot be displaced by EDTA; thus, the reaction

$$AlF_6^{3-}(aq) + Y^{4-}(aq) \rightleftharpoons AlY^{-}(aq) + 6F^{-}(aq)$$
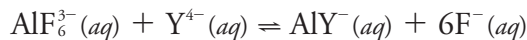
has an equilibrium constant of K_1/β_6, or 3.2×10^{-4}.

20. Cyanide, CN^-, is a weak base, which means at more acidic pH levels it converts to its conjugate weak acid form, HCN. For example, consider the equilibria in a solution of $Ag(CN)_2^-$

$$Ag(CN)_2^-(aq) \rightleftharpoons Ag^+(aq) + 2CN^-(aq)$$

$$CN^-(aq) + H_3O^+(aq) \rightleftharpoons H_2O(l) + HCN(aq)$$

Adding acid pushes the second reaction to the right, decreasing the concentration of CN^-; in turn, the decrease in the concentration of CN^- pushes the first reaction to the right, decreasing the extent of complexation.

21. There are several approaches that we can use; here is one. First, make the solution strongly basic by adding NaOH, precipitating tin as SnO_2, copper as $Cu(OH)_2$, and lead as $Pb(OH)_2$, leaving zinc in solution as $Zn(OH)_4^{2-}$. After isolating the precipitates by filtration, dissolve the $Cu(OH)_2$ and the $Pb(OH)_2$ using a solution of HNO_3, leaving behind solid SnO_2. Next, we make the solution of Cu^{2+} and of Pb^{2+} basic using a NH_4^+/NH_3 buffer, precipitating the lead as $Pb(OH)_2$ and leaving the copper behind as $Cu(NH_3)_6^{2+}$.

22. For n identical extractions, the amount of solute remaining in the aqueous phase after the last extraction, $(Q_{aq})_n$ is given by equation 7.27

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}} \right)^n$$

where V_{aq} is the volume of aqueous phase, V_{org} is the volume of organic extracting phase, and D is the distribution ratio. The extraction efficiency is $1 - (Q_{aq})_n$; thus, for (a) we have

$$(Q_{aq})_1 = \left(\frac{50.0}{(7.5)(50.0) + 50.0} \right)^1 = 0.118$$

or an extraction efficiency of 0.882 or 88.2%; for (b) we have

$$(Q_{aq})_2 = \left(\frac{50.0}{(7.5)(25.0) + 50.0} \right)^2 = 0.0443$$

or an extraction efficiency of 0.956 or 95.6%; for (c) we have

$$(Q_{aq})_4 = \left(\frac{50.0}{(7.5)(12.5) + 50.0} \right)^4 = 0.0146$$

or an extraction efficiency of 0.985 or 98.5%; for (d) we have

$$(Q_{aq})_5 = \left(\frac{50.0}{(7.5)(10.0) + 50.0} \right)^5 = 0.0102$$

or an extraction efficiency of 0.990 or 99.0%. As expected, we see a greater extraction efficiency when we divide the organic extracting phase into smaller portions and carry out more extractions.

23. To extract 99.9% of the solute we need an extraction efficiency of 0.999; in turn, this requires that $(Q_{aq})_n = 0.001$. Beginning with equation 7.27

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}} \right)^n$$

we solve for V_{org} by taking the nth root of each side of the equation

$$\sqrt[n]{(Q_{aq})_n} = \frac{V_{aq}}{DV_{org} + V_{aq}}$$

multiplying through by $DV_{org} + V_{aq}$

$$DV_{org}\sqrt[n]{(Q_{aq})_n} + V_{aq}\sqrt[n]{(Q_{aq})_n} = V_{aq}$$

and then gathering terms

$$V_{org} = \frac{V_{aq} - V_{aq}\sqrt[n]{(Q_{aq})_n}}{D\sqrt[n]{(Q_{aq})_n}}$$

For (a) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times 0.001}{7.5 \times 0.001} = 6600 \text{ mL/extraction}$$

or a total volume of 6600 mL for one extraction; for (b) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times \sqrt{0.001}}{7.5 \times \sqrt{0.001}} = 204 \text{ mL/extraction}$$

or a total volume of 408 mL for two extractions; for (c) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times \sqrt[4]{0.001}}{7.5 \times \sqrt[4]{0.001}} = 30.8 \text{ mL/extraction}$$

or a total volume of 123.2 mL for four extractions; and for (d) the minimum volume needed is

$$V_{org} = \frac{50.0 - 50.0 \times \sqrt[5]{0.001}}{7.5 \times \sqrt[5]{0.001}} = 19.9 \text{ mL/extraction}$$

or a total volume of 79.5 mL for five extractions. As expected, we use less total solvent when we use multiple extractions.

24. To extract 99% of the solute we need an extraction efficiency of 0.99; in turn, this requires that $(Q_{aq})_n = 0.01$. Beginning with equation 7.27

$$(Q_{aq})_n = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^n$$

we solve for D by taking the nth root of each side of the equation

$$\sqrt[n]{(Q_{aq})_n} = \frac{V_{aq}}{DV_{org} + V_{aq}}$$

multiplying through by $DV_{org} + V_{aq}$

$$DV_{org}\sqrt[n]{(Q_{aq})_n} + V_{aq}\sqrt[n]{(Q_{aq})_n} = V_{aq}$$

and then gathering terms

$$D = \frac{V_{aq} - V_{aq}\sqrt[n]{(Q_{aq})_n}}{V_{org}\sqrt[n]{(Q_{aq})_n}}$$

For (a) we need a D of

$$D = \frac{50.0 - 50.0 \times 0.01}{50.0 \times 0.01} = 99.0$$

and for (b) we need a D of

$$D = \frac{50.0 - 50.0 \times \sqrt{0.01}}{25.0 \times \sqrt{0.01}} = 18.0$$

25. From equation 7.27, an extraction efficiency of 99.9%, requires that

$$Q_{aq} = 0.001 = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{D \times 50.0 + 50.0}$$

for a single extraction of 50.0 mL of sample using 50.0 mL of organic solvent. Solving gives the minimum value of D as 999. Because the analyte is a weak acid, the distribution ratio's value depends on the pH of the aqueous phase, with more acidic pH levels favoring a larger value for D. From equation 7.31, we know that

$$D = \frac{K_D[H_3O^+_{aq}]}{[H_3O^+_{aq}] + K_a}$$

$$999 = \frac{(1200)[H_3O^+_{aq}]}{[H_3O^+_{aq}] + (1.00 \times 10^{-5})}$$

$$999[H_3O^+_{aq}] + 9.99 \times 10^{-3} = 1200[H_3O^+_{aq}]$$

$$9.99 \times 10^{-3} = 201[H_3O^+_{aq}]$$

gives $[H_3O^+_{aq}]$ as 4.97×10^{-5}, or a maximum pH of 4.30.

26. For a pH of 7.00 ($[H_3O^+_{aq}] = 1.00 \times 10^{-7}$), the distribution ratio, D, is

$$D = \frac{K_D[H_3O^+_{aq}]}{[H_3O^+_{aq}] + K_a} = \frac{(1200) \times (1.00 \times 10^{-7})}{(1.00 \times 10^{-7}) + (1.00 \times 10^{-5})} = 11.9$$

To find the number of extractions, we make appropriate substitutions into equation 7.27 and solve for n

$$0.001 = \left(\frac{50.0}{11.9 \times 50.0 + 50.0}\right)^n$$

$$\log(0.001) = n\log(0.0775)$$

$$-3.00 = -1.11n$$

finding that n is 2.7; thus, we need to complete at least three extractions to achieve an extraction efficiency of 99.9%.

27. From equation 7.27, an extraction efficiency of 99.9%, requires that

$$(Q_{aq})_2 = 0.001 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^2 = \left(\frac{50.0}{D \times 25.0 + 50.0}\right)^2$$

for two extractions of 50.0 mL of sample using 25.0 mL of organic solvent per extraction. Taking the square root of both sides

$$0.03162 = \frac{50.0}{D \times 25.0 + 50.0}$$

and solving for D gives its minimum value of as 61.3. Because the analyte is a weak base, the distribution ratio's value depends on the pH of the aqueous phase, with more basic pH levels favoring a larger value for D. From Practice Exercise 7.9, we know that

$$D = \frac{K_D[\text{OH}^-_{aq}]}{[\text{OH}^-_{aq}] + K_b}$$

$$61.3 = \frac{(5.00 \times 10^2)[\text{OH}^-_{aq}]}{[\text{OH}^-_{aq}] + (1.0 \times 10^{-3})}$$

$$61.3[\text{OH}^-_{aq}] + 0.0613 = (5.00 \times 10^2)[\text{OH}^-_{aq}]$$

$$0.0613 = 438.7[\text{OH}^-_{aq}]$$

gives $[\text{OH}^-_{aq}]$ as 1.40×10^{-4}, or a minimum pH of 10.15.

28. (a) To calculate the extraction efficiencies for HA and HB, we first find their respective distribution ratios at a pH of 7.00

$$D_{\text{HA}} = \frac{K_{D,\text{HA}}[\text{H}_3\text{O}^+_{aq}]}{[\text{H}_3\text{O}^+_{aq}] + K_{a,\text{HA}}} = \frac{(5.00 \times 10^2)(1.0 \times 10^{-7})}{1.0 \times 10^{-7} + 1.0 \times 10^{-3}} = 0.0500$$

$$D_{\text{HB}} = \frac{K_{D,\text{HB}}[\text{H}_3\text{O}^+_{aq}]}{[\text{H}_3\text{O}^+_{aq}] + K_{a,\text{HB}}} = \frac{(5.00 \times 10^2)(1.0 \times 10^{-7})}{1.0 \times 10^{-7} + 1.0 \times 10^{-7}} = 250$$

and then calculate the fraction of HA and HB that remain in the aqueous phase when the extraction is complete

$$Q_{aq,\text{HA}} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{0.0500 \times 50.0 + 50.0} = 0.952$$

$$Q_{aq,\text{HB}} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{250 \times 50.0 + 50.0} = 0.00398$$

Thus, the extraction efficiency for HA is 0.048 or 4.8% and for HB is 0.996 or 99.6%

(b) The aqueous phase is enriched in the analyte, HA, with 95.2% of HA remaining unextracted.

(c) The recovery for HA in the aqueous phase, R_{HA}, is 0.952 or 95.2%; for HB, R_{HB} is 0.00398 or 0.398%.

(d) The separation factor, $S_{\text{HB,HA}}$, is

$$S_{\text{HB,HA}} = \frac{R_{\text{HB}}}{R_{\text{HA}}} = \frac{0.00398}{0.952} = 4.18 \times 10^{-3}$$

(e) The error is

$$E = (R_{\text{HA}} - 1) + \frac{K_{\text{HA,HB}}(C_{\text{HB}})_o}{(C_{\text{HA}})_o} \times R_{\text{HB}}$$

$$E = (0.952 - 1) + \frac{0.500 \times 10}{1} \times 0.00398 = -0.0281$$

or an error of –2.81%.

29. (a) Decreasing the concentration of I^- pushes the equilibrium reaction between I_2 and I_3^- to the left, which increases the concentration of $I_2(aq)$; in turn, this pushes the equilibrium reaction between $I_2(aq)$ and $I_2(org)$ toward the organic phase, increasing the extraction efficiency.

(b) We start by writing equations for K_D and for K_f for the two equilibrium reactions; these are

$$K_D = \frac{[I_2]_{org}}{[I_2]_{aq}} \qquad K_f = \frac{[I_3^-]_{aq}}{[I_2]_{aq}[I^-]_{aq}}$$

and the distribution ratio for the extraction

$$D = \frac{[I_2]_{org}}{[I_2]_{aq} + [I_3^-]_{aq}}$$

Solving K_f for $[I_3^-]_{aq}$ and substituting into the equation for the distribution ratio

$$D = \frac{[I_2]_{org}}{[I_2]_{aq} + K_f[I_2]_{aq}[I^-]_{aq}}$$

factoring our $[I_2](aq)$ in the denominator

$$D = \frac{[I_2]_{org}}{[I_2]_{aq}\{1 + K_f[I^-]_{aq}\}}$$

and simplifying by replacing $[I_2]_{org}/[I_2]_{aq}$ with K_D leaves us with the desired final equation

$$D = \frac{K_D}{1 + K_f[I^-]_{aq}}$$

30. (a) We start by writing equations for K_D and for β_2 for the two equilibrium reactions; these are

$$K_D = \frac{[ML_2]_{org}}{[ML_2]_{aq}} \qquad \beta_2 = \frac{[ML_2]_{aq}}{[M^{2+}]_{aq}[L^-]_{aq}^2}$$

and the distribution ratio for the extraction

$$D = \frac{[ML_2]_{org}}{[ML_2]_{aq} + [M^{2+}]_{aq}}$$

Solving β_2 for $[M^{2+}]_{aq}$ and substituting into the equation for the distribution ratio

$$D = \frac{[ML_2]_{org}}{[ML_2]_{aq} + \dfrac{[ML_2]_{aq}}{\beta_2[L^-]_{aq}^2}}$$

factoring out $[ML_2]_{aq}$ in the denominator

$$D = \frac{[ML_2]_{org}}{[ML_2]_{aq}\left\{1 + \dfrac{1}{\beta_2[L^-]_{aq}^2}\right\}}$$

and simplifying by replacing $[ML_2]_{org}/[ML_2]_{aq}$ with K_D leaves us with the desired final equation

$$D = \frac{K_D}{1 + \dfrac{1}{\beta_2[L^-]_{aq}^2}} = \frac{K_D\beta_2[L^-]_{aq}^2}{1 + \beta_2[L^-]_{aq}^2}$$

(b) Because the initial concentration of L^- (0.12 M) is much greater than the initial concentration of M^{2+} (0.15 mM), we can assume that $[L^-]_{aq}$ is 0.12 M. Substituting known values into the equation for D from part (a) gives the distribution ratio as

$$D = \frac{K_D\beta_2[L^-]_{aq}^2}{1 + \beta_2[L^-]_{aq}^2} = \frac{(10.3)(560)(0.12)^2}{1 + (560)(0.12)^2} = 9.16$$

the fraction remaining in the aqueous phase as

$$Q_{aq} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{9.16 \times 25.0 + 50.0} = 0.179$$

and an extraction efficiency of 0.821 or 82.1%.

31. We start by writing equations for $K_{D,c}$, $K_{D,L}$, K_a, and β_n for the four equilibrium reactions; these are

$$K_{D,c} = \frac{[ML_n]_{org}}{[ML_n]_{aq}} \qquad K_{D,HL} = \frac{[HL]_{org}}{[HL]_{aq}}$$

$$\beta_n = \frac{[ML_n]_{aq}}{[M^{n+}]_{aq}[L^-]_{aq}^n} \qquad K_a = \frac{[H_3O^+]_{aq}[L^-]_{aq}}{[HL]_{aq}}$$

and the distribution ratio for the extraction

$$D = \frac{[ML_n]_{org}}{[ML_n]_{aq} + [M^{n+}]_{aq}}$$

Solving β_n for $[M^{n+}]_{aq}$ and substituting into the equation for the distribution ratio

$$D = \frac{[ML_n]_{org}}{[ML_n]_{aq} + \dfrac{[ML_n]_{aq}}{\beta_n[L^-]_{aq}^n}}$$

and factoring out $[ML_n]_{aq}$ in the denominator gives

$$D = \frac{[ML_n]_{org}}{[ML_n]_{aq}\left\{1 + \dfrac{1}{\beta_n[L^-]_{aq}^n}\right\}} = \frac{K_{D,c}}{1 + \dfrac{1}{\beta_n[L^-]_{aq}^n}} = \frac{K_{D,c}\beta_n[L^-]_{aq}^n}{1 + \beta_n[L^-]_{aq}^n}$$

Next we solve K_a for $[L^-]_{aq}$ and substitute into the equation for the distribution ratio, giving

$$D = \frac{K_{D,c}\beta_n\left(\dfrac{K_a[HL]_{aq}}{[H_3O^+]_{aq}}\right)^n}{1 + \beta_n\left(\dfrac{K_a[HL]_{aq}}{[H_3O^+]_{aq}}\right)^n} = \frac{K_{D,c}(K_a)^n\beta_n[HL]_{aq}^n}{[H_3O^+]_{aq}^n + \beta_n(K_a)^n[HL]_{aq}^n}$$

Next, we solve $K_{D,L}$ for $[HL]_{aq}$ and substitute into the equation for the distribution ratio

$$D = \frac{K_{D,c}(K_a)^n\beta_n\left(\dfrac{[HL]_{org}}{K_{D,HL}}\right)^n}{[H_3O^+]_{aq}^n + \beta_n(K_a)^n\left(\dfrac{[HL]_{org}}{K_{D,HL}}\right)^n}$$

$$D = \frac{K_{D,c}(K_a)^n\beta_n[HL]_{org}^n}{(K_{D,HL})^n[H_3O^+]_{aq}^n + \beta_n(K_a)^n[HL]_{org}^n}$$

Finally, because the solubility of HL in the aqueous phase is so poor, we make the following assumption for a mass balance on HL

$$C_{HL} = [HL]_{org} + [HL]_{aq} \approx [HL]_{org}$$

and substitute back into the equation for the distribution ratio to yield equation 7.32.

$$D = \frac{\beta_n K_{D,c}(K_a)^n(C_{HL})^n}{(K_{D,HL})^n[H_3O^+]_{aq}^n + \beta_n(K_a)^n(C_{HL})^n}$$

32. We begin by calculating the distribution ration using equation 7.32

$$D = \frac{(5\times10^{22})(7\times10^4)(3\times10^{-5})^2(4.0\times10^{-4})^2}{(1.1\times10^4)^2(1)^2 + (5\times10^{22})(3\times10^{-5})^2(4.0\times10^{-4})^2}$$

$$D = 3930$$

and then calculate the fraction of Cu^{2+} remaining in the aqueous phase

$$Q_{aq} = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{100}{3930\times10.0 + 100.0} = 0.00254$$

finding that the extraction efficiency is 0.997 or 99.7%.

33. (a) One approach is to start by adjusting the pH of the aqueous phase to 1.0 and extract the Hg^{2+}. We can then raise the pH to 4.0 and extract the Pb^{2+}. Finally, we can raise the pH to 9.0 (or 10.0) and extract the Zn^{2+}.

(b) After three extractions, the fraction of Hg^{2+} that remains in the aqueous phase is

$$(Q_{aq})_3 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^3 = \left(\frac{50.0}{3.3\times50.0 + 50.0}\right)^3 = 0.0126$$

or 1.26%; the extraction efficiency is 98.7%

(c) The minimum volume of solvent needed to extract 99.5% of the Pb^{2+} in the aqueous phase is

$$Q_{aq} = 0.005 = \frac{V_{aq}}{DV_{org} + V_{aq}} = \frac{50.0}{9999V_{org} + 50.0}$$

$$49.995V_{org} + 0.25 = 50.0$$

$$V_{org} = 0.995 \text{ mL}$$

or a minimum volume of 1 mL of the organic solvent.

(d) The number of extractions needed to remove 99.5% of the Zn^{2+} is

$$(Q_{aq})_n = 0.005 = \left(\frac{V_{aq}}{DV_{org} + V_{aq}}\right)^n = \left(\frac{50.0}{2.57 \times 25.0 + 50.0}\right)^n$$

$$\log(0.005) = n\log(0.4376)$$

$$-2.301 = -0.3589n$$

$$n = 6.41$$

or a minimum of 7 extractions.

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 Ag^+, Cl^-, and $AgCl_{(s)}$

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

    For reactions 8.3–8.5, the equilibrium constant expressions are

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

    $$K_2 = \frac{[AgCl_2^-]}{[AgCl(aq)][Cl^-]}$$

    $$K_3 = \frac{[AgCl_3^{2-}]}{[AgCl_2^-][Cl^-]}$$

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

    $$S_{AgCl} = [Ag^+] + [AgCl(aq)] + [AgCl_2^-] + [AgCl_3^{2-}]$$

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

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

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

    $$[AgCl_2^-] = K_2[AgCl(aq)][Cl^-] = K_1K_2K_{sp}[Cl^-]$$

    $$[AgCl_3^{2-}] = K_3[AgCl_2^-][Cl^-] = K_1K_2K_3K_{sp}[Cl^-]^2$$

    and substituting back into the equation for S_{AgCl}

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

    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 Ag^+ in all its forms. We also can express the solubility of AgCl in terms of the total concentration of Cl^- in all its form; thus

    $$S_{AgCl} = [Cl^-] + [AgCl(aq)] + 2[AgCl_2^-] + 3[AgCl_3^{2-}]$$

    where we multiply the concentration of $AgCl_2^-$ by 2 and the concentration of $AgCl_3^{2-}$ by 3 to account for chloride's stoichiometry in the

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

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

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

$$K_2 = \frac{[AgCl_2^-]}{[AgCl(aq)][Cl^-]} = 83.2$$

$$K_3 = \frac{[AgCl_3^{2-}]}{[AgCl_2^-][Cl^-]} = 6.03$$

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

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

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

$$[AgCl_2^-] = K_2[AgCl(aq)][Cl^-] = \frac{K_1K_2K_{sp}^2}{[Ag^+]}$$

$$[AgCl_3^-] = K_3[AgCl_2^-][Cl^-] = \frac{K_1K_2K_3K_{sp}^3}{[Ag^+]^2}$$

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

$$S_{AgCl} = \frac{K_{sp}}{[Ag^+]} + K_1K_{sp} + \frac{2K_1K_2K_{sp}^2}{[Ag^+]} + \frac{3K_1K_2K_3K_{sp}^3}{[Ag^+]^2}$$

Figure SM8.1 shows a plot of $\log(S_{AgCl})$ as a function of pAg. For smaller concentrations of Ag^+, the solubility of AgCl is determined by the K_{sp} reaction alone; thus, the solubility for pAg > 4 is identical to that seen in Figure 8.1. The solubility of AgCl in the presence of a larger concentration of Ag^+ is dominated by the formation of AgCl(aq); thus, the solubility shown for pAg < 4 is independent of $[Ag^+]$ and much less than that seen in Figure 8.1 where the higher concentration of Cl^- allows for the formation of the soluble $AgCl_2^-$ and $AgCl_3^{2-}$ ions.
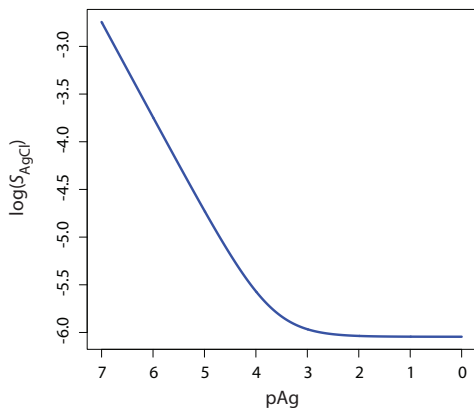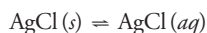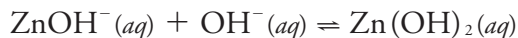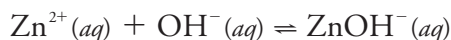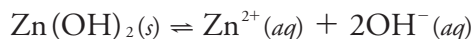

Figure SM8.1 Solubility of AgCl as a function of pAg based on reaction 8.1 and reactions 8.3–8.5. Solubility is displayed on the y-axis in logarithmic form. For pAg > 4, solubility is controlled by the reaction

$$AgCl(aq) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

For pAg < 4, solubility is controlled by the reaction

$$AgCl(s) \rightleftharpoons AgCl(aq)$$
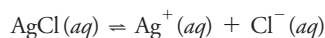
3. The relevant equilibrium reactions are

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

$$Zn^{2+}(aq) + OH^-(aq) \rightleftharpoons ZnOH^-(aq)$$

$$ZnOH^-(aq) + OH^-(aq) \rightleftharpoons Zn(OH)_2(aq)$$

$$Zn(OH)_2(aq) + OH^-(aq) \rightleftharpoons Zn(OH)_3^-(aq)$$

$$Zn(OH)_3^-(aq) + OH^-(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$$

for which the equilibrium constant expressions are

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

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

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

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

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

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

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

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

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

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

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

$$[HF] = \frac{[H_3O^+][F^-]}{K_a}$$

and substitute this into equation 8.10

$$[Ca^{2+}] = \frac{1}{2}\{[F^-] + [HF]\} = \frac{1}{2}\left([F^-] + \frac{[H_3O^+][F^-]}{K_a}\right)$$

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

$$[Ca^{2+}] = \frac{1}{2}[F^-]\left(1 + \frac{[H_3O^+]}{K_a}\right)$$

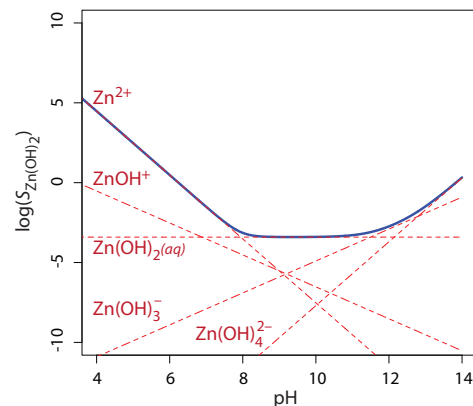$$[F^-] = \frac{2[Ca^{2+}]}{\left(1 + \frac{[H_3O^+]}{K_a}\right)}$$

Figure SM8.2 Solubility of $Zn(OH)_2$ as a function of pH. The contribution of the various soluble forms of 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 $Zn(OH)_2(aq)$ 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

$$K_{sp} = [Ca^{2+}][F^-]^2 = [Ca^{2+}]\left\{\frac{2[Ca^{2+}]}{\left(1 + \frac{[H_3O^+]}{K_a}\right)}\right\}^2$$

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

$$K_{sp} = [Ca^{2+}]\left\{\frac{2[Ca^{2+}]}{\left(1 + \frac{[H_3O^+]}{K_a}\right)}\right\}^2 = \frac{4[Ca^{2+}]^3}{\left(1 + \frac{[H_3O^+]}{K_a}\right)^2}$$

$$[Ca^{2+}]^3 = \frac{K_{sp}}{4}\left(1 + \frac{[H_3O^+]}{K_a}\right)^2$$

$$[Ca^{2+}] = \left\{\frac{K_{sp}}{4}\left(1 + \frac{[H_3O^+]}{K_a}\right)^2\right\}^{1/3}$$

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 CaC_2O_4, the upper-left ladder diagram suggests that we maintain the pH above 4.27 where $C_2O_4^{2-}$ is the only important form of oxalate. (b) For $PbCrO_4$, the ladder diagram at the bottom indicates that we must keep the pH level above 6.5 where 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 $BaSO_4$ as SO_4^{2-} is the only important form of sulfate. (d) The middle-left ladder diagram suggests that to minimize the solubility of $SrCO_3$, we must maintain a pH more basic than 10.33 to ensure that 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 S^{2-} is the only important form of sulfide, to minimize the solubility of ZnS.

6. Pure $KClO_4$ is white and pure $KMnO_4$ is a dark purple; the presence of a purple color in a precipitate of $KClO_4$ indicates that $KMnO_4$ is present and the depth of the color is proportional to the amount of $KMnO_4$ in the precipitate. In Experiment 1, the concentration of MnO_4^- is much greater than the concentration of ClO_4^-. As $KClO_4$ precipitates, the high concentration of MnO_4^- makes more likely the formation of inclusions of $KMnO_4$ that impart the deep purple color to the white precipitate of $KClO_4$. In experiment 2, the concentration of MnO_4^- is much smaller than that of ClO_4^-; as a result, inclusions of $KMnO_4$ are less likely and the precipitate's color is less intensely pink.
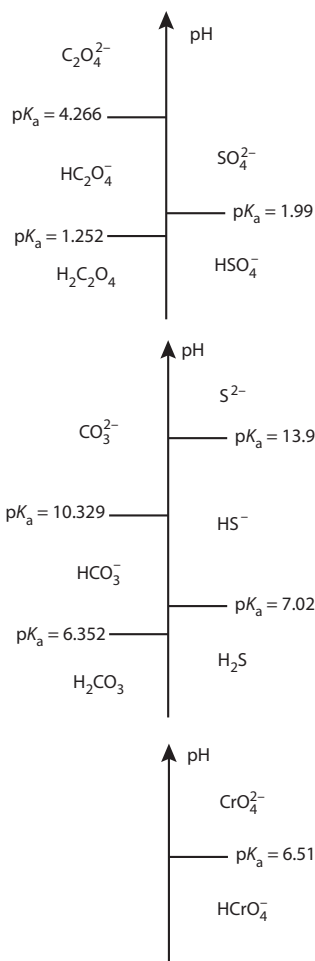

Figure SM8.3 Ladder diagrams for the weak base anions in Problem 8.5. Note that the ladder diagram for SO_4^{2-} does not include H_2SO_4 because it is a strong acid, and that the ladder diagram for CrO_4^{2-} does not include H_2CrO_4 because its pK_a of –0.2 means that it is an important species only 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 deceases the RSS; and (*iii*) digesting the precipitate provides time to allow for additional particle growth.

(b) If we isolate one mole of Al as $Al(OH)_3$, we obtain 78.0 g of product, and if we isolate one mole of Al as Al_2O_3, we obtain 51.0 g of product. Failing to convert some of the $Al(OH)_3$ to Al_2O_3 results in a larger than expected final mass—a positive determinate error—and we report a %w/w Al that is too high.

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.

(c) Both are added to help us control the solution's pH, which is important as $Al(OH)_3$ becomes more soluble at higher pHs due to the formation of complex ions, such as $Al(OH)_4^-$. The presence of NH_4^+ slows the rise in pH as it 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 NH_3 to complete the precipitation of Al^{3+}.

(d) If we isolate one mole of Al as Al_2O_3, we obtain 51.0 g of product, and if we isolate one mole of Al as $Al(C_9H_6NO)_3$, we obtain 459 g of product. With a greater mass, isolating Al as $Al(C_9H_6NO)_3$ improves the method's sensitivity.

9. (a) At first glance, we might expect that $CaC_2O_4 \cdot H_2O$ is a more desirable final product as it yields more grams of product per mole of Ca than does $CaCO_3$. 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 $CaCO_3$, we obtain 100.1 g of product. If we accidentally convert some of the $CaCO_3$ to CaO, the

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 Fe_3O_4, we obtain 77.2 g of product, and if we isolate one mole of Fe as Fe_2O_3, we obtain 79.8 g of product. As a result, if we isolate some of the Fe as Fe_3O_4 instead of as Fe_2O_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 NH_4NO_3 is added to prevent peptization of the precipitate.

(c) Ammonia, which is a weak base, is the source of OH^- for precipitating $Fe(OH)_3$. As NH_3 is volatile and has a distinct odor, once all the Fe^{3+} is precipitated as $Fe(OH)_3$, the excess NH_3 is easy to detect.

(d) One way to test the filtrate for Cl^- is to use Ag^+ and look for the formation of precipitate of AgCl. To carry out the test, we remove a small portion of the filtrate, add a small amount of acid to neutralize any NH_3 present so it does not form the stable complex $Ag(NH_3)_2^+$, and then add a few drops of a NaCl solution. If a precipitate forms, then we need to continue rinsing the precipitate.

11. First, we need to calculate the expected mass of 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 MoO_3. The volume of 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 $C_{13}H_{11}NO_2$, 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 Fe_2O_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 Fe_2O_3. Each mole (159.7 g) of Fe_2O_3 contains two moles (2×55.845 g = 111.7 g) of Fe.

13. To report the concentration of arsenic as %w/w As_2O_3, we first need to convert the mass of $Mg_2As_2O_7$ recovered into an equivalent mass of As_2O_3; thus

$$0.1065 \text{ g } Mg_2As_2O_7 \times \frac{197.84 \text{ g } As_2O_3}{310.45 \text{ g } Mg_2As_2O_7} = 0.0679 \text{ g } As_2O_3$$

which leave us with a %w/w As_2O_3 of

$$\frac{0.0679 \text{ g } As_2O_3}{1.627 \text{ g sample}} \times 100 = 4.17\%\text{w/w } As_2O_3$$

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

$$0.1357 \text{ g } Al_2O_3 \times \frac{53.96 \text{ g Al}}{101.96 \text{ g } Al_2O_3} = 0.07182 \text{ g Al}$$

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 Fe_2O_3 to an equivalent mass of iron and then covert the mass of Fe to the mass of $FeSO_4 \cdot 7H_2O$ in the original sample; thus

$$0.355 \text{ g } Fe_2O_3 \times \frac{111.69 \text{ g Fe}}{159.69 \text{ g } Fe_2O_3} = 0.2483 \text{ g Fe}$$

$$0.2483 \text{ g Fe} \times \frac{278.01 \text{ g } FeSO_4 \cdot 7H_2O}{55.845 \text{ g Fe}} = 1.236 \text{ g } FeSO_4 \cdot 7H_2O$$

The mass of $FeSO_4 \cdot 7H_2O$ per tablet, therefore, is

$$\frac{1.236 \text{ g } FeSO_4 \cdot 7H_2O}{3.116 \text{ g}} \times \frac{20.505 \text{ g}}{15 \text{ tablets}} = 0.542 \frac{\text{g } FeSO_4 \cdot 7H_2O}{\text{tablet}}$$

16. Because we isolate iron in a form, Fe_2O_3, identical to how we report its concentration, the calculation is straightforward

$$\frac{0.0357 \text{ g } Fe_2O_3}{1.4639 \text{ g sample}} \times 100 = 2.44\%\text{w/w } Fe_2O_3$$

For calcium, we isolate it as $CaSO_4$ but report it as 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 $Mg_2P_2O_7$ but report it as 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 $R(OCH_2CH_3)_x$ consumes x moles of HI, which means there are

$$6.296 \times 10^{-4} \text{ mol HI} \times \frac{\text{mol R}(OCH_2CH_3)_x}{x \text{ mol HI}}$$

$$= \frac{(6.296 \times 10^{-4}) \text{ mol R}(OCH_2CH_3)_x}{x}$$

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

$$\frac{0.03692 \text{ g R}(OCH_2CH_3)_x}{\dfrac{(6.296 \times 10^{-4}) \text{ mol R}(OCH_2CH_3)_x}{x}} = \frac{176 \text{ g R}(OCH_2CH_3)_x}{\text{mol R}(OCH_2CH_3)_x}$$

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

18. Because the mixture contains only K_2SO_4 and $(NH_4)_2SO_4$, we know that

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

where x is the mass of K_2SO_4 and y is the mass of $(NH_4)_2SO_4$. With one equation and two unknowns, we need an additional equation to define the system. Because K_2SO_4, $(NH_4)_2SO_4$, and $BaSO_4$ each contain a single mole of SO_4^{2-}, we know that

$$\text{mol BaSO}_4 = \text{mol K}_2SO_4 + \text{mol (NH}_4)\,SO_4$$

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

$$\frac{0.8635 \text{ g BaSO}_4}{233.39 \dfrac{\text{g BaSO}_4}{\text{mol}}} = \frac{x}{174.26 \dfrac{\text{g K}_2SO_4}{\text{mol}}} + \frac{y}{132.14 \dfrac{\text{g (NH}_4)_2SO_4}{\text{mol}}}$$

With two equations we have sufficient information to grind through the algebra and determine the mass of K_2SO_4 and $(NH_4)_2SO_4$ in the sample. Using the first equation, we solve for the mass of $(NH_4)_2SO_4$ in terms of K_2SO_4

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

substitute it into the second equation

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

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

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

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

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

where L_{Fe} is the ligand bound to iron and L_{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 FeL_3

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

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

and between Mn and MnL_2

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

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

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

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

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

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 FeL_3 as 0.6915 g. Substituting back gives the mass of MnL_2 as 0.1763 g.

Finally, we convert the mass of FeL_3 and the mass of 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

$$(\text{g AgCl})_{\text{AgBr}} = \text{g AgBr} \times \frac{1 \text{mol AgBr}}{187.77 \text{ g AgBr}} \times$$

$$\frac{1 \text{ mol (AgCl)}_{\text{AgBr}}}{\text{mol AgBr}} \times \frac{143.32 \text{ g (AgCl)}_{\text{AgBr}}}{\text{mol (AgCl)}_{\text{AgBr}}} = \text{g AgBr} \times 0.7633$$

$$(\text{g AgCl})_{\text{AgI}} = \text{g AgI} \times \frac{1 \text{mol AgI}}{234.77 \text{ g AgI}} \times$$

$$\frac{1 \text{ mol (AgCl)}_{\text{AgI}}}{\text{mol AgI}} \times \frac{143.32 \text{ g (AgCl)}_{\text{AgBr}}}{\text{mol (AgCl)}_{\text{AgBr}}} = \text{g AgI} \times 0.6105$$

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

$$0.1528 \times g\ AgBr = 0.09065$$

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

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

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

Finally, the mass of $NaNO_3$ is

$$0.8612\ g - 0.3248\ g\ NaBr - 0.2714\ g\ NaI = 02650\ g\ NaNO_3$$

and the mass percent of $NaNO_3$ is

$$\frac{0.2650\ g\ NaNO_3}{0.8612\ g\ sample} \times 100 = 30.77\%w/s\ NaNO_3$$

21. We begin by calculating the moles of AgBr formed

$$12.53112\ g\ AgBr \times \frac{1\ mol\ AgBr}{187.772\ g\ AgBr} = 0.667358\ mol\ AgBr$$

and then convert this to the moles of $MnBr_2$

$$0.0667358\ mol\ AgBr \times \frac{1\ mol\ MnBr_2}{2\ mol\ AgBr} = 0.0333679\ mol\ MnBr_2$$

The formula weight for $MnBr_2$ is

$$\frac{7.16539\ g\ MnBr_2}{0.0333679\ g\ MnBr_2} = 214.739\ g/mol$$

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:

$$AgCl\ (white) \quad AgI\ (yellow) \quad BaSO_4\ (white)$$
$$PbCl_2\ (white) \quad PbI_2\ (yellow) \quad PbSO_4\ (white)$$

We identify solution C as KI because I^- is the only species that forms two yellow precipitates. Solution E is $BaCl_2$ as it is the only solution that forms three white precipitates (one that contains Ba^{2+} and two that contain SO_4^{2-}). The yellow precipitates when KI (solution C) is mixed with solutions A and B tell us that one of these solutions

contains Ag^+ and that the other contains Pb^{2+}; because $Pb(NO_3)_2$ forms two white precipitates, we know that it is solution B, which leaves solution A as $AgNO_3$. Finally, the one remaining solution, D, is Na_2SO_4.

23. We know that the initial precipitate is completely soluble in dilute HNO_3, which means the precipitate contains one or more of the following compounds

$$Ag_2CO_3 \quad ZnCO_3 \quad MgCO_3 \quad BaCO_3$$

and that it cannot include $AgCl$ or $BaSO_4$ as neither is soluble in acid; note that this means that the original sample cannot contain both $AgNO_3$ and $ZnCl_2$, nor can it contain both $MgSO_4$ and $Ba(C_2H_3O_2)_2$.

Although the initial precipitate is soluble in HNO_3, at least one of its constituents does not dissolve in HCl. The solid that remains must be $AgCl$, as Zn^{2+}, Mg^{2+}, and Ba^{2+} form soluble chloride salts; this also means that the original sample must include $AgNO_3$ and K_2CO_3, and that it cannot include $ZnCl_2$.

$Ag_2CO_3\,(s) + 2HCl\,(aq) \longrightarrow$

$2AgCl\,(s) + H_2CO_3\,(aq)$
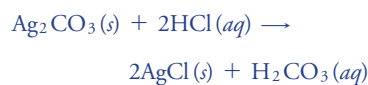
The filtrate that remains after adding HCl to the initial precipitate forms a precipitate with NH_3, which is a source of OH^-. The only possible precipitate is $Mg(OH)_2$ as Zn^{2+} forms a soluble complex of $Zn(OH)_4^{2-}$; thus, $MgSO_4$ is present in the original sample. Because $MgSO_4$ is present, we know that $Ba(C_2H_3O_2)_2$ is not present.

Finally, we have insufficient information to determine whether NH_4NO_3 is present.

24. When we analyze for the sulfur in pyrite, the relationship between the mass of analyte, FeS_2, and the mass of the precipitate, $BaSO_4$, is

$$\text{g BaSO}_4 = \text{g FeS}_2 \times \frac{2 \text{ mol S}}{119.96 \text{ g FeS}_2} \times \frac{233.39 \text{ g BaSO}_4}{1 \text{ mol S}}$$

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

When we analyze for the iron in pyrite, the relationship between the mass of analyte, FeS_2, and the mass of the final product, Fe_2O_3, is

$$\text{g Fe}_2O_3 = \text{g FeS}_2 \times \frac{1 \text{ mol Fe}}{119.96 \text{ g FeS}_2} \times \frac{159.69 \text{ g Fe}_2O_3}{2 \text{ mol Fe}}$$

$$\text{g Fe}_2O_3 = 0.666 \times \text{g FeS}_2$$

Based on these results, we see that the more sensitive analysis is to precipitate the sulfur in FeS_2 as $BaSO_4$ as this yields the greater mass of product for a given mass of FeS_2. This assumes, of course, that 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 $BaSO_4$, 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_2, 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 $AgNO_3$ to use, we first need to determine which analyte has the greatest amount of Cl^- on a per gram basis. This is easy to determine if we compare the %w/w Cl^- 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_4Cl has the greatest %w/w Cl^-, we assume that the sample contains only NH_4Cl and calculate the volume of $AgNO_3$ 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 $PbCrO_4$ 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_4^{2-} 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 $Pb(CrO_4)_{1.005}$.

(c) The effect of the non-stoichiometric ratio between Pb^{2+} and 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 Fe_3O_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

$$\%\text{w/w } Fe_3O_4 = \frac{2 \times m_{Fe_2O_3} \times FW_{Fe_3O_4}}{3 \times m_{sample} \times FW_{Fe_2O_3}} \times 100$$

where 2 and 3 account for the stoichiometry of iron in Fe_2O_3 and Fe_3O_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 Fe_2O_3 and the mass of Fe_3O_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 Fe_2O_3 is 0.8525 ± 0.00014 g and the mass of Fe_3O_4 is 1.5419 ± 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 ± 0.001 g/mol; thus, for Fe_2O_3 the formula weight is 159.691 ± 0.001 g/mol, and for Fe_3O_4 the formula weight is 231.537 ± 0.001 g/mol.

The %w/w Fe_2O_3 in the sample is

$$\frac{2 \times 0.8525 \times 231.537}{3 \times 1.5419 \times 159.691} \times 100 = 53.44\%\text{w/w } Fe_3O_4$$

and the estimated relative uncertainty in this value is

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

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 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 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 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

$$2KO_3\,(s) \longrightarrow 2KO_2\,(s) + O_2\,(g)$$

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 SiO_2, all of which is lost during the volatilization step. For each mole of 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

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

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

The compound's empirical formula, therefore, is $FeC_{10}H_{10}$.

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

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

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

polymer A	$m_{polymer}$ (g)	m_{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	$m_{polymer}$ (g)	m_{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

$$H_0: \overline{X}_A = \overline{X}_B \qquad H_A: \overline{X}_A \neq \overline{X}_B$$

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

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

finding that F_{exp}

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

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

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

The experimental value for t is

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

Because t_{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

$$d = \frac{\text{mol } H_2O}{m^2}$$

$$d = \frac{0.006 \text{ g } H_2O \times \dfrac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \dfrac{2 \text{ mol } OH^-}{\text{mol } H_2O} \times \dfrac{10^6 \text{ } \mu mol}{\text{mol}}}{1 \text{ g } ZrO_2 \times \dfrac{33 \text{ m}^2}{\text{g } ZrO_2}}$$

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

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

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

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

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

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

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, $\overline{X}$, to the expected mean, μ, for which the null and alternative hypotheses are

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

The experimental value for t is

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

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

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

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

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

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

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

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_{sample} (g)	$m_{organic}$ (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 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.
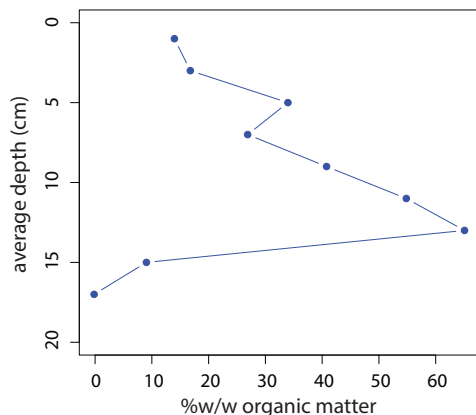
Figure SM8.4 Sediment profile showing the concentration of organic matter as a function of depth. Although normally we plot the dependent variable (%w/w organic matter, in this case) on the y-axis, we flip the axes here so that depth is aligned vertically as it is in a sediment column; note that we also 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.

38. (a) A 100-µL 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

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

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

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

$$7.71 \times 10^{-7} \text{ M} \pm 1.20 \times 10^{-7} \text{ M}$$
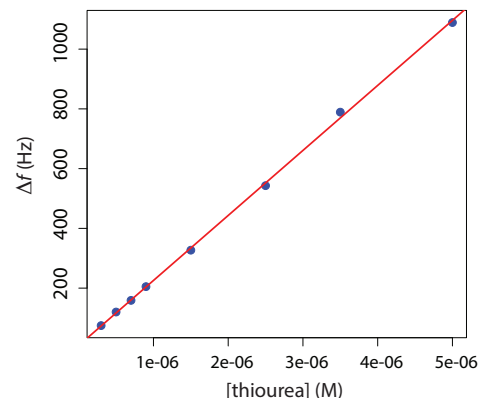
Figure SM8.5 Calibration curve for the data in Problem 8.38.

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

Chapter 9

Some of the problems in this chapter ask you to calculate or to sketch a titration curve. In general, you will find a discussion of calculations for a few representative points on each titration curve; to visualize the titration curve, you will need to calculate additional points. Brief comments on how to sketch the titration curve using a minimum number of calculations are included as sidebar comments. The exact titration curves in the accompanying figures were calculated using R; see the appendix for a discussion of the scripts used to create the figures.

1. (a) The titration of NaOH using HCl is an example of a strong base/strong acid titration curve. The equivalence point is reached when

$$n_{HCl} = M_{HCl} V_{HCl} = M_{NaOH} V_{NaOH} = n_{NaOH}$$

where n is the moles of HCl or of NaOH; thus

$$V_{eq.pt.} = V_{HCl} = \frac{M_{NaOH} V_{NaOH}}{M_{HCl}} = \frac{(0.100\ M)\,(25.0\ mL)}{0.0500\ M} = 50.0\ mL$$

The sample's initial pH is determined by the concentration of NaOH

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.100} = 1.00 \times 10^{-13}\ M$$

$$pH = -\log[H_3O^+] = -\log(1.00 \times 10^{-13}) = 13.00$$

For volumes less than the equivalence point volume, the pH is determined by the concentration of excess NaOH. After adding 10.0 mL of HCl, for example

$$[OH^-] = \frac{M_{NaOH} V_{NaOH} - M_{HCl} V_{HCl}}{V_{NaOH} + V_{HCl}}$$

$$[OH^-] = \frac{(0.100\ M)\,(25.0\ mL) - (0.0500\ M)\,(10.0\ mL)}{25.0\ mL + 10.0\ mL}$$

$$[OH^-] = 0.0571\ M$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.0571} = 1.75 \times 10^{-13}\ M$$

the pH is 12.76. For volumes greater than the equivalence point volume, the pH is determined by the concentration of excess HCl. After adding 60.0 mL of HCl, for example

$$[H_3O^+] = [HCl] = \frac{M_{HCl} V_{HCl} - M_{NaOH} V_{NaOH}}{V_{HCl} + V_{NaOH}}$$

$$[H_3O^+] = \frac{(0.0500\ M)\,(60.0\ mL) - (0.100\ M)\,(25.0\ mL)}{60.0\ mL + 25.0\ mL}$$

$$[H_3O^+] = 5.88 \times 10^{-3}\ M$$

the pH is 2.23. Figure SM9.1 shows the full titration curve.

For the titration curves in this problem, we will calculate the initial pH, the pH for one volume before each equivalence point, and the pH for one volume after the last equivalence point. In Problem 2, we will consider how to calculate the pH for each equivalence point.
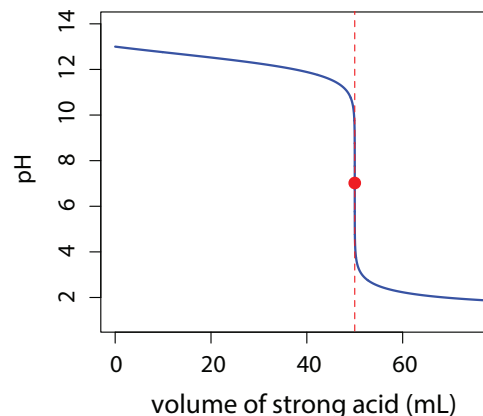

Figure SM9.1 The titration curve for 0.100 M NaOH using 0.100 M HCl as the titrant is shown in **blue**. The **red** dashed line marks the volume of titrant at the equivalence point and the **red** dot shows the equivalence point (see Problem 2a).

To sketch an approximate titration curve, calculate the pH for any two volumes before the equivalence point and the pH for any two volumes after equivalence point. Use the line passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.

(b) The titration of formic acid, HCOOH, using NaOH is an example of a monoprotic weak acid/strong base titration curve. The equivalence point is reached when

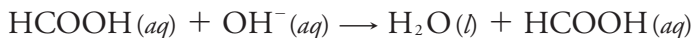$$n_{NaOH} = M_{NaOH} V_{NaOH} = M_{HCOOH} V_{HCOOH} = n_{HCOOH}$$

where n is the moles of NaOH or of HCOOH; thus

$$V_{eq.pt.} = V_{NaOH} = \frac{M_{HCOOH} V_{HCOOH}}{M_{NaOH}} =$$

$$\frac{(0.0500 \text{ M}) (50.0 \text{ mL})}{0.100 \text{ M}} = 25.0 \text{ mL}$$

The sample's initial pH of 2.54 is determined by the initial concentration of formic acid and its K_a value

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{(x)(x)}{0.0500 - x} = 1.80 \times 10^{-4}$$

$$x = [H_3O^+] = 2.91 \times 10^{-3} \text{ M}$$

Before the equivalence point, the solution is a buffer that consists of excess HCOOH and HCOO$^-$ from the reaction

$$HCOOH(aq) + OH^-(aq) \longrightarrow H_2O(l) + HCOOH(aq)$$

After adding 10.0 mL of HCl, for example, the pH is

$$[HCOOH] = \frac{M_{HCOOH} V_{HCOOH} - M_{NaOH} V_{NaOH}}{V_{HCOOH} + V_{NaOH}}$$

$$[HCOOH] = \frac{(0.0500 \text{ M}) (50.0 \text{ mL}) - (0.100 \text{ M}) (10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}}$$

$$[HCOOH] = 0.025 \text{ M}$$

$$[HCOO^-] = \frac{M_{NaOH} V_{NaOH}}{V_{HCOOH} + V_{NaOH}} =$$

$$\frac{(0.100 \text{ M}) (10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0167 \text{ M}$$

$$pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]} = 3.745 + \log \frac{(0.0167)}{(0.0250)} = 3.57$$

For volumes greater than the equivalence point volume, the pH is determined by the concentration of excess NaOH. After adding 35.0 mL of NaOH, for example

$$[OH^-] = \frac{M_{NaOH} V_{NaOH} - M_{HCOOH} V_{HCOOH}}{V_{HCOOH} + V_{NaOH}}$$

$$[OH^-] = \frac{(0.100 \text{ M}) (35.0 \text{ mL}) - (0.0500 \text{ M}) (50.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}}$$

$$[OH^-] = 0.0118 \text{ M}$$

the pOH is 1.93, or a pH of 12.07. Figure SM9.2 shows the full titration curve.
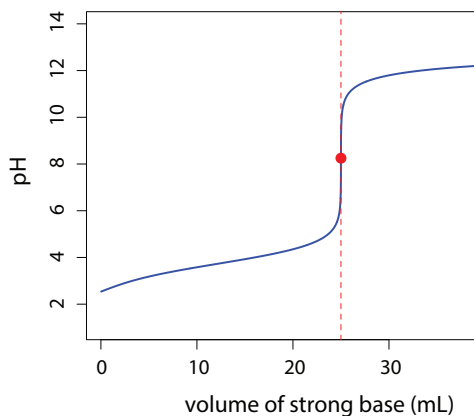

Figure SM9.2 The titration curve for 0.0500 M using 0.100 M NaOH as the titrant is shown in **blue**. The **red** dashed line marks the volume of titrant at the equivalence point and the **red** dot shows the equivalence point (see Problem 2b).

(c) The titration of ammonia, NH_3, using HCl is an example of a monoprotic weak base/strong acid titration curve. The equivalence point is reached when

$$n_{HCl} = M_{HCl} V_{HCl} = M_{NH_3} V_{NH_3} = n_{NH_3}$$

where n is the moles of HCl or of NH_3; thus

$$V_{eq.pt.} = V_{HCl} = \frac{M_{NH_3} V_{NH_3}}{M_{HCl}} =$$

$$\frac{(0.100\ M)\,(50.0\ mL)}{0.100\ M} = 50.0\ mL$$

The sample's initial pOH of 2.88, or a pH of 11.12, is determined by the initial concentration of ammonia and its K_b value

$$K_b = \frac{[OH^-]\,[NH_4^+]}{[NH_3]} = \frac{(x)\,(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [OH^-] = 1.31 \times 10^{-3}\ M$$

Before the equivalence point, the solution is a buffer that consists of excess NH_3 and NH_4^+ from the reaction

$$NH_3\,(aq) + H_3O^+\,(aq) \longrightarrow H_2O\,(l) + NH_4^+\,(aq)$$
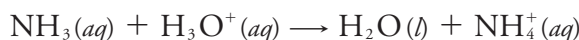
After adding 20.0 mL of HCl, for example, the pH is

$$[NH_3] = \frac{M_{NH_3} V_{NH_3} - M_{HCl} V_{HCl}}{V_{NH_3} + V_{HCl}}$$

$$[NH_3] = \frac{(0.100\ M)\,(50.0\ mL) - (0.100\ M)\,(20.0\ mL)}{50.0\ mL + 20.0\ mL}$$

$$[NH_3] = 0.0429\ M$$

$$[NH_4^+] = \frac{M_{HCl} V_{HCl}}{V_{NH_3} + V_{HCl}} =$$

$$\frac{(0.100\ M)\,(20.0\ mL)}{50.0\ mL + 20.0\ mL} = 0.0286\ M$$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = 9.244 + \log\frac{(0.0429)}{(0.0286)} = 9.42$$

For volumes greater than the equivalence point volume, the pH is determined by the amount of excess HCl. After adding 60.0 mL of HCl, for example

$$[H_3O^+] = \frac{M_{HCl} V_{HCl} - M_{NH_3} V_{NH_3}}{V_{NH_3} + V_{HCl}}$$

$$[H_3O^+] = \frac{(0.100\ M)\,(60.0\ mL) - (0.100\ M)\,(50.0\ mL)}{50.0\ mL + 60.0\ mL}$$

$$[H_3O^+] = 0.00909\ M$$

the pH is 2.04. Figure SM9.3 shows the full titration curve.
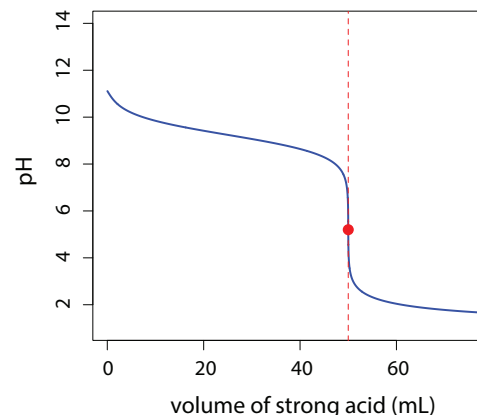
Figure SM9.3 The titration curve for 0.100 M NH_3 using a 0.100 M HCl as the titrant is shown in **blue**. The **red** dashed line marks the volume of titrant at the equivalence point and the **red** dot shows the equivalence point (see Problem 2c).

To sketch an approximate titration curve, use a ladder diagram for NH_3 to place points at 10% and at 90% of the equivalence point's volume, and calculate the pH for two points after the equivalence point. Use the line passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.

(d) The titration of ethylenediamine, which we abbreviate here as en, using HCl is an example of a diprotic weak base/strong acid titration curve. Because en is diprotic, the titration curve has two equivalence points; the first equivalence point is reached when

$$n_{HCl} = M_{HCl} V_{HCl} = M_{en} V_{en} = n_{en}$$

where n is the moles of HCl or of en; thus

$$V_{eq.pt.1} = V_{HCl} = \frac{M_{en} V_{en}}{M_{HCl}} =$$

$$\frac{(0.0500 \text{ M}) (50.0 \text{ mL})}{0.100 \text{ M}} = 25.0 \text{ mL}$$

The second equivalence point is reached after adding an additional 25.0 mL of HCl, for a total volume of 50.0 mL.

The sample's initial pOH of 2.69, or a pH of 11.31, is determined by the initial concentration of en and its K_{b1} value

$$K_{b1} = \frac{[OH^-][Hen^+]}{[en]} = \frac{(x)(x)}{0.0500 - x} = 8.47 \times 10^{-5}$$

$$x = [OH^-] = 2.06 \times 10^{-3} \text{ M}$$

Before the first equivalence point the pH is fixed by an Hen^+/en buffer; for example, after adding 10.0 mL of HCl, the pH is

$$[en] = \frac{M_{en} V_{en} - M_{HCl} V_{HCl}}{V_{en} + V_{HCl}}$$

$$[en] = \frac{(0.0500 \text{ M}) (50.0 \text{ mL}) - (0.100 \text{ M}) (10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}}$$

$$[en] = 0.0250 \text{ M}$$

$$[Hen^+] = \frac{M_{HCl} V_{HCl}}{V_{en} + V_{HCl}} =$$

$$\frac{(0.100 \text{ M}) (10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}} = 0.0167 \text{ M}$$

Be sure to use pK_{a2} in the Henderson-Hasselbach equation, not pK_{a1}, as the latter describes the acid-base equilibrium between H_2en^{2+} and Hen^+.

$$pH = pK_{a2} + \log\frac{[en]}{[Hen^+]} = 9.928 + \log\frac{(0.0250)}{(0.0167)} = 10.10$$

Between the two equivalence points, the pH is fixed by a buffer of H_2en^{2+} and en; for example, after adding 35.0 mL of HCl the pH is

$$[Hen^+] = \frac{M_{en} V_{en} - M_{HCl}(V_{HCl} - V_{eq.pt.1})}{V_{en} + V_{HCl}}$$

$$[Hen^+] = \frac{(0.0500 \text{ M}) (50.0 \text{ mL}) - (0.100 \text{ M}) (35.0 - 25.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}}$$

$$[Hen^+] = 0.0176 \text{ M}$$

$$[H_2en^{2+}] = \frac{M_{HCl}(V_{HCl} - V_{eq.pt.1})}{V_{en} + V_{HCl}}$$

$$[H_2en^{2+}] = \frac{(0.100 \text{ M})(35.0 - 25.0 \text{ mL})}{50.0 \text{ mL} + 35.0 \text{ mL}}$$

$$[H_2en^{2+}] = 0.0118 \text{ M}$$

$$pH = pK_{a1} + \log\frac{[Hen^+]}{[H_2en^{2+}]} = 6.848 + \log\frac{(0.0176)}{(0.0118)} = 7.02$$

For volumes greater than the second equivalence point volume, the pH is determined by the concentration of excess HCl. After adding 60.0 mL of HCl, for example

$$[H_3O^+] = \frac{M_{HCl}(V_{HCl} - V_{eq.pt2})}{V_{en} + V_{HCl}}$$

$$[H_3O^+] = \frac{(0.100 \text{ M})(60.0 - 50.0 \text{ mL})}{50.0 \text{ mL} + 60.0 \text{ mL}}$$

$$[H_3O^+] = 0.00909 \text{ M}$$

the pH is 2.04. Figure SM9.4 shows the full titration curve.

(e) The titration of citric acid, which we abbreviate here as H_3A, using NaOH is an example of a triprotic weak acid/strong base titration curve. Because H_3A is triprotic, the titration curve has three equivalence points; the first equivalence point is reached when

$$n_{NaOH} = M_{NaOH}V_{NaOH} = M_{H_3A}V_{H_3A} = n_{H_2A}$$

where n is the moles of HCl or of H_3A; thus

$$V_{eq.pt.1} = V_{NaOH} = \frac{M_{H_3A}M_{H_3A}}{M_{NaOH}} =$$

$$\frac{(0.0400 \text{ M})(50.0 \text{ mL})}{0.120 \text{ M}} = 16.7 \text{ mL}$$

The second equivalence point occurs after adding an additional 16.7 mL of HCl, for a total volume of 33.33 mL, and the third equivalence point after adding an additional 16.7 mL of HCl, for a total volume of 50.0 mL.

The sample's initial pH of 2.29 is determined by the initial concentration of citric acid and its K_{a1} value

$$K_{a1} = \frac{[H_3O^+][H_2A^-]}{[H_3A]} = \frac{(x)(x)}{0.0400 - x} = 7.45 \times 10^{-4}$$

$$x = [H_3O^+] = 5.10 \times 10^{-3} \text{ M}$$

Adding NaOH creates, in succession, an H_3A/H_2A^- buffer, an H_2A^-/HA^{2-} buffer, and an HA^{2-}/A^{3-} buffer. We can calculate the pH in these buffer regions using the same approach outlined in the previous three problems; however, because citric acid's pK_a values are sufficiently similar in value (see Figure SM9.5) we must be careful to avoid pHs where two buffer regions overlap. After adding 5.00 mL of NaOH, for example, the pH is

To sketch an approximate titration curve, use a ladder diagram for en to place points at 10% and at 90% of each of the two equivalence point volumes, and calculate the pH for two points after the second equivalence point. Use the line passing through each pair of points and the vertical lines at the equivalence point volumes to sketch the titration curve.
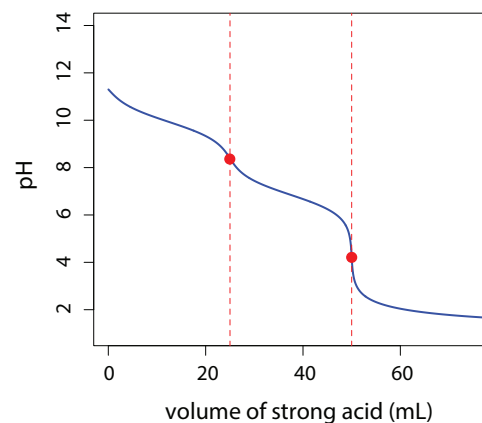

Figure SM9.4 The titration curve for 0.0500 M ethylenediamine using 0.100 M HCl as the titrant is shown in **blue**. The **red** dashed lines mark the volumes of titrant at the equivalence points and the **red** dots mark the equivalence points (see Problem 2d).
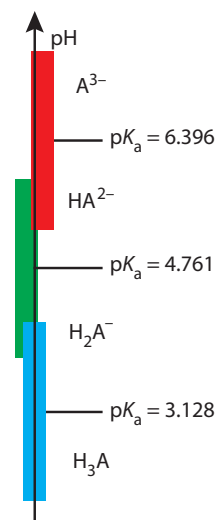

Figure SM9.5 Ladder diagram for citric acid with buffer regions for H_3A/H_2A^- (in **blue**), for H_2A^-/HA^{2-} (in **green**), and for HA^{2-}/A^{3-} (in **red**). The assumptions in the Henderson-Hasselbalch equation hold at pH levels where the buffers do not overlap.

$$[H_3A] = \frac{M_{H_3A} V_{H_3A} - M_{NaOH} V_{NaOH}}{V_{H_3A} + V_{NaOH}}$$

$$[H_3A] = \frac{(0.0400 \text{ M})(50.0 \text{ mL}) - (0.120 \text{ M})(5.00 \text{ mL})}{50.0 \text{ mL} + 5.00 \text{ mL}}$$

$$[H_3A] = 0.0255 \text{ M}$$

$$[H_2A^-] = \frac{M_{NaOH} V_{NaOH}}{V_{H_3A} + V_{NaOH}} =$$

$$\frac{(0.120 \text{ M})(5.00 \text{ mL})}{50.0 \text{ mL} + 5.00 \text{ mL}} = 0.0109 \text{ M}$$

$$pH = pK_{a1} + \log\frac{[H_2A^-]}{[H_3A]} = 3.128 + \log\frac{(0.0109)}{(0.0255)} = 2.76$$

After adding 30.00 mL of NaOH the pH is

$$[H_2A^-] = \frac{M_{H_3A} V_{H_3A} - M_{NaOH}(V_{NaOH} - V_{eq.pt.1})}{V_{H_3A} + V_{NaOH}}$$

$$[H_2A^-] = \frac{(0.0400 \text{ M})(50.0 \text{ mL}) - (0.120 \text{ M})(30.0 - 16.7 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}}$$

$$[H_2A^-] = 5.05 \times 10^{-3} \text{ M}$$

$$[HA^{2-}] = \frac{M_{NaOH}(V_{NaOH} - V_{eq.pt.1})}{V_{H_3A} + V_{NaOH}}$$

$$[HA^{2-}] = \frac{(0.120 \text{ M})(30.0 - 16.7 \text{ mL})}{50.0 \text{ mL} + 30.0 \text{ mL}}$$

$$[HA^{2-}] = 0.0200 \text{ M}$$

$$pH = pK_{a2} + \log\frac{[HA^{2-}]}{[H_2A^-]} = 4.761 + \log\frac{(0.0200)}{(0.00505)} = 5.36$$

and after adding 45.0 mL of NaOH the pH is

$$[HA^{2-}] = \frac{M_{H_3A} V_{H_3A} - M_{NaOH}(V_{NaOH} - V_{eq.pt.2})}{V_{H_3A} + V_{NaOH}}$$

$$[HA^{2-}] = \frac{(0.0400 \text{ M})(50.0 \text{ mL}) - (0.120 \text{ M})(45.0 - 33.3 \text{ mL})}{50.0 \text{ mL} + 45.0 \text{ mL}}$$

$$[HA^{2-}] = 0.00627 \text{ M}$$

$$[A^{3-}] = \frac{M_{NaOH}(V_{NaOH} - V_{eq.pt.2})}{V_{H_3A} + V_{NaOH}}$$

$$[A^{3-}] = \frac{(0.120 \text{ M})(45.0 - 33.3 \text{ mL})}{50.0 \text{ mL} + 45.0 \text{ mL}}$$

$$[A^{3-}] = 0.0148 \text{ M}$$

$$pH = pK_{a3} + \log\frac{[A^{3-}]}{[HA^{2-}]} = 6.396 + \log\frac{(0.0148)}{(0.00627)} = 6.77$$

For volumes greater than the third equivalence point volume, the pH is determined by the concentration of excess NaOH. After adding 60.0 mL of NaOH, for example

$$[OH^-] = \frac{M_{NaOH}(V_{NaOH} - V_{eq.pt.3})}{V_{H_3A} + V_{NaOH}}$$

$$[OH^-] = \frac{(0.120\ M)(60.0 - 50.0\ mL)}{50.0\ mL + 60.0\ mL}$$

$$[OH^-] = 0.0109\ M$$

the pOH is 1.96, or a pH of 12.04. Figure SM9.6 shows the full titration curve.

(f) With one exception, the calculations for the titration of phosphoric acid, H_3PO_4, with NaOH are identical to those for citric acid in part (e), and are left to you. The interesting exception is that the calculated pH values between the second and the third equivalence point hover around phosphoric acid's pK_{a3} of 12.35, but following the third equivalence point the calculated pH values are just a bit greater than 12; clearly this is impossible as the pH cannot become more acidic as we add NaOH. The problem is in calculating the pH between the second and the third equivalence point where a key assumption fails: because HPO_4^{2-} is such a weak acid, its reaction with NaOH is not complete. Figure SM97 shows the full titration curve.

2. The dashed lines in Figures SM9.1–SM9.4, in Figure SM9.6, and in Figure SM9.7 indicate the location of the equivalence. Of these equivalence points, the first and second for citric acid (Figure SM9.6) and the third for phosphoric acid (Figure SM9.7) are not discernible and not considered further in this problem.

(a) For any titration of an aqueous strong acid and an aqueous strong base, the pH at the equivalence point is equivalent to $\frac{1}{2}pK_w$, or 7.00. At the equivalence point, each mole of HCl has reacted with one mole of NaOH.

(b) At the equivalence point the solution contains the formate ion with a concentration of

$$[HCOO^-] = \frac{M_{HCOOH}V_{HCOOH}}{V_{HCOOH} + V_{NaOH}} =$$

$$\frac{(0.0500\ M)(50.0\ mL)}{50.0\ mL + 25.0\ mL} = 0.0333\ M$$

The pOH of 5.87, or a pH of 8.13, is determined by the concentration of formate and its K_b value

$$K_b = \frac{[OH^-][HCOOH]}{[HCOO^-]} = \frac{(x)(x)}{0.0333 - x} = 5.56 \times 10^{-11}$$

$$x = [OH^-] = 1.36 \times 10^{-6}\ M$$

To sketch an approximate titration curve, use a ladder diagram for citric acid to place points at 10% and at 90% of each of the three equivalence point volumes, and calculate the pH for two points after the third equivalence point. Use the line passing through each pair of points and the vertical lines at the equivalence point volumes to sketch the titration curve. Remember that the pH can only increase.
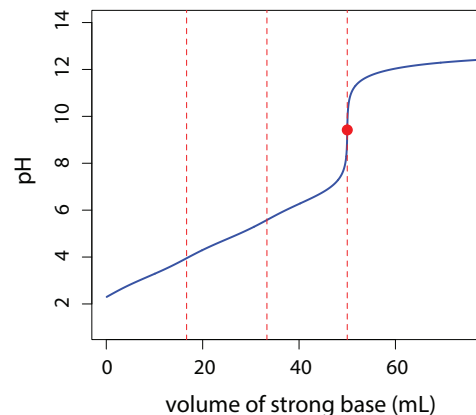

Figure SM9.6 The titration curve for 0.040 M citric acid using 0.120 M NaOH as the titrant is shown in **blue**. The **red** dashed lines mark the volumes of titrant at the equivalence points and the **red** dot marks the third equivalence point (see Problem 2e). Note that the pK_a values are sufficiently close in value that the first two equivalence points are not discernible.

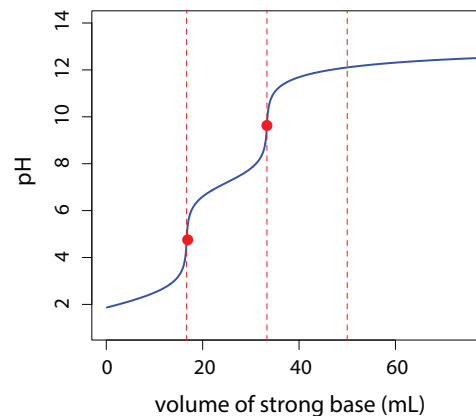**Figure SM9.7** The titration curve for 0.040 M H_3PO_4 using 0.120 M NaOH as the titrant is shown in **blue**. The **red** dashed lines mark volumes of titrant at the equivalence points and the **red** dots marks the first two equivalence points (see Problem 2f). Note that third equivalence point is not discernible.

At the equivalence point, each mole of formic acid has reacted with one mole of NaOH.

(c) At the equivalence point the solution contains the ammonium ion with a concentration of

$$[NH_4^+] = \frac{M_{NH_3} V_{NH_3}}{V_{NH_3} + V_{HCl}} =$$

$$\frac{(0.100\ M)(50.0\ mL)}{50.0\ mL + 50.0\ mL} = 0.0500\ M$$

The pH of 5.27, is determined by the concentration of the ammonium ion and its K_a value

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{(x)(x)}{0.0500 - x} = 5.70 \times 10^{-10}$$

$$x = [H_3O^+] = 5.34 \times 10^{-6}\ M$$

At the equivalence point, each mole of ammonia reacts with one mole of HCl.

(d) The titration of ethylenediamine (en) has two equivalence points. The pH at the first equivalence point is determined by the concentration of Hen^+, which is

$$[Hen^+] = \frac{M_{en} V_{en}}{V_{en} + V_{HCl}} =$$

$$\frac{(0.0500\ M)(50.0\ mL)}{50.0\ mL + 25.0\ mL} = 0.0333\ M$$

Because Hen^+ is amphiprotic, the pH at the equivalence point of 8.39 is determine by its concentration and by the K_a values for both H_2en^{2+} and for Hen^+

$$[H_3O^+] = \sqrt{\frac{K_{a1} K_{a2} C_{Hen^+} + K_{a1} K_w}{C_{Hen^+} + K_{a1}}}$$

$$[H_3O^+] = \sqrt{\frac{\left[\begin{array}{c} (1.42 \times 10^{-7})(1.18 \times 10^{-10})(0.0333) \\ + (1.42 \times 10^{-7})(1.00 \times 10^{-14}) \end{array} \right]}{(0.0333) + (1.42 \times 10^{-7})}}$$

$$[H_3O^+] = 4.1 \times 10^{-9}$$

At the second equivalence point, the pH of 4.23 is determined by the concentration of H_2en^{2+}, which is

$$[H_2en^{2+}] = \frac{M_{en} V_{en}}{V_{en} + V_{HCl}} =$$

$$\frac{(0.0500\ M)(50.0\ mL)}{50.0\ mL + 50.0\ mL} = 0.0250\ M$$

and by K_{a1} for the dissociation of H_2en^{2+}

$$K_{a1} = \frac{[H_3O^+][Hen^+]}{[H_2en^{2+}]} = \frac{(x)(x)}{0.0250 - x} = 1.42 \times 10^{-7}$$

$$[H_3O^+] = 5.95 \times 10^{-5}$$

At the first equivalence point, each mole of en reacts with one mole of HCl; at the second equivalence point, each mole of en reacts with two moles of HCl.

(e) For citric acid the only discernible equivalence point is the third, which corresponds to the conversion of monohydrogen citrate, HA^{2-}, to citrate, A^{3-}. The concentration of citrate is

$$[A^{3-}] = \frac{M_{H_3A} V_{H_3A}}{V_{H_3A} + V_{HCl}} =$$

$$\frac{(0.0400\ M)(50.0\ mL)}{50.0\ mL + 50.0\ mL} = 0.0200\ M$$

for which

$$K_{b1} = \frac{[OH^-][HA^{2-}]}{[A^{3-}]} = \frac{(x)(x)}{0.0200 - x} = 2.49 \times 10^{-8}$$

$$[OH^-] = 2.23 \times 10^{-5}$$

the pOH is 4.65, or a pH of 9.35. At this equivalence point, each mole of citric acid reacts with three moles of NaOH.

(f) For phosphoric acid, the first and the second equivalence points are the only useful equivalence points. The first equivalence point corresponds to the conversion of H_3PO_4 to $H_2PO_4^-$ and the second equivalence point corresponds to the conversion of $H_2PO_4^-$ to HPO_4^{2-}. The pH at the first equivalence point is determined by the concentration of $H_2PO_4^-$, which is

$$[H_2PO_4^-] = \frac{M_{H_3PO_4} V_{H_3PO_4}}{V_{NaOH} + V_{H_3PO_4}} =$$

$$\frac{(0.0400\ M)(50.0\ mL)}{16.7\ mL + 50.0\ mL} = 0.0300\ M$$

Because $H_2PO_4^-$ is amphiprotic, the pH of 4.72 is given by

$$[H_3O^+] = \sqrt{\frac{K_{a1} K_{a2} C_{H_2PO_4^-} + K_{a1} K_w}{C_{H_2PO_4^-} + K_{a1}}}$$

$$[H_3O^+] = \sqrt{\frac{\left[\begin{array}{c} (7.11 \times 10^{-3})(6.32 \times 10^{-8})(0.0300) \\ + (7.11 \times 10^{-3})(1.00 \times 10^{-14}) \end{array} \right]}{(0.0300) + (7.11 \times 10^{-3})}}$$

$$[H_3O^+] = 1.91 \times 10^{-5}$$

The pH at the second equivalence point is determined by the concentration of HPO_4^{2-}, which is

$$[HPO_4^{2-}] = \frac{M_{H_3PO_4} V_{H_3PO_4}}{V_{NaOH} + V_{H_3PO_4}} =$$

$$\frac{(0.0400\ M)(50.0\ mL)}{33.3\ mL + 50.0\ mL} = 0.0240\ M$$

Because HPO_4^{2-} is amphiprotic, the pH of 9.63 is given by

$$[H_3O^+] = \sqrt{\frac{K_{a2}K_{a3}C_{HPO_4^{2-}} + K_{a2}K_w}{C_{HPO_4^{2-}} + K_{a2}}}$$

$$[H_3O^+] = \sqrt{\frac{\left[\begin{array}{r}(6.32 \times 10^{-8})(4.5 \times 10^{-13})(0.0240) \\ + (6.32 \times 10^{-8})(1.00 \times 10^{-14})\end{array}\right]}{(0.0240) + (6.32 \times 10^{-8})}}$$

$$[H_3O^+] = 2.34 \times 10^{-10}$$

At the first equivalence point, each mole of H_3PO_4 reacts with one mole of NaOH; at the second equivalence point, each mole of H_3PO_4 reacts with two moles of NaOH.

3. For each titration curve, an appropriate indicator is determined by comparing the indicator's pK_a and its pH range to the pH at the equivalence point. Using the indicators in Table 9.4, good choices are:

    (a) bromothymol blue; (b) cresol red; (c) methyl red; (d) cresol red for the first equivalence point (although the lack of a large change in pH at this equivalence point makes it the less desirable choice) and congo red for the second equivalence point; (e) phenolphthalein; and (f) bromocresol green for the first equivalence point and phenolphthalein for the second equivalence point.

    The margin note reads:

    > The choice of indicator for (d) illustrates an important point: for a polyprotic weak acid or weak base, you can choose the equivalence point that best meets your needs.

    Other indicators from Table 9.4 are acceptable choices as well, provided that the change in color occurs wholly within the sharp rise in pH at the equivalence point.

4. To show that this is the case, let's assume we are titrating the weak acid HA with NaOH and that we begin with x moles of HA. The reaction between HA and OH^- is very favorable, so before the equivalence point we expect that the moles of HA will decrease by an amount equivalent to the moles of OH^- added. If we add sufficient OH^- to react with 10% of the HA, then the moles of HA that remain is $0.9x$. Because we produce a mole of A^- for each mole of HA consumed, we have $0.1x$ moles of A^-. From the Henderson-Hasselbalch equation we know that

    $$pH = pK_a + \log\frac{\text{mol } A^-}{\text{mol HA}}$$

    $$pH = pK_a + \log\frac{0.1x}{0.9x} = pK_a - 0.95 \approx pK_a - 1$$

    After adding sufficient OH^- to consume 90% of the HA, $0.1x$ moles of HA remain and $0.9x$ moles of A^-; thus

    $$pH = pK_a + \log\frac{0.9x}{0.1x} = pK_a + 0.95 \approx pK_a + 1$$

5. Tartaric acid is a diprotic weak acid, so our first challenge is to decide which of its two endpoints is best suited for our analysis. As the two

pK_a values are not widely separated from each other, you might expect that the first equivalence point does not provide a strong signal (see, for example, the titration curve for citric acid in Problem 1e); this is correct, as shown in Figure SM9.8 for the titration of 0.10 M tartaric acid with 0.10 M NaOH.

Our second challenge is to determine an appropriate indicator for the titration. From Figure SM9.8, any indicator with a pH range between a pH of 7 and a pH of 10 is suitable: cresol red, thymol blue, and phenolphthalein are suitable options.

Finally, our third challenge is to determine the mass of sample to take. At the second equivalence point, each mole of tartaric acid consumes two moles of NaOH. Although the second equivalence point for the titration curve in Figure SM9.8 is at 100 mL, we want to limit our titration to a volume of less than 50 mL so that we do not need to refill the buret. Let's aim, therefore, for an equivalence point of approximately 45 mL. If we calculate the sample's mass assuming it is 100% pure, then we know that the equivalence point will occur between approximately 36 mL of NaOH (80% of 45) and 45 mL of NaOH; thus, we need

$$0.045 \text{ L NaOH} \times \frac{0.10 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol H}_2\text{C}_4\text{H}_4\text{O}_6}{2 \text{ mol NaOH}}$$

$$\times \frac{150.1 \text{ g H}_2\text{C}_4\text{H}_4\text{O}_6}{\text{mol H}_2\text{C}_4\text{H}_4\text{O}_6} = 0.34 \text{ g H}_2\text{C}_4\text{H}_4\text{O}_6$$

We use this same equation to calculate the actual mass of tartaric acid in the sample, replacing the 45 mL of NaOH with the actual volume of NaOH at the equivalence point. The %w/w tartaric acid is

$$\frac{\text{g H}_2\text{C}_4\text{H}_4\text{O}_6}{\text{g sample}} \times 100 = \text{\%w/w H}_2\text{C}_4\text{H}_4\text{O}_6$$

6. Figure SM9.9a shows a normal titration curve in which we plot pH on the y-axis as a function of volume on the x-axis. The equivalence point is where the titration curve has its greatest slope.

    To plot the first derivative, we calculate the change in pH as a function of the change in volume; for example, the first point is

    $$\frac{\Delta \text{pH}}{\Delta V} = \frac{3.2 - 3.0}{0.86 - 0.25} = 0.328$$

    and is plotted at the average of the two volumes, or 0.555 mL. Figure SM9.9b shows the resulting titration curve, where the equivalence point corresponds to the volume that has the greatest signal.

    To plot the second derivative, we calculate the change in $\Delta \text{pH}/\Delta V$ as a function of the volume of titrant. For example, the first two points in Figure SM9.9b are (0.555,0.328) and (1.245,0.260), which makes the second derivative
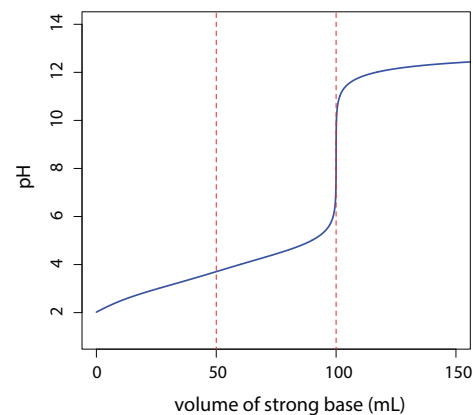

Figure SM9.8 The titration curve for 0.10 M tartaric acid using 0.10 M NaOH as the titrant is shown in **blue**. The **red** dashed lines mark the volumes of titrant at the equivalence points. Note that first equivalence point is not discernible.
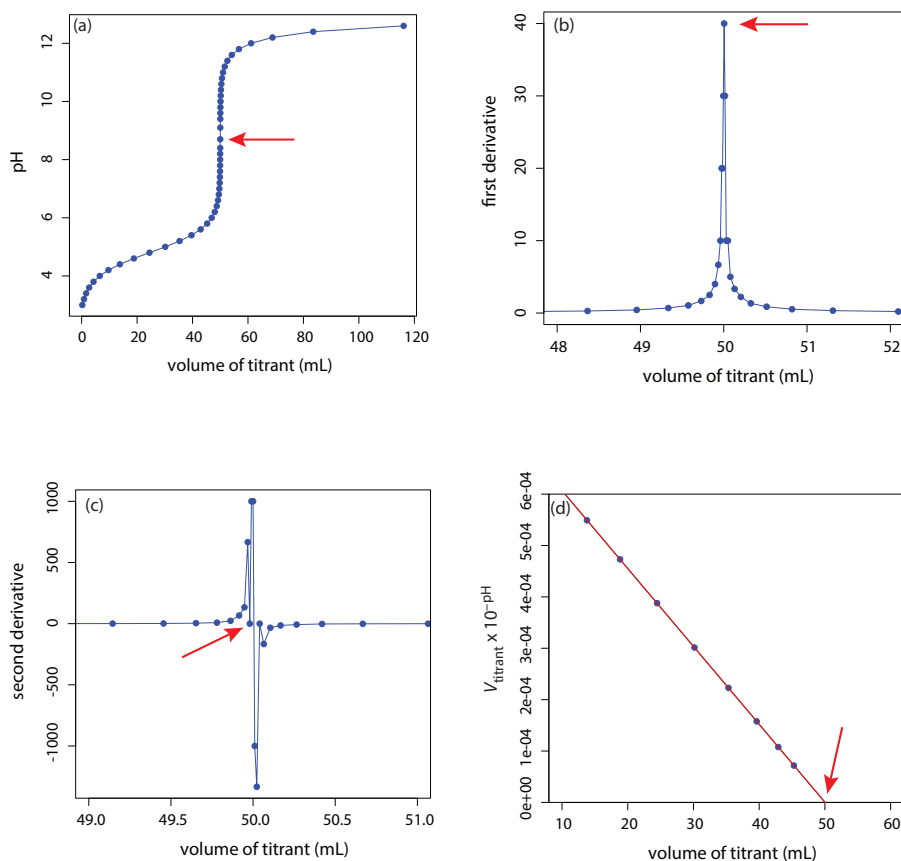
Figure SM9.9 Titration curves for a monoprotic weak acid using a strong base as the titrant: (a) normal titration curve; (b) first-derivative titration curve; (c) second-derivative titration curve; and (d) Gran's plot titration curve. For all four titration curves, the location of the equivalence point is shown by the **red** arrow. Note that titration curves in (b), (c), and (d) display the volume over a limited range of values.

$$\frac{\Delta^2 pH}{\Delta V^2} = \frac{0.260 - 0.328}{1.245 - 0.555} = -0.099$$

with an average volume of 0.90 mL. Figure SM9.9c shows the resulting titration curve, where the equivalence point corresponds to the volume where the second-derivative crosses the x-axis.

For a monoprotic weak acid, a Gran's plot displays $V_{NaOH} \times 10^{-pH}$ on the y-axis as a function of V_{NaOH} on the x-axis. Figure SM9.9d shows the resulting titration curve using data for volumes of NaOH between 10 and 45 mL. The equivalence point is the x-intercept of the line through these points.

7. The theoretical equivalence point for this titration occurs when the moles of titrant equal the initial moles of weak acid; thus
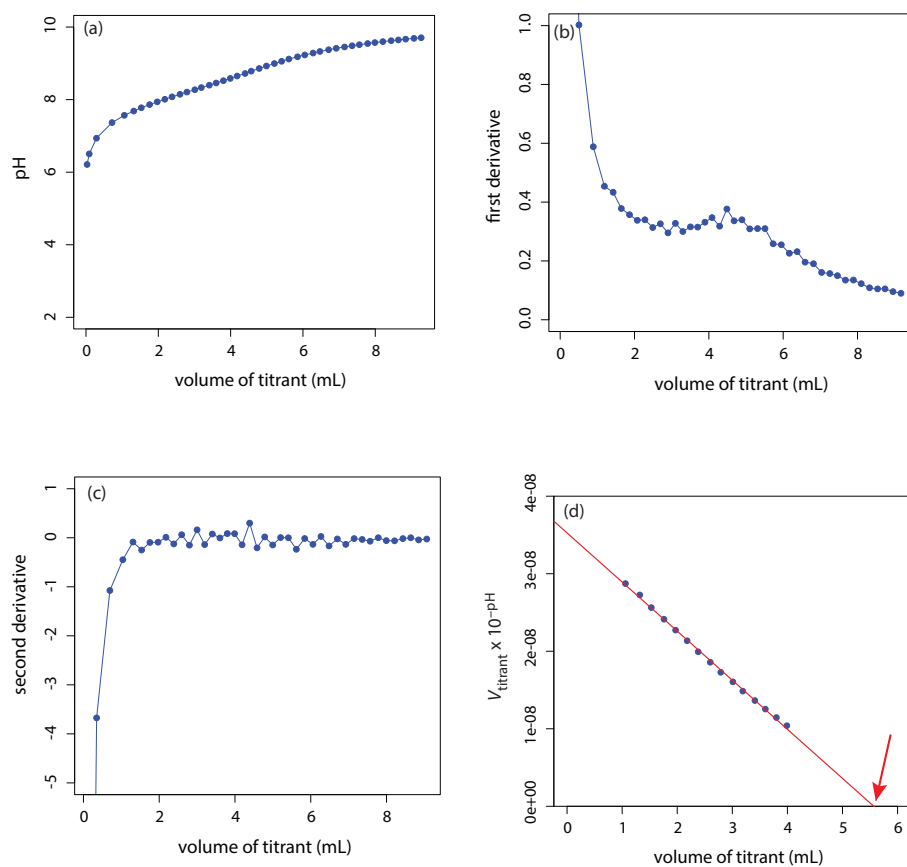
Figure SM9.10 Titration curves for the titration of a monoprotic weak acid with a strong base: (a) normal titration curve; (b) first-derivative titration curve; (c) second-derivative titration curve; and (d) Gran's plot titration curve. The experimental equivalence point for the Gran plot is shown by the **red** arrow.

$$n_{NaOH} = M_{NaOH} V_{NaOH} = M_{HA} V_{HA} = n_{HA}$$

$$(1.004 \times 10^{-3} \text{ M}) V_{NaOH} = (1.02 \times 10^{-4} \text{ M})(0.04994 \text{ L})$$

$$V_{NaOH} = V_{eq.pt.} = 5.07 \text{ mL}$$

Figure SM9.10 shows all four titration curves. As we expect for the titration of a weak acid of low concentration, the normal titration curve does not have a distinct equivalence point. The first-derivative titration curve and the second-derivative titration curve also do not have distinct equivalence points. The Gran plot, however, shows a distinct equivalence point. A linear regression of the Gran plot's data yields an equivalence point of 5.5 mL, an error of 8.5%.

8. Figure SM9.11 shows the titration curve in each solvent. To calculate or sketch the titration curves, see Problem 9.1b, but use K_w or K_s, as appropriate, to calculate the pH. Note that the two titration curves are identical before the equivalence point because the pH is determined by the weak acid's K_a value, which is unaffected by the solvent. The pH after the equivalence point is determined by the concentration of excess base in which the pH is a function of the solvent's dissociation constant; because K_s is greater than K_w, the pH after the equivalence point is greater for the non-aqueous solvent.
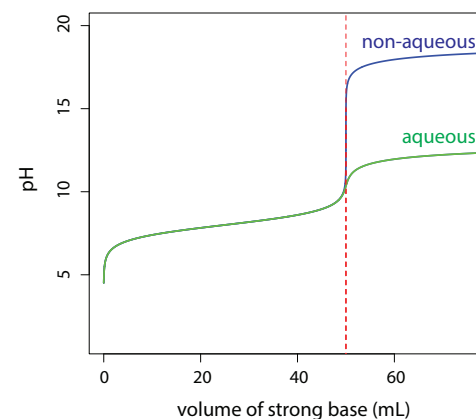

Figure SM9.11 Titration curves for Problem 9.8. The titration curve in **green** is in an aqueous solution with a pK_w of 14; the titration curve in **blue** is in a non-aqueous solvent with a pK_s of 20. The volume of titrant at the equivalence point is shown by the dashed **red** line.
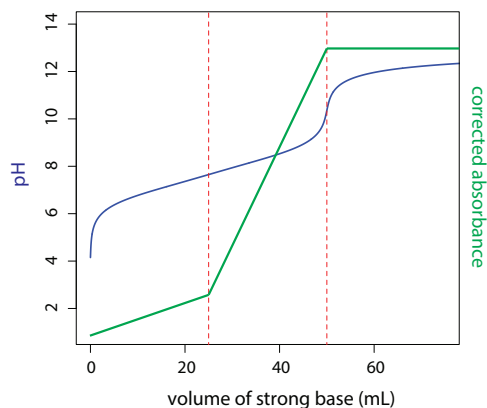
Figure SM9.12 Titration curves for Problem 9.9 with the volume of titrant at the equivalence points shown by the dashed **red** lines. The potentiometric titration curve is shown in **blue**. Of the two equivalence points, only the second—for *m*-nitrophenol—is discernible. The spectrophotometric titration curve, which is shown by the **green** line, has a distinct equivalence point for each analyte.
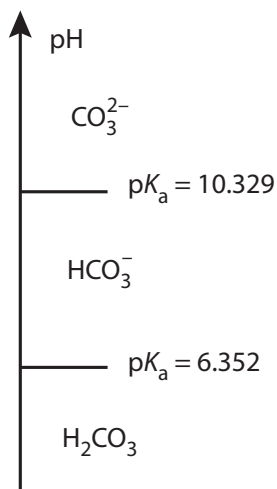

Figure SM9.13 Ladder diagram for H_2CO_3.

9. This is an interesting example of a situation where we cannot use a visual indicator. As we see in Figure SM9.12, because the two analytes have pK_a values that are not sufficiently different from each other, the potentiometric titration curve for *o*-nitrophenol does not show a discernible equivalence point.

    For the spectrophotometric titration curve, the corrected absorbance increases from the first addition of NaOH as *o*-nitrophenol reacts to form *o*-nitrophenolate. After the first equivalence point we begin to convert *m*-nitrophenol to *m*-nitrophenolate; the rate of change in the corrected absorbance increases because *m*-nitrophenolate absorbs light more strongly than does *o*-nitrophenolate. After the second equivalence point, the corrected absorbance remains constant because there is no further increase the amounts of *o*-nitrophenolate or of *m*-nitrophenolate.

10. (a) With a K_b of 3.94×10^{-10}, aniline is too weak of a base to titrate easily in water. In an acidic solvent, such as glacial acetic acid, aniline behaves as a stronger base.

    (b) At a higher temperature, the molar concentration of $HClO_4$ decreases because the moles of $HClO_4$ remain unchanged but the volume of solution is larger. Titrating the solution of aniline at 27°C, therefore, requires a volume of titrant that is greater than when we complete the titration at 25°C. As a result, we overestimate the moles of $HClO_4$ needed to reach the equivalence point and report a concentration of $HClO_4$ that is too large.

    (c) A sample that contains 3-4 mmol of aniline will require

    $$V_{HClO_4} = \frac{3\text{–}4 \times 10^{-3} \text{ mol aniline}}{0.1000 \text{ M}} = 0.030\text{–}0.040 \text{ L}$$

    30–40 mL of $HClO_4$ to reach the equivalence point. If we take a sample with significantly more aniline, we run the risk of needing more than 50 mL of titrant. This requires that we stop the titration and refill the buret, introducing additional uncertainty into the analysis.

11. Figure SM9.13 shows the ladder diagram for H_2CO_3. When we standardize a solution of NaOH we must ensure that the pH at the endpoint is below 6 so that dissolved CO_2, which is present as H_2CO_3, does not react with NaOH. If the endpoint's pH is between 6 and 10, then NaOH reacts with H_2CO_3, converting it to HCO_3^-; as a result, we overestimate the volume of NaOH that reacts with our primary standard and underestimate the titrant's concentration.

12. Figure SM9.14 shows the full titration curve, although our focus in this problem is on the first two equivalence points. At the titration's first equivalence point, the pH is sufficiently acidic that a reaction is unlikely between NaOH and any weak acids in the sample. The ladder diagram for H_2CO_3 in Figure SM9.13, for example, shows

that H_2CO_3 is the only significant species at this pH. The volume of NaOH needed to reach a pH of 3.7, therefore, is a measure of the amount of available strong acids.

At a pH of 8.3, most weak acids will have reacted with the titrant. For example, the ladder diagram for H_2CO_3 in Figure SM9.13 shows that the conversion of H_2CO_3 to HCO_3^- is complete by the time we reach a pH of 8.3; thus, the total volume of titrant needed to reach a pH of 8.3 is a measure of total acidity, and the difference between the two equivalence points is a measure of the amount of available weak acids.
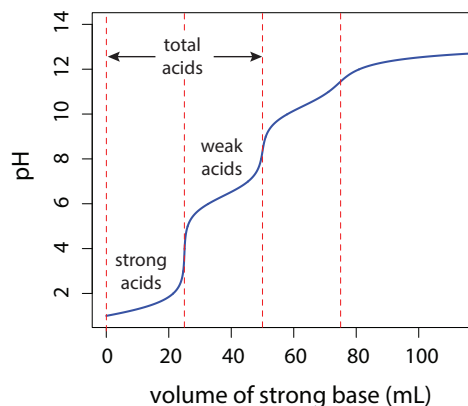

Figure SM9.14 Titration curve for a mixture of 0.10 M HCl and 0.10 M H_2CO_3 using 0.20 M NaOH as the titrant showing the contribution of strong acid acidity and weak acidity to the sample's total acidity.

13. The titration curve shows three equivalence points instead of the four we might expect given that H_4Y has four acid dissociation constants. Clearly one of the equivalence points is not visible, either because two of the acid dissociation constants are too similar to each other (see, for example, the titration curve for citric acid in Figure SM9.6), or one of the acid dissociation constants is too small to give a discernible equivalence point (see, for example, the titration curve for phosphoric acid in Figure SM9.7). In this case, we see equivalence points at approximately 12 mL, 18 mL, and 24 mL of titrant. For the titration curve of a multiprotic weak acid, the equivalence points must be spaced equally. The first visible equivalence point requires 12 mL of titrant, but the remaining visible equivalence points require 6 mL of titrant each; the first visible equivalence point, therefore, is for the reaction

$$H_4Y(aq) + 2OH^-(aq) \longrightarrow H_2Y^{2-}(aq) + 2H_2O(l)$$
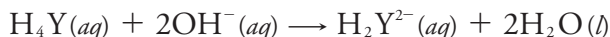
and the second visible equivalence point—the one of interest to us—is for the reaction

$$H_2Y^{2-}(aq) + OH^-(aq) \longrightarrow HY^{3-}(aq) + H_2O(l)$$
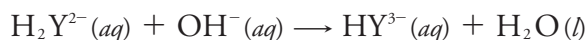
At this equivalence point, each mole of H_4Y reacts with three moles of NaOH.

14. The Gran plot for this system uses the following equation

$$V_b = V_{E1} + \frac{K_a V_{E2}}{[H_3O^+] + K_a} - \frac{(V_a + V_b)d}{M_b}$$

where V_b is the volume of NaOH, V_a is the volume of sample, V_{E1} is the volume of NaOH needed to titrate HCl, V_{E2} is the volume of NaOH needed to titrate CH_3COOH, K_a is the acid dissociation constant for CH_3COOH, M_b is the molarity of NaOH, and d is $[H_3O^+] - [OH^-]$. Before the first equivalence point, the second term on the right side of the equation is much smaller than the first term, which means we can simplify the equation to

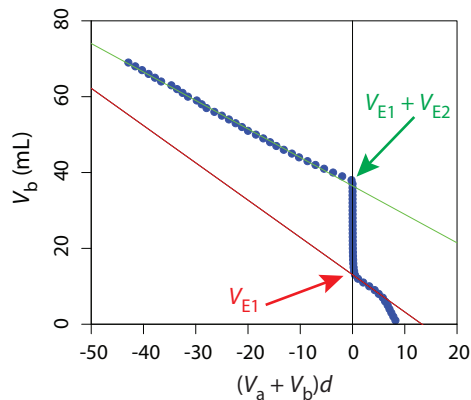$$V_b = V_{E1} - \frac{(V_a + V_b)d}{M_b}$$

Figure SM9.15 Gran plot for the data in Problem 9.14. The linear regression lines are used to determine V_{E1} and $V_{E1} + V_{E2}$; see the solution for more details. The data, which I collected specifically for this problem, is a bit wonky as the two regression lines should have identical slopes of $1/M_b$. The slope of the data used to determine V_{E1} gives M_b as 0.093 M, which is close to its actual value of 0.0916 M; however, the slope of the data used to determine $V_{E1} + V_{E2}$ gives M_b as 0.121. One possible source for this difference is drift over time in the potentiometric measurement of pH.

and a plot of V_b versus $(V_a + V_b)d$ is a straight-line with a y-intercept of V_{E1}. After the second equivalence point, the $[H_3O^+]$ is much smaller than K_a and the full Gran plot equation reduces to

$$V_b = V_{E1} + V_{E2} - \frac{(V_a + V_b)d}{M_b}$$

and a plot of V_b versus $(V_a + V_b)d$ is a straight-line with a y-intercept of $V_{E1} + V_{E2}$.

Figure SM9.15 shows the full Gran plot for our data. Although the data after the second equivalence point is linear, the data before the first equivalence point shows some curvature for the first few additions of NaOH. A linear regression analysis for volumes of NaOH from 8–12 mL gives V_{E1} as 13.1 mL, and a linear regression analysis of the data for volumes of NaOH from 39–69 mL gives the sum of V_{E1} and V_{E2} as 36.5 mL; thus, V_{E2} is 23.4 mL.

At the first equivalence point, the moles of NaOH equal the moles of HCl; thus

$$M_{HCl} = \frac{M_{NaOH} V_{E1}}{V_{HCl}} = \frac{(0.09186 \text{ M}) (13.1 \text{ mL})}{50.00 \text{ mL}} = 0.0241 \text{ M}$$

At the second equivalence point, the additional moles of NaOH equal the moles of CH_3COOH; thus

$$M_{CH_3COOH} = \frac{M_{NaOH} (V_{E2} - V_{E1})}{V_{CH_3COOH}} =$$

$$\frac{(0.09186 \text{ M}) (36.5 \text{ mL} - 13.1 \text{ mL})}{50.00 \text{ mL}} = 0.0430 \text{ M}$$

15. The equilibrium constant for the reaction between OH^- and HCO_3^-

$$OH^- (aq) + HCO_3^- (aq) \rightleftharpoons CO_3^{2-} (aq) + H_2O (l)$$
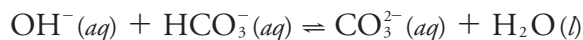
$$K = \frac{[CO_3^{2-}]}{[HCO_3^-] [OH^-]} = \frac{1}{K_{b,CO_3^{2-}}} =$$

$$\frac{K_{a,HCO_3^-}}{K_w} = \frac{4.69 \times 10^{-11}}{1.00 \times 10^{-14}} = 4690$$

which means the two will react until the limiting reagent is used up.

16. (a) Because the two endpoints are similar, only OH^- is present in the sample. Using the average volume of 21.37 mL, the mass of OH^- in the sample is

$$0.02137 \text{ L} \times \frac{(0.1198 \text{ mol HCl})}{L} \times \frac{1 \text{ mol OH}^-}{\text{mol HCl}}$$

$$\times \frac{17.01 \text{ g OH}^-}{\text{mol OH}^-} \times \frac{1000 \text{ mg}}{g} = 43.5 \text{ mg OH}^-$$

which makes its concentration

$$\frac{43.5 \text{ mg OH}^-}{0.02500 \text{ L}} = 1740 \text{ ppm OH}^-$$

(b) Because the volume to reach the bromocresol green end point is more than twice that to reach the phenolphthalein end point, the sample must contain a mixture of CO_3^{2-} and HCO_3^-. Only CO_3^{2-} is neutralized when we titrate to the phenolphthalein end point, forming HCO_3^- as a product; thus

$$0.00567\ L \times \frac{(0.1198\ mol\ HCl)}{L} \times \frac{1\ mol\ CO_3^{2-}}{mol\ HCl}$$

$$\times \frac{60.01\ g\ CO_3^{2-}}{mol\ CO_3^{2-}} \times \frac{1000\ mg}{g} = 40.8\ mg\ CO_3^{2-}$$

$$\frac{40.8\ mg\ CO_3^{2-}}{0.02500\ L} = 1630\ ppm\ CO_3^{2-}$$

We know that it takes 5.67 mL of HCl to titrate CO_3^{2-} to HCO_3^-, which means it takes 2×5.67 mL, or 11.34 mL of HCl to reach the second end point for CO_3^{2-}. The volume of HCl used to titrate HCO_3^- is 21.13 mL − 11.34 mL, or 9.79 mL; thus, the concentration of HCO_3^- in the sample is

$$0.00979\ L \times \frac{(0.1198\ mol\ HCl)}{L} \times \frac{1\ mol\ HCO_3^-}{mol\ HCl}$$

$$\times \frac{61.02\ g\ HCO_3^-}{mol\ HCO_3^-} \times \frac{1000\ mg}{g} = 71.6\ mg\ HCO_3^-$$

$$\frac{71.6\ mg\ HCO_3^-}{0.02500\ L} = 2860\ ppm\ HCO_3^-$$

(c) A sample that requires no HCl to reach the phenolphthalein end point contains HCO_3^- only; thus, the concentration of HCO_3^- in the sample is

$$0.01428\ L \times \frac{(0.1198\ mol\ HCl)}{L} \times \frac{1\ mol\ HCO_3^-}{mol\ HCl}$$

$$\times \frac{61.02\ g\ HCO_3^-}{mol\ HCO_3^-} \times \frac{1000\ mg}{g} = 104.4\ mg\ HCO_3^-$$

$$\frac{104.4\ mg\ HCO_3^-}{0.02500\ L} = 4180\ ppm\ HCO_3^-$$

(d) If the volume to reach the bromocresol end point is twice that to reach the phenolphthalein end point, then the sample contains CO_3^{2-} only; thus, using the volume of HCl used to reach the phenolphthalein end point, we find that the concentration of CO_3^{2-} is

$$0.01712\ L \times \frac{(0.1198\ mol\ HCl)}{L} \times \frac{1\ mol\ CO_3^{2-}}{mol\ HCl}$$

$$\times \frac{60.01\ g\ CO_3^{2-}}{mol\ CO_3^{2-}} \times \frac{1000\ mg}{g} = 123.1\ mg\ CO_3^{2-}$$

$$\frac{123.1\ mg\ CO_3^{2-}}{0.02500\ L} = 4920\ ppm\ CO_3^{2-}$$

We can use the volume to reach the bromocresol green end point as well, substituting

$$\frac{1\ mol\ CO_3^{2-}}{2\ mol\ HCl}$$

for

$$\frac{1\ mol\ CO_3^{2-}}{1\ mol\ HCl}$$

(e) If the volume to reach the bromocresol green end point is less than twice the volume to reach the phenolphthalein end point, then we know the sample contains CO_3^{2-} and OH^-. Because OH^- is neutralized completely at the phenolphthalein end point, the difference of 4.33 mL in the volumes between the two end points is the volume of HCl used to titrate CO_3^{2-}; thus, its concentration is

$$0.00433\,L \times \frac{(0.1198\,\text{mol HCl})}{L} \times \frac{1\,\text{mol CO}_3^{2-}}{\text{mol HCl}}$$

$$\times \frac{60.01\,\text{g CO}_3^{2-}}{\text{mol CO}_3^{2-}} \times \frac{1000\,\text{mg}}{g} = 31.1\,\text{mg CO}_3^{2-}$$

$$\frac{31.1\,\text{mg CO}_3^{2-}}{0.02500\,L} = 1240\,\text{ppm CO}_3^{2-}$$

At the phenolphthalein end point, the volume of HCl used to neutralize OH^- is the difference between the total volume, 21.36 mL, and the volume used to neutralize CO_3^{2-}, 4.33 mL, or 17.03 mL; thus, its concentration is

$$0.01703\,L \times \frac{(0.1198\,\text{mol HCl})}{L} \times \frac{1\,\text{mol OH}^-}{\text{mol HCl}}$$

$$\times \frac{17.01\,\text{g OH}^-}{\text{mol OH}^-} \times \frac{1000\,\text{mg}}{g} = 34.7\,\text{mg OH}^-$$

$$\frac{34.7\,\text{mg OH}^-}{0.02500\,L} = 1390\,\text{ppm OH}^-$$

17. (a) When using HCl as a titrant, a sample for which the volume to reach the methyl orange end point is more than twice the volume to reach the phenolphthalein end point is a mixture of HPO_4^{2-} and PO_4^{3-}. The titration to the phenolphthalein end point involves PO_4^{3-} only; thus, its concentration is

$$M_{PO_4^{3-}} = \frac{M_{HCl}\,V_{HCl}}{V_{sample}} = \frac{(0.1198\,M)\,(11.54\,\text{mL})}{25.00\,\text{mL}} = 0.0553\,M$$

We know that it takes 11.54 mL of HCl to titrate PO_4^{3-} to HPO_4^{2-}, which means it takes 2×11.54 mL, or 23.08 mL of HCl to reach the second end point for PO_4^{3-}. The volume of HCl used to titrate HPO_4^{2-} is 35.29 mL − 23.08 mL, or 12.21 mL; thus, the concentration of HPO_4^{2-} in the sample is

$$M_{HPO_4^{2-}} = \frac{M_{HCl}\,V_{HCl}}{V_{sample}} = \frac{(0.1198\,M)\,(12.21\,\text{mL})}{25.00\,\text{mL}} = 0.0585\,M$$

(b) When using NaOH as the titrant, a sample for which the volume to reach the phenolphthalein end point is twice the volume to reach the methyl orange end point contains H_3PO_4 only; thus, the concentration of H_3PO_4 is

$$M_{H_3PO_4} = \frac{M_{NaOH}\,V_{NaOH}}{V_{sample}} = \frac{(0.1198\,M)\,(9.89\,\text{mL})}{25.00\,\text{mL}} = 0.0474\,M$$

(c) When using HCl as a titrant, a sample that requires identical volumes to reach the methyl orange and the phenolphthalein end points contains OH^- only; thus, the concentration of OH^- is

$$M_{OH^-} = \frac{M_{HCl} V_{HCl}}{V_{sample}} = \frac{(0.1198 \text{ M}) (22.77 \text{ mL})}{25.00 \text{ mL}} = 0.1091 \text{ M}$$

(d) When using NaOH as the titrant, a sample for which the volume to reach the phenolphthalein end point is more than twice the volume to reach the methyl orange end point contains a mixture of H_3PO_4 and $H_2PO_4^-$. The titration to the methyl orange end point involves H_3PO_4 only; thus, its concentration is

$$M_{H_3PO_4} = \frac{M_{NaOH} V_{NaOH}}{V_{sample}} = \frac{(0.1198 \text{ M}) (17.48 \text{ mL})}{25.00 \text{ mL}} = 0.0838 \text{ M}$$

We know that it takes 17.48 mL of NaOH to titrate H_3PO_4 to $H_2PO_4^-$, which means it takes 2×17.48 mL, or 34.96 mL of NaOH to reach the second end point for H_3PO_4. The volume of NaOH used to titrate $H_2PO_4^-$ is 39.42 mL – 34.96 mL, or 4.46 mL; thus, the concentration of $H_2PO_4^-$ in the sample is

$$M_{H_2PO_4^-} = \frac{M_{NaOH} V_{NaOH}}{V_{sample}} = \frac{(0.1198 \text{ M}) (4.46 \text{ mL})}{25.00 \text{ mL}} = 0.0214 \text{ M}$$

18. For this back titration, the moles of HCl must equal the combined moles of NH_3 and of NaOH; thus

$$n_{NH_3} = n_{HCl} - n_{NaOH} = M_{HCl} V_{HCl} - M_{NaOH} V_{NaOH}$$

$$n_{NH_3} = (0.09552 \text{ M}) (0.05000 \text{ L}) - (0.05992 \text{ M}) (0.03784 \text{ L})$$

$$n_{NH_3} = 2.509 \times 10^{-3} \text{ mol NH}_3$$

$$2.509 \times 10^{-3} \text{ mol NH}_3 \times \frac{14.007 \text{ g N}}{\text{mol NH}_3} = 0.03514 \text{ g N}$$

$$0.03514 \text{ g N} \times \frac{1 \text{ g protein}}{0.1754 \text{ g N}} = 0.2003 \text{ g protein}$$

$$\frac{0.2003 \text{ g protein}}{1.2846 \text{ g sample}} \times 100 = 15.59\% \text{ w/w protein}$$

19. The sulfur in SO_2 is converted to H_2SO_4, and titrated with NaOH to the phenolphthalein end point, converting H_2SO_4 to SO_4^{2-} and consuming two moles of NaOH per mole of H_2SO_4; thus, there are

$$0.01008 \text{ L} \times \frac{0.0244 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{2 \text{ mol NaOH}}$$

$$\times \frac{1 \text{ mol SO}_2}{\text{mol H}_2\text{SO}_4} \times \frac{64.06 \text{ g SO}_2}{\text{mol SO}_2} \times \frac{1000 \text{ mg}}{\text{g}} = 7.88 \text{ mg SO}_2$$

in the sample. The volume of air sampled is 1.25 L/min × 60 min, or 75.0 L, which leaves us with an SO_2 concentration of

$$\dfrac{7.78 \text{ mg SO}_2 \times \dfrac{1 \text{ mL}}{2.86 \text{ mg SO}_2} \times \dfrac{1000 \text{ μL}}{\text{mL}}}{75.0 \text{ L}} = 36.7 \text{ μL/L SO}_2$$

20. We begin the analysis with

$$\dfrac{0.0200 \text{ mol Ba(OH)}_2}{\text{L}} \times 0.05000 \text{ L} = 1.00 \times 10^{-3} \text{ mol Ba(OH)}_2$$

The titration of $Ba(OH)_2$ by HCl consumes two moles of HCl for every mole of $Ba(OH)_2$; thus,

$$0.03858 \text{ mL} \times \dfrac{0.0316 \text{ M HCl}}{\text{L}} \times$$

$$\dfrac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HCl}} = 6.10 \times 10^{-4} \text{ mol Ba(OH)}_2$$

react with HCl, leaving

$$1.00 \times 10^{-3} \text{ mol Ba(OH)}_2 - 6.10 \times 10^{-4} \text{ mol Ba(OH)}_2$$

or 3.90×10^{-4} mol $Ba(OH)_2$ to react with CO_2. Because each mole of CO_2 reacts with one mole of $Ba(OH)_2$ to form $BaCO_3$, we know that the sample of air has 3.90×10^{-4} mol CO_2; thus, the concentration of CO_2 is

$$3.90 \times 10^{-4} \text{ mol CO}_2 \times \dfrac{44.01 \text{ g CO}_2}{\text{mol CO}_2} = 0.01716 \text{ g CO}_2$$

$$\dfrac{0.01716 \text{ g CO}_2 \times \dfrac{1 \text{ L CO}_2}{1.98 \text{ g CO}_2} \times \dfrac{10^6 \text{ μL}}{\text{L}}}{3.5 \text{ L}} = 2480 \text{ μL/L CO}_2$$

21. From the reaction in Table 9.8, we see that each mole of methylethyl ketone, C_4H_8O, releases one mole of HCl; thus, the moles of NaOH used in the titration is equal to the moles of C_4H_8O in the sample. The sample's purity, therefore, is

$$0.03268 \text{ mL} \times \dfrac{0.9989 \text{ mol NaOH}}{\text{L}} \times$$

$$\dfrac{1 \text{ mol C}_4\text{H}_8\text{O}}{\text{mol NaOH}} \times \dfrac{72.11 \text{ g C}_4\text{H}_8\text{O}}{\text{mol C}_4\text{H}_8\text{O}} = 2.354 \text{ g C}_4\text{H}_8\text{O}$$

$$\dfrac{2.354 \text{ g C}_4\text{H}_8\text{O} \times \dfrac{1 \text{ mL}}{0.805 \text{ g}}}{3.00 \text{ mL sample}} \times 100 = 97.47\%$$

22. For this back titration, the total moles of KOH used is equal to the moles that react with HCl in the titration and the moles that react with the butter. The total moles of KOH is

$$0.02500 \text{ L} \times \dfrac{0.5131 \text{ mol KOH}}{\text{L}} = 0.01283 \text{ mol KOH}$$

and the moles of KOH that react with HCl is

$$0.01026 \text{ L} \times \frac{0.5000 \text{ mol HCl}}{\text{L}} \times$$

$$\frac{1 \text{ mol KOH}}{\text{mol HCl}} = 0.00513 \text{ mol KOH}$$

which means that

$$(0.01283 \text{ mol KOH} - 0.00513 \text{ mol KOH}) \times$$

$$\frac{56.10 \text{ g KOH}}{\text{mol KOH}} \times \frac{1000 \text{ mg}}{\text{g}} = 432.0 \text{ mg KOH}$$

react with the butter. The saponification number for butter is

$$\frac{432.0 \text{ mg KOH}}{2.085 \text{ g butter}} = 207$$

23. To calculate the weak acid's equivalent weight, we treat the titration reaction as if each mole of weak acid reacts with one mole of strong base; thus, the weak acid's equivalent weight is

$$0.03258 \text{ L} \times \frac{0.0556 \text{ mol NaOH}}{\text{L}} \times$$

$$\frac{1 \text{ mol acid}}{\text{mol NaOH}} = 0.001811 \text{ mol acid}$$

$$\frac{0.2500 \text{ g acid}}{0.001811 \text{ mol acid}} = 138 \text{ g/mol}$$

24. To identify the amino acid, we use the titration curve to determine its equivalent weight and its K_a value. The titration's equivalence point is approximately 34 mL. The pH at half this volume provides an estimate of the amino acid's pK_a; this is approximately 8.6, or a K_a of 2.5×10^{-9}. From the list of possible amino acids, taurine and asparagine are likely candidates.

Using our estimate of 34 mL for the equivalence point, the amino acid's equivalent weight is

$$0.034 \text{ L} \times \frac{0.1036 \text{ mol NaOH}}{\text{L}} \times$$

$$\frac{1 \text{ mol acid}}{\text{mol NaOH}} = 0.00352 \text{ mol acid}$$

$$\frac{0.4300 \text{ g acid}}{0.00352 \text{ mol acid}} = 120 \text{ g/mol}$$

As this is closer to the formula weight of taurine than of asparagine, taurine is the most likely choice for the amino acid.

25. From Figure SM9.9, we see that the equivalence point is at 50.0 mL of NaOH. The pH at half this volume is approximately 4.8, which makes the pK_a 4.8 and the K_a value 1.6×10^{-5}.

26. The method illustrated in Figure 9.24 uses a sample of approximately 20 μL; if we assume a density of 1 g/mL, this is equivalent to a sample that weighs 20 mg, or a meso sample. The method illustrated in

A density of 1 g/ml is the same as 1 mg/μL; thus, a 20 μL sample weighs 20 mg.

A density of 1 g/mL is equivalent to 1 ng/pL; thus, a 1 pL sample weighs 1 ng.

Figure 9.27 uses an approximately 1 pL sample; if we assume a density of 1 g/mL, this corresponds to a sample that weight 1 ng, or an ultramicro sample. For both methods, the need to see the titration's visual end point requires a major or, perhaps, a minor analyte.

27. To determine an analyte's formula weight requires that we know the stoichiometry between the analyte and the titrant. Even if a titration curve shows a single equivalence point, we cannot be sure if it represents the titration of a single proton or if it represents the titration of two or more protons that are too similar in their acid-base strength. To calculate the equivalent weight we simply assume that for any equivalence point, one mole of acid reacts with one mole of base.

Look back, for example, at the titration curve for citric acid in Figure SM9.6 in which the single equivalence point occurs when each mole of citric acid has reacted with three moles of NaOH.

28. An titration is designed to use most of the buret's volume without exceeding its maximum volume. The latter point is important because refilling the buret introduces additional uncertainty. Because the procedure is designed for a sample that is 30–40%w/w Na_2CO_3, using the procedure for a sample that is more than 98%w/w Na_2CO_3 will require approximately 2.5–3.3×more titrant. To reduce the amount of titrant we can do one or more of the following: we can reduce the sample's mass; we can dissolve the sample of washing soda in a larger volume of water; we can take a smaller portion of the dissolved sample; or we can increase the concentration of NaOH.

29. (a) Systematic error. Because the actual mass of KHP is greater than we think, by 0.15 g, we report a concentration for NaOH that is smaller than its actual concentration.

(b) Systematic error. Because KHP is a weak acid, the actual equivalence point for its titration is at a pH that is greater than 7. If the indicator signals the end point when the pH is between 3 and 4, we will use less NaOH than expected, which means we will report a concentration for NaOH that is greater than its actual concentration.

(c) Systematic error. The loss of an air bubble in the buret's tip means that the volume of NaOH in the buret decreases without actually adding NaOH to the solution of KHP. The effect is to increase the apparent volume of NaOH, which means we report a concentration that is smaller than its actual value.

The change in volume of NaOH in the buret is equivalent to the volume of the air bubble.

(d) Random error. Because each flask has a different mass, some of our flasks will weigh more than the flask we used to tare the balance; other flasks, of course, will weigh less.

(e) Systematic error. The reason we dry the KHP is to ensure it is free from moisture so that we can calculate the moles of KHP from its mass. Because the reported mass of KHP is too large, we report a concentration of NaOH that is greater than its actual concentration.

(f) No affect on error. We do not use the mass of NaOH in our calculations; thus, any uncertainty in its mass has no effect on our results.

(g) No affect on error. The volume of water used to dissolve the KHP is not used to calculate the concentration of NaOH.

30. (a) If we carry out the titration too quickly, we may neutralize the extracted *o*-phthalic acid—triggering the end point's signal—and stop the titration long before the remaining *o*-phthalic acid has time to extract. As a result, we underestimate the concentration of *o*-phthalic acid.

> This is not a fatal error if we allow time for additional *o*-phthalic acid to extract into the aqueous solution, reversing the end point's signal, and then continue the titration more slowly. If the end point signal does not reverse, however, then we must discard the sample.

(b) If we wish to carry out the titration more quickly, we can add an excess of NaOH to the sample, allow time for the *o*-phthalic acid to extract into the NaOH and react, and then back-titrate the excess NaOH using a strong acid.

31. The titration of Mg^{2+} with EDTA is an example of a complexation titration. The titration's equivalence point is reached when

$$n_{Mg} = M_{Mg} V_{Mg} = M_{EDTA} V_{EDTA} = n_{EDTA}$$

> For the titration curves in this problem and in the next problem, we will calculate the initial pMetal, the pMetal for one volume before the equivalence point, and the pMetal for one volume after the equivalence point.

where n is the moles of Mg^{2+} or of EDTA; thus

$$V_{eq.pt.} = V_{EDTA} = \frac{M_{Mg} V_{Mg}}{M_{EDTA}} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{(0.100 \text{ M})} = 50.0 \text{ mL}$$

The sample's initial pMg is determined by its concentration of Mg^{2+}

$$pMg = -\log[Mg^{2+}] = -\log(0.100) = 1.00$$

For volumes less that the equivalence point volume, pMg is determined by the concentration of excess Mg^{2+} in solution. After adding 10.0 mL of EDTA, for example

$$[Mg^{2+}] = \frac{M_{Mg} V_{Mg} - M_{EDTA} V_{EDTA}}{V_{Mg} + V_{EDTA}}$$

$$[Mg^{2+}] = \frac{(0.100 \text{ M})(50.0 \text{ mL}) - (0.100 \text{ M})(10.0 \text{ mL})}{50.0 \text{ mL} + 10.0 \text{ mL}}$$

$$[Mg^{2+}] = 0.0667 \text{ M}$$

> For this problem there is no auxiliary complexing agent; thus, $\alpha_{Cd^{2+}} = 1$ and the total concentration of magnesium, C_{Mg}, is identical to the concentration of free magnesium, $[Mg^{2+}]$. In the next problem, which involves the titration of Cu^{2+} with EDTA in the presence of NH_3, we will need to account for an auxiliary complexing agent.

the pMg is 1.18. For volumes of titrant greater than the equivalence point volume, pMg is determined by the dissociation of the MgY^{2-} complex in the presence of excess EDTA. After adding 60.0 mL of EDTA, for example, the concentrations of MgY^{2-} and of EDTA are

$$[MgY^{2-}] = \frac{M_{Mg} V_{Mg}}{V_{EDTA} + V_{Mg}} = \frac{(0.100 \text{ M})(50.0 \text{ mL})}{60.0 \text{ mL} + 50.0 \text{ mL}}$$

$$[MgY^{2-}] = 4.55 \times 10^{-2} \text{ M}$$

$$C_{EDTA} = \frac{M_{EDTA} V_{EDTA} - M_{Mg} V_{Mg}}{V_{EDTA} + V_{Mg}}$$

> At the pH of the titration, only some of the EDTA is present in solution as Y^{4-}; here, we calculate the total concentration of EDTA, C_{EDTA}, instead of the concentration of free EDTA, $[Y^{4-}]$. We account for the difference between the two by using conditional formation constant for MgY^{2-} in place of its formation constant.

To sketch an approximate titration curve, calculate pMg for any two volumes before the equivalence point and use a ladder diagram for Mg^{2+}/MgY^{2-} to place points at 110% and 200% of the equivalence point volume. Use the lines passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.
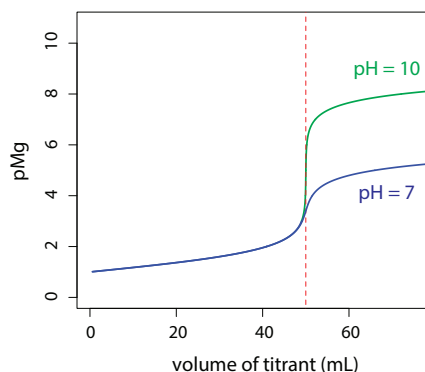

Figure SM9.16 Complexometric titration curves for 50.0 mL of 0.100 M Mg^{2+} using 0.100 M EDTA as the titrant at a pH of 7 (**blue**) and at a pH of 10 (**green**). The volume of titrant at the equivalence point for both titrations is shown by the dashed **red** line.

Values for $\alpha_{Cu^{2+}}$ in Table 9.4.

$$C_{EDTA} = \frac{(0.100 \text{ M})(60.0 \text{ mL}) - (0.100 \text{ M})(50.0 \text{ mL})}{60.0 \text{ mL} + 50.0 \text{ mL}}$$

$$C_{EDTA} = 9.09 \times 10^{-3} \text{ M}$$

For a pH of 10, substituting these concentrations into the conditional formation constant for MgY^{2-} and solving for $[Mg^{2+}]$

$$\frac{[MgY^{2-}]}{[Mg^{2+}] C_{EDTA}} = K_f \alpha_{Y^{4-}} = (6.2 \times 10^8)(0.367) = 2.3 \times 10^8$$

$$\frac{4.55 \times 10^{-2}}{[Mg^{2+}](9.09 \times 10^{-3})} = 2.3 \times 10^8$$

gives $[Mg^{2+}]$ as 2.18×10^{-8}, or a pMg of 7.66. A similar calculation at a pH of 7 gives $[Mg^{2+}]$ as 1.60×10^{-5}, or a pMg of 4.80. Figure SM9.16 shows the full titration curves for both pHs.

32. The titration of Cu^{2+} with EDTA is an example of a complexation titration. The titration's equivalence point is reached when

$$n_{Cu} = M_{Cu} V_{Cu} = M_{EDTA} V_{EDTA} = n_{EDTA}$$

where n is the moles of Cu^{2+} or of EDTA; thus

$$V_{eq.pt.} = V_{EDTA} = \frac{M_{Cu} V_{Cu}}{M_{EDTA}} = \frac{(0.0500 \text{ M})(25.0 \text{ mL})}{(0.0250 \text{ M})} = 50.0 \text{ mL}$$

The sample's initial pCu is determined by the concentration of free Cu^{2+}, which means we must account for the presence of Cu^{2+}–NH_3 complexes; for example, when the concentration of NH_3 is 10^{-3} M, the initial concentration of free Cu^{2+} is

$$[Cu^{2+}] = C_{Cu} \times \alpha_{Cu^{2+}} = (0.0500 \text{ M})(0.00415) = 2.08 \times 10^{-4} \text{ M}$$

or a pCu of 3.68; a similar calculation when the concentration of NH_3 is 10^{-1} M gives a pCu of 10.64.

For volumes of titrant less than the equivalence point volume, pCu is determined by the concentration of excess free Cu^{2+} in solution. For example, when the concentration of NH_3 is 10^{-3} M, after adding 10.0 mL of EDTA we find that

$$C_{Cu} = \frac{M_{Cu} V_{Cu} - M_{EDTA} V_{EDTA}}{V_{Cu} + V_{EDTA}}$$

$$C_{Cu} = \frac{(0.0500 \text{ M})(25.0 \text{ mL}) - (0.0250 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}}$$

$$C_{Cu} = 2.86 \times 10^{-2} \text{ M}$$

$$[Cu^{2+}] = C_{Cu} \times \alpha_{Cu^{2+}} = (0.0286 \text{ M})(0.00415) = 1.19 \times 10^{-4} \text{ M}$$

or a pCu of 3.92; a similar calculation when the concentration of NH_3 is 10^{-1} M gives a pCu of 10.88. For volumes of titrant greater than the equivalence point volume, pCu is determined by the disso-

ciation of the CuY^{2-} complex in the presence of excess EDTA. After adding 60.0 mL of EDTA, for example, the concentrations of CuY^{2-} and of EDTA are

$$[CuY^{2-}] = \frac{M_{Cu} V_{Cu}}{V_{EDTA} + V_{Cu}} = \frac{(0.0500 \text{ M})(25.0 \text{ mL})}{60.0 \text{ mL} + 25.0 \text{ mL}}$$

$$[CuY^{2-}] = 1.47 \times 10^{-2} \text{ M}$$

$$C_{EDTA} = \frac{M_{EDTA} V_{EDTA} - M_{Cu} V_{Cu}}{V_{EDTA} + V_{Cu}}$$

$$C_{EDTA} = \frac{(0.0250 \text{ M})(60.0 \text{ mL}) - (0.0500 \text{ M})(25.0 \text{ mL})}{60.0 \text{ mL} + 25.0 \text{ mL}}$$

$$C_{EDTA} = 2.94 \times 10^{-3} \text{ M}$$

For a pH of 10, substituting these concentrations into the conditional formation constant for CuY^{2-} and solving for $[Cu^{2+}]$

$$\frac{[CuY^{2-}]}{C_{Cu} C_{EDTA}} = K_f \alpha_{Cu^{2+}} \alpha_{Y^{4-}} =$$

$$(6.3 \times 10^{18})(0.00415)(0.367) = 9.6 \times 10^{15}$$

$$\frac{1.47 \times 10^{-2}}{C_{Cu}(2.94 \times 10^{-3})} = 9.6 \times 10^{15}$$

$$C_{Cu} = 5.0 \times 10^{-16} \text{ M}$$

$$[Cu^{2+}] = C_{Cu} \times \alpha_{Cu^{2+}} =$$

$$(5.00 \times 10^{-16} \text{ } M)(0.00415) = 2.1 \times 10^{-18} \text{ M}$$

or a pCu of 17.68. A similar calculation when the concentration of NH_3 is 10^{-1} M gives the same result. Figure SM9.17 shows the full titration curves for both concentrations of NH_3.

33. The reaction of EDTA and Bi^{3+} ($K_f = 6 \times 10^{27}$) is more favorable than the reaction of EDTA and Cu^{2+} ($K_f = 6.3 \times 10^{18}$), which means EDTA reacts with Bi^{3+} before it reacts with Cu^{2+}. As we add EDTA, the absorbance remains at zero until we reach the equivalence point for the titration of Bi^{3+} when we begin to form CuY^{2-}. Because CuY^{2-} absorbs light at the selected wavelength, the absorbance increases until we reach the equivalence point for the titration of Cu^{2+}, after which the absorbance remains constant. To avoid a change in absorbance due to dilution, we plot a corrected absorbance

$$A_{corr} = A \times \frac{V_{EDTA} + V_{sample}}{V_{sample}}$$

where V_{EDTA} is the volume of titrant and V_{sample} is the volume of sample. A sketch of the spectrophotometric titration curve is shown in Figure SM9.18.

34. The reaction between EDTA and Ca^{2+} ($K_f = 4.9 \times 10^{10}$) is more favorable than the reaction between EDTA and Mg^{2+} ($K_f = 6.2 \times 10^{8}$),

To sketch an approximate titration curve, calculate pMg for any two volumes before the equivalence point and use a ladder diagram for Mg^{2+}/MgY^{2-} to place points at 110% and 200% of the equivalence point volume. Use the lines passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.
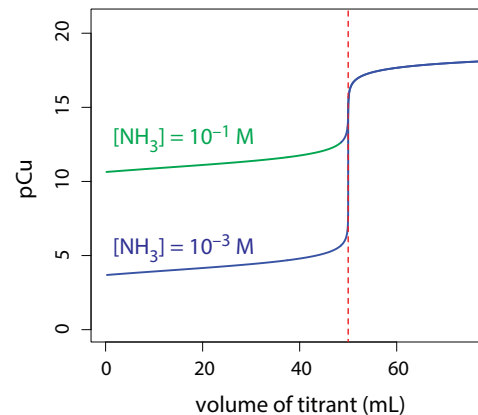

Figure SM9.17 Complexometric titration curves for 25.0 mL of 0.0500 M Cu^{2+} in the presence of 10^{-3} M NH_3 (**blue**) and 10^{-1} M NH_3 (**green**) using 0.0250 M EDTA as the titrant. The pH is 10 for both titration curves. The volume of titrant at the equivalence point for both titrations is shown by the dashed **red** line.
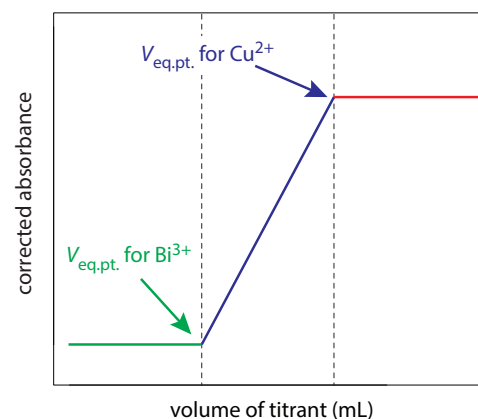

Figure SM9.18 Spectrophotometric titration curve for Problem 9.33. The **green** branch of the titration curve is the reaction between Bi^{3+} and EDTA and the **blue** branch of the titration curve is the reaction between Cu^{2+} and EDTA. Once the titration of Cu^{2+} is complete, the absorbance remains constant, as shown by the titration curve's **red** branch.
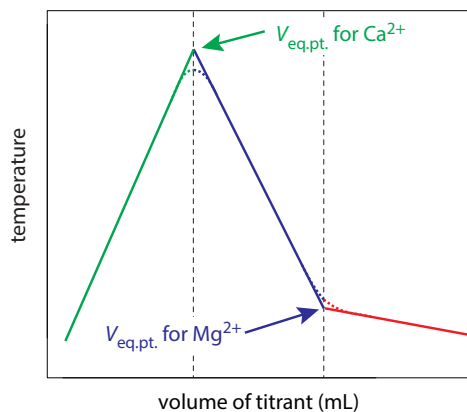
Figure SM9.19 Thermometric titration curve for Problem 9.34. The **green** branch of the titration curve is the titration of Ca^{2+} using EDTA and the **blue** branch of the titration curve is the titration of Mg^{2+} with EDTA. Once the titration of Mg^{2+} is complete, the temperature continues to decrease, as shown by the curve's **red** branch. The straight-line segments represent an idealized titration curve; as suggested by the dashed lines, the actual shape of the titration curve at each equivalence point depends on the reaction conditions.

which means EDTA reacts with Ca^{2+} before it reacts with Mg^{2+}. As we add EDTA, the exothermic reaction of EDTA and Ca^{2+} causes the temperature to increase. Once we reach this reaction's equivalence point , the temperature begins to drop as the endothermic reaction of EDTA and Mg takes over. After the second equivalence point, the temperature will continue to decrease as the solution cools. Figure SM9.19 shows an idealized thermometric titration curve for this system; note that actual shape of the titration curve at each equivalence point and the rate of change in temperature after the second equivalence point will depend upon the reaction conditions, including the properties of the vessel in which the titration is carried out.

35. The best choice is the titrant with the largest difference in $\log K_f$ values; in this case, the best choice is EGTA.

36. At the equivalence point, the moles of Ca^{2+} in the sample equal the moles of EDTA; thus

$$2.68 \times 10^{-4}\,L \times \frac{0.0119\ \text{mol EDTA}}{L} \times \frac{1\ \text{mol Ca}}{\text{mol EDTA}} \times$$

$$\frac{40.08\ \text{g Ca}}{\text{mol Ca}} \times \frac{1000\ \text{mg}}{g} = 0.128\ \text{mg Ca}$$

This is the mass of calcium in 0.100 mL; scaling up by a factor of 1000 gives the concentration of calcium as 128 mg per 100 mL.

37. The mass of $CaCO_3$ in the sample as analyzed is

$$0.04411\,L \times \frac{0.04988\ \text{mol EDTA}}{L} \times$$

$$\frac{1\ \text{mol Ca}}{\text{mol EDTA}} \times \frac{100.09\ \text{g CaCO}_3}{\text{mol Ca}} = 0.2202\ \text{g CaCO}_3$$

This is the mass of $CaCO_3$ in a 10.00-mL portion of the solution that contains the dissolved eggshell; thus, the %w/w $CaCO_3$ in the eggshell is

$$\frac{0.2002\ \text{g CaCO}_3 \times \dfrac{250.0\ \text{mL}}{10.00\ \text{mL}}}{5.613\ \text{g sample}} \times 100 = 98.08\%\text{w/w CaCO}_3$$

38. The mass of NaCN in the sample as analyzed is

$$0.02736\,L \times \frac{0.1012\ \text{mol AgNO}_3}{L} \times \frac{2\ \text{mol NaCN}}{1\ \text{mol AgNO}_3}$$

$$\times \frac{49.01\ \text{g NaCN}}{\text{mol NaCN}} \times \frac{1000\ \text{mg}}{g} = 271.4\ \text{mg NaCN}$$

This is the mass of NaCN in a 5.00-mL sample drawn from the electroplating bath; thus, the concentration of NaCN in the electroplating bath is

$$\frac{271.4\ \text{mg NaCN}}{5.00 \times 10^{-3}\,L\ \text{sample}} = 5.43 \times 10^4\ \text{ppm NaCN}$$

Note that we do not need to worry about the fact that the original 5.00 mL sample is diluted to 250.0 mL prior to its analysis. The only source of the 271.4 mg of NaCN is the 5.00 mL sample drawn from the electroplating bath. Contrast this with the previous problem where the source of the 0.2002 g of $CaCO_3$ is a 10.00-mL sample drawn from a much larger volume of sample that contains the dissolved eggshell.

39. In this back-titration, KCN reacts with both the analyte, Cd^{2+}, and with the titrant, Ag^+. The total moles of KCN available are

$$0.02000 \text{ L} \times \frac{0.5000 \text{ mol KCN}}{\text{L}} = 0.01000 \text{ mol KCN}$$

of which

$$0.01398 \text{ L} \times \frac{0.1518 \text{ mol AgNO}_3}{\text{L}} \times$$

$$\frac{2 \text{ mol KCN}}{\text{mol AgNO}_3} = 4.244 \times 10^{-3} \text{ mol KCN}$$

were used to titrate Ag^+; this means that

$$0.01000 \text{ mol KCN} - 4.224 \times 10^{-3} \text{ mol KCN}$$

$$= 5.756 \times 10^{-3} \text{ mol KCN}$$

reacted with Cd^{2+}. The mass of Cd^{2+} in the sample, therefore, is

$$5.756 \times 10^{-3} \text{ mol KCN} \times \frac{1 \text{ mol Cd}^{2+}}{4 \text{ mol KCN}} \times$$

$$\frac{112.41 \text{ g Cd}^{2+}}{\text{mol Cd}^{2+}} = 0.1617 \text{ g Cd}^{2+}$$

and its concentration is

$$\frac{0.1617 \text{ g Cd}^{2+}}{0.3000 \text{ g sample}} \times 100 = 53.90\% \text{w/w Cd}^{2+}$$

40. (a) To evaluate the relative stabilities for the EDTA complexes of Fe^{3+} and of Al^{3+}, we need to compare their conditional formation complexes. At a pH of 2 the value of $\alpha_{Y^{4-}}$ is 3.47×10^{-14}, which gives conditional formation constants of

$$K'_{f,Fe^{3+}} = \alpha_{Y^{4-}} K_{f,Fe^{3+}} = (3.47 \times 10^{-14})(1.3 \times 10^{25}) = 4.5 \times 10^{11}$$

$$K'_{f,Al^{3+}} = \alpha_{Y^{4-}} K_{f,Al^{3+}} = (3.47 \times 10^{-14})(2.0 \times 10^{16}) = 690$$

The conditional formation constant for Fe^{3+} is 6.5×10^8 times larger than the conditional formation constant for Al^{3+}; thus, the reaction of EDTA with Fe^{3+} is more favorable than its reaction with Al^{3+}.

(b) In the first titration only Fe^{3+} reacts with EDTA; thus, the concentration of Fe^{3+} is

$$M_{Fe} = \frac{M_{EDTA} V_{EDTA}}{V_{Fe}} =$$

$$\frac{(0.05002 \text{ M})(24.82 \text{ mL})}{50.00 \text{ mL}} = 0.02483 \text{ M Fe}^{3+}$$

The second titration is a back-titration. The total moles of EDTA added is

$$0.05000 \text{ L} \times \frac{0.05002 \text{ mol EDTA}}{\text{L}} = 2.501 \times 10^{-3} \text{ mol EDTA}$$

of which

$$0.01784 \text{ L} \times \frac{0.04109 \text{ mol Fe}^{3+}}{\text{L}} \times$$

$$\frac{1 \text{ mol EDTA}}{\text{mol Fe}^{3+}} = 7.33 \times 10^{-4} \text{ mol EDTA}$$
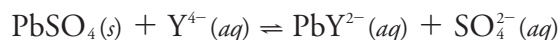
react with Fe^{3+}, leaving us with

$$2.501 \times 10^{-3} - 7.33 \times 10^{-4} = 1.768 \times 10^{-3} \text{ mol EDTA}$$

to react with Al^{3+}. The concentration of Al^{3+}, therefore, is

$$\frac{1.768 \times 10^{-3} \text{ mol EDTA} \times \frac{1 \text{ mol Al}^{3+}}{\text{mol EDTA}}}{0.05000 \text{ L}} = 0.03536 \text{ M Al}^{3+}$$

41. (a) To show that a precipitate of $PbSO_4$ is soluble in a solution of EDTA, we add together the first two reactions to obtain the reaction
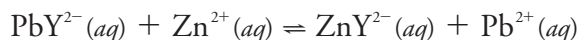
$$PbSO_4(s) + Y^{4-}(aq) \rightleftharpoons PbY^{2-}(aq) + SO_4^{2-}(aq)$$

for which the equilibrium constant is

$$K = K_{sp} K_{f,PbY^{2-}} = (1.6 \times 10^{-8})(1.1 \times 10^{18}) = 1.8 \times 10^{10}$$

The large magnitude of the equilibrium constant means that $PbSO_4$ is soluble in EDTA.

(b) The displacement of Pb^{2+} from PbY^{4-} by Zn^{2+} is the reaction

$$PbY^{2-}(aq) + Zn^{2+}(aq) \rightleftharpoons ZnY^{2-}(aq) + Pb^{2+}(aq)$$

for which the equilibrium constant is

$$K = \frac{K_{f,ZnY^{2-}}}{K_{f,PbY^{2-}}} = \frac{3.2 \times 10^{16}}{1.1 \times 10^{18}} = 0.029$$

Although less than 1, the equilibrium constant does suggest that there is some displacement of Pb^{2+} when using Zn^{2+} as the titrant. When using Mg^{2+} as the titrant, the potential displacement reaction

$$PbY^{2-}(aq) + Mg^{2+}(aq) \rightleftharpoons MgY^{2-}(aq) + Pb^{2+}(aq)$$
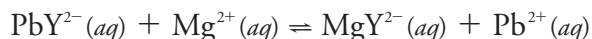
has an equilibrium constant of

$$K = \frac{K_{f,MgY^{2-}}}{K_{f,PbY^{2-}}} = \frac{4.9 \times 10^8}{1.1 \times 10^{18}} = 4.5 \times 10^{-10}$$

As this is a much smaller equilibrium constant, the displacement of Pb^{2+} by Mg^{2+} is not likely to present a problem. Given the equilibrium constants, we will underestimate the amount of sulfate in the sample if we use Zn^{2+} as the titrant. To see this, we note that for this back-titration the total moles of EDTA used is equal to the combined moles of Pb^{2+} and of Zn^{2+}. If some of the Zn^{2+} displaces Pb^{2+}, then we use more Zn^{2+} than expected, which means we underreport the moles of Pb^{2+} and, therefore, the moles of sulfate.

(c) The total moles of EDTA used is

$$0.05000\ \text{L} \times \frac{0.05000\ \text{mol EDTA}}{\text{L}} = 0.002500\ \text{mol EDTA}$$

of which

$$0.01242\ \text{L} \times \frac{0.1000\ \text{mol Mg}^{2+}}{\text{L}} \times$$

$$\frac{1\text{mol EDTA}}{\text{mol Mg}^{2+}} = 0.001242\ \text{mol EDTA}$$

react with Mg^{2+}; this leaves

$$0.002500 - 0.001242 = 0.001258\ \text{mol EDTA}$$

to react with Pb^{2+}. The concentration of sulfate in the sample, there-fore, is

$$0.001258\ \text{mol EDTA} \times \frac{1\ \text{mol Pb}^{2+}}{\text{mol EDTA}} \times$$

$$\frac{1\ \text{mol SO}_4^{2-}}{\text{mol Pb}^{2+}} = 0.001258\ \text{mol SO}_4^{2-}$$

$$\frac{0.001258\ \text{mol SO}_4^{2-}}{0.02500\ \text{L}} = 0.05032\ \text{M SO}_4^{2-}$$

42. Let's start by writing an equation for $\alpha_{Y^{4-}}$ that includes all seven forms of EDTA in solution

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{\left\{ \begin{array}{l} [H_6Y^{2+}] + [H_5Y^{+}] + [H_4Y] + \\ \qquad [H_3Y^{-}] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}] \end{array} \right\}}$$

Next, we define the concentration of each species in terms of the con-centration of Y^{4-}; for example, using the acid dissociation constant, K_{a6}, for HY^{3-}

$$K_{a6} = \frac{[Y^{4-}][H_3O^{+}]}{[HY^{3-}]}$$

we have

$$[HY^{3-}] = \frac{[Y^{4-}][H_3O^{+}]}{K_{a6}}$$

and using the acid dissociation constant, K_{a5}, for H_2Y^{2-}

$$K_{a5} = \frac{[HY^{3-}][H_3O^{+}]}{[H_2Y^{2-}]}$$

we have

$$[H_2Y^{2-}] = \frac{[HY^{3-}][H_3O^{+}]}{K_{a5}} = \frac{[Y^{4-}][H_3O^{+}]^2}{K_{a5}K_{a6}}$$

Continuing in this fashion—the details are left to you—we find that

$$[H_3Y^-] = \frac{[Y^{4-}][H_3O^+]^3}{K_{a4}K_{a5}K_{a6}}$$

$$[H_4Y] = \frac{[Y^{4-}][H_3O^+]^4}{K_{a3}K_{a4}K_{a5}K_{a6}}$$

$$[H_5Y^+] = \frac{[Y^{4-}][H_3O^+]^5}{K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}$$

$$[H_6Y^{2+}] = \frac{[Y^{4-}][H_3O^+]^6}{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}$$

Now things get a bit messy (!) as we substitute each of the last six equations back into our equation for $\alpha_{Y^{4-}}$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{\left\{ \begin{array}{c} \dfrac{[Y^{4-}][H_3O^+]^6}{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[Y^{4-}][H_3O^+]^5}{K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \\[3mm] \dfrac{[Y^{4-}][H_3O^+]^4}{K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[Y^{4-}][H_3O^+]^3}{K_{a4}K_{a5}K_{a6}} + \\[3mm] \dfrac{[Y^{4-}][H_3O^+]^2}{K_{a5}K_{a6}} + \dfrac{[Y^{4-}][H_3O^+]}{K_{a6}} + [Y^{4-}] \end{array} \right\}}$$

This equation looks imposing, but we can simplify it by factoring $[Y^{4-}]$ out of the denominator and simplifying

$$\alpha_{Y^{4-}} = \frac{1}{\left\{ \begin{array}{c} \dfrac{[H_3O^+]^6}{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[H_3O^+]^5}{K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \\[3mm] \dfrac{[H_3O^+]^4}{K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[H_3O^+]^3}{K_{a4}K_{a5}K_{a6}} + \\[3mm] \dfrac{[H_3O^+]^2}{K_{a5}K_{a6}} + \dfrac{[H_3O^+]}{K_{a6}} + 1 \end{array} \right\}}$$

and then multiplying through by $K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}$ to arrive at our final equation

$$\alpha_{Y^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}{\left\{ \begin{array}{c} [H_3O^+]^6 + K_{a1}[H_3O^+]^5 + K_{a1}K_{a2}[H_3O^+]^4 + \\[2mm] K_{a1}K_{a2}K_{a3}[H_3O^+]^3 + K_{a1}K_{a2}K_{a3}K_{a4}[H_3O^+]^2 + \\[2mm] K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}[H_3O^+] + K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6} \end{array} \right\}}$$

For the titration curves in this problem, we will calculate the potential for one volume of titrant before the equivalence point and the potential for one volume of titrant after the equivalence point.
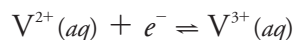
43. (a) The titration of V^{2+} with Ce^{4+} is an example of a redox titration. The titration's equivalence point is reached when

$$n_V = M_V V_V = M_{Ce} V_{Ce} = n_{Ce}$$

where n is the moles of V^{2+} or of Ce^{4+}; thus

$$V_{eq.pt.} = V_{Ce} = \frac{M_V V_V}{M_{Ce}} = \frac{(0.0100 \text{ M})(25.0 \text{ mL})}{(0.0100 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, the potential is easiest to calculate by using the Nernst equation for the analyte's half-reaction

$$V^{2+}(aq) + e^- \rightleftharpoons V^{3+}(aq)$$

$$E = E^\circ_{V^{3+}/V^{2+}} - 0.05916\log\frac{[V^{2+}]}{[V^{3+}]}$$

$$E = -0.255 - 0.05916\log\frac{[V^{2+}]}{[V^{3+}]}$$

Although the analyte's reaction is an oxidation, the Nernst equation is still written for the corresponding reduction reaction.

For example, after adding 10.0 mL of titrant, the concentrations of V^{2+} and of V^{3+} are

$$[V^{2+}] = \frac{M_V V_V - M_{Ce} V_{Ce}}{V_V + V_{Ce}}$$

$$[V^{2+}] = \frac{(0.0100 \text{ M})(25.0 \text{ mL}) - (0.0100 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}}$$
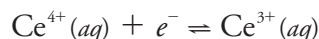
$$[V^{2+}] = 4.29 \times 10^{-3} \text{ M}$$

$$[V^{3+}] = \frac{M_{Ce} V_{Ce}}{V_V + V_{Ce}} = \frac{(0.0100 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 2.86 \times 10^{-3} \text{ M}$$

which gives us a potential of

$$E = -0.255 - 0.05916\log\frac{4.29 \times 10^{-3}}{2.86 \times 10^{-3}} = -0.265 \text{ V}$$

After the equivalence point, the potential is easiest to calculate by using the Nernst equation for the titrant's half-reaction

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$$

$$E = E^\circ_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E = +1.72 - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

To sketch an approximate titration curve, use a ladder diagram for V^{3+}/V^{2+} to plot points at 10% and 90% of the equivalence point volume and use a ladder diagram for Ce^{4+}/Ce^{3+} to plot two points at 110% and 200% of the equivalence point volume. Use the lines passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.
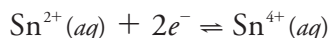
For example, after adding 35.0 mL of titrant, the concentrations of Ce^{3+} and of Ce^{4+} are

$$[Ce^{4+}] = \frac{M_{Ce} V_{Ce} - M_V V_V}{V_{Ce} + V_V}$$

$$[Ce^{4+}] = \frac{(0.0100 \text{ M})(35.0 \text{ mL}) - (0.0100 \text{ M})(25.0 \text{ mL})}{35.0 \text{ mL} + 25.0 \text{ mL}}$$

$$[Ce^{4+}] = 1.67 \times 10^{-3} \text{ M}$$

$$[Ce^{3+}] = \frac{M_V V_V}{V_V + V_{Ce}} = \frac{(0.0100 \text{ M})(25.0 \text{ mL})}{25.0 \text{ mL} + 35.0 \text{ mL}} = 4.17 \times 10^{-3} \text{ M}$$

which gives us a potential of

$$E = +1.72 - 0.05916\log\frac{4.17 \times 10^{-3}}{1.67 \times 10^{-3}} = +1.70 \text{ V}$$

Figure SM9.20 shows the full titration curve.

(b) The titration of Sn^{2+} with Ce^{4+} is an example of a redox titration. The titration's equivalence point is reached when
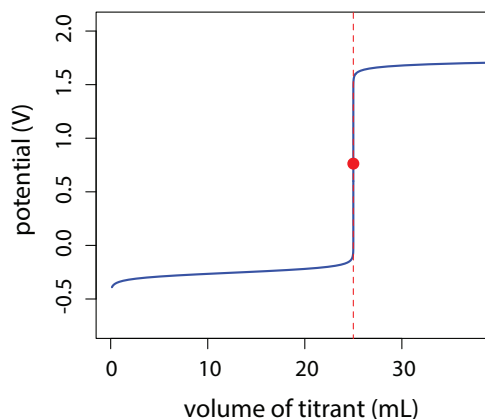
Figure SM9.20 The titration curve for 0.0100 M V^{2+} using 0.0100 M Ce^{3+} as the titrant is shown in **blue**. The **red** dashed lines mark the volume of titrant at the equivalence point and the **red** dot marks the equivalence point (see Problem 44a).

$$n_{Sn} = 2 \times M_{Sn} V_{Sn} = M_{Ce} V_{Ce} = n_{Ce}$$

where n is the moles of Sn^{2+} or of Ce^{4+}; thus

$$V_{eq.pt.} = V_{Ce} = \frac{2 \times M_{Sn} V_{Sn}}{M_{Ce}} =$$

$$\frac{(2)(0.0100 \text{ M})(25.0 \text{ mL})}{(0.0100 \text{ M})} = 50.0 \text{ mL}$$

Before the equivalence point, the potential is easiest to calculate by using the Nernst equation for the analyte's half-reaction

$$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn^{4+}(aq)$$

$$E = E^\circ_{Sn^{4+}/Sn^{2+}} - \frac{0.05916}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

$$E = +0.154 - \frac{0.05916}{2} \log \frac{[Sn^{2+}]}{[Sn^{4+}]}$$

For example, after adding 10.0 mL of titrant, the concentrations of Sn^{2+} and of Sn^{4+} are

$$[Sn^{2+}] = \frac{M_{Sn} V_{Sn} - 0.5 \times M_{Ce} V_{Ce}}{V_{Sn} + V_{Ce}}$$

$$[Sn^{2+}] = \frac{(0.0100 \text{ M})(25.0 \text{ mL}) - (0.5)(0.0100 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}}$$
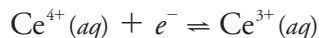
$$[Sn^{2+}] = 5.71 \times 10^{-3} \text{ M}$$

$$[Sn^{4+}] = \frac{0.5 \times M_{Ce} V_{Ce}}{V_{Sn} + V_{Ce}} =$$

$$\frac{(0.5)(0.0100 \text{ M})(10.0 \text{ mL})}{25.0 \text{ mL} + 10.0 \text{ mL}} = 1.43 \times 10^{-3} \text{ M}$$

which gives us a potential of

$$E = 0.154 - \frac{0.05916}{2} \log \frac{5.71 \times 10^{-3}}{1.43 \times 10^{-3}} = 0.136 \text{ V}$$

After the equivalence point, the potential is easiest to calculate by using the Nernst equation for the titrant's half-reaction

$$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$$

$$E = E^\circ_{Ce^{4+}/Ce^{3+}} - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E = +1.72 - 0.05916 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and of Ce^{4+} are

$$[Ce^{4+}] = \frac{M_{Ce} V_{Ce} - 2 \times M_{Sn} V_{Sn}}{V_{Ce} + V_{Sn}}$$

$$[Ce^{4+}] = \frac{(0.0100 \text{ M})(60.0 \text{ mL}) - (2)(0.0100 \text{ M})(25.0 \text{ mL})}{60.0 \text{ mL} + 25.0 \text{ mL}}$$

$$[Ce^{4+}] = 1.18 \times 10^{-3} \text{ M}$$

$$[Ce^{3+}] = \frac{2 \times M_{Sn} V_{Sn}}{V_{Sn} + V_{Ce}} =$$

$$\frac{(2)(0.0100 \text{ M})(25.0 \text{ mL})}{25.0 \text{ mL} + 60.0 \text{ mL}} = 5.88 \times 10^{-3} \text{ M}$$

which gives us a potential of

$$E = +1.72 - 0.05916 \log \frac{5.88 \times 10^{-3}}{1.18 \times 10^{-3}} = +1.68 \text{ V}$$

Figure SM9.21 shows the full titration curve.

(c) The titration of Fe^{2+} with MnO_4^- is an example of a redox titration. The titration's equivalence point is reached when

$$n_{Fe} = M_{Fe} V_{Fe} = 5 \times M_{Mn} V_{Mn} = 5 \times n_{Mn}$$

where n is the moles of Fe^{2+} or the moles of MnO_4^-; thus

$$V_{eq.pt.} = V_{Mn} = \frac{M_{Fe} V_{Fe}}{5 \times M_{Mn}} = \frac{(0.0100 \text{ M})(25.0 \text{ mL})}{(5)(0.0100 \text{ M})} = 5.00 \text{ mL}$$

Before the equivalence point, the potential is easiest to calculate by using the Nernst equation for the analyte's half-reaction

$$Fe^{2+}(aq) + e^- \rightleftharpoons Fe^{3+}(aq)$$
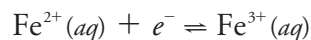
$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E = +0.771 - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

For example, after adding 3.00 mL of titrant, the concentrations of Fe^{2+} and of Fe^{3+} are

$$[Fe^{2+}] = \frac{M_{Fe} V_{Fe} - 5 \times M_{Mn} V_{Mn}}{V_{Fe} + V_{Mn}}$$

$$[Fe^{2+}] = \frac{(0.0100 \text{ M})(25.0 \text{ mL}) - (5)(0.0100 \text{ M})(3.00 \text{ mL})}{25.0 \text{ mL} + 3.00 \text{ mL}}$$

$$[Fe^{2+}] = 3.57 \times 10^{-3} \text{ M}$$

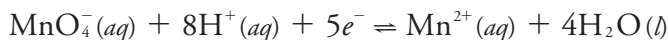$$[Fe^{3+}] = \frac{5 \times M_{Mn} V_{Mn}}{V_{Fe} + V_{Mn}} =$$

$$\frac{(5)(0.0100 \text{ M})(3.00 \text{ mL})}{25.0 \text{ mL} + 3.00 \text{ mL}} = 5.36 \times 10^{-3} \text{ M}$$

which gives us a potential of

$$E = 0.771 - 0.05916 \log \frac{3.57 \times 10^{-3}}{5.36 \times 10^{-3}} = 0.781 \text{ V}$$

After the equivalence point, the potential is easiest to calculate by using the Nernst equation for the titrant's half-reaction

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

To sketch an approximate titration curve, use a ladder diagram for Sn^{4+}/Sn^{2+} to plot points at 10% and 90% of the equivalence point volume and use a ladder diagram for Ce^{4+}/Ce^{3+} to plot two points at 110% and 200% of the equivalence point volume. Use the lines passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.

Figure SM9.21 The titration curve for 0.0100 M Sn^{2+} using 0.0100 M Ce^{3+} as the titrant is shown in **blue**. The **red** dashed lines mark the volume of titrant at the equivalence point and the **red** dot marks the equivalence point (see Problem 44b).

To sketch an approximate titration curve, use a ladder diagram for Fe^{3+}/Fe^{2+} to plot points at 10% and 90% of the equivalence point volume and use a ladder diagram for MnO_4^-/Mn^{2+} to plot two points at 110% and 200% of the equivalence point volume. Use the lines passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.
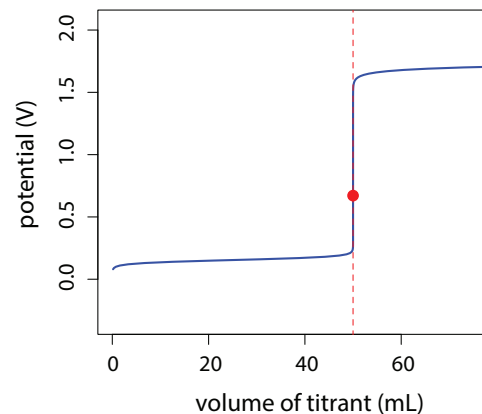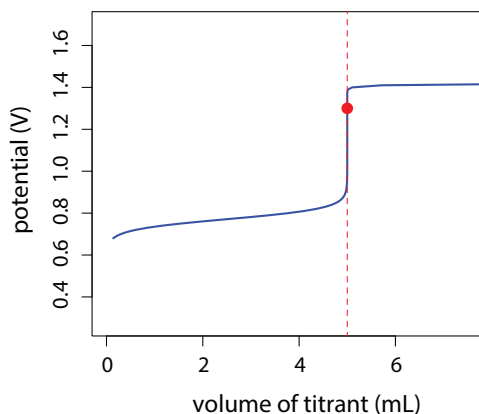

Figure SM9.22 The titration curve for 0.0100 M Fe^{2+} using 0.0100 M MnO_4^- as the titrant is shown in **blue**. The **red** dashed lines mark the volume of titrant at the equivalence point and the **red** dot marks the equivalence point (see Problem 44c).

$$E = E^\circ_{MnO_4^-/Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$E = +1.51 - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

For example, after adding 7.00 mL of titrant, the concentrations of MnO_4^- and of Mn^{2+} are

$$[MnO_4^-] = \frac{5 \times M_{Mn} V_{Mn} - M_{Fe} V_{Fe}}{V_{Mn} + V_{Fe}}$$

$$[MnO_4^-] = \frac{(5)(0.0100\ M)(7.00\ mL) - (0.0100\ M)(25.0\ mL)}{7.00\ mL + 25.0\ mL}$$

$$[MnO_4^-] = 3.12 \times 10^{-3}\ M$$

$$[Mn^{2+}] = \frac{0.2 \times M_{Fe} V_{Fe}}{V_{Fe} + V_{Mn}} =$$

$$\frac{(0.2)(0.0100\ M)(25.0\ mL)}{25.0\ mL + 7.00\ mL} = 1.56 \times 10^{-3}\ M$$

which gives us a potential of

$$E = +1.51 - \frac{0.05916}{5} \log \frac{1.56 \times 10^{-3}}{(3.12 \times 10^{-3})(0.1)^8} = +1.42\ V$$

Figure SM9.22 shows the full titration curve.

44. (a) When the titration reaction's stoichiometry is a 1:1 ratio, then the potential at the equivalence point is the average of the analyte's and the titrant's standard state potentials; thus

$$E_{eq.pt.} = \frac{E^\circ_{V^{3+}/V^{2+}} + E^\circ_{Ce^{4+}/Ce^{3+}}}{2} = \frac{-0.255\ V + 1.72V}{2} = 0.73\ V$$

(b) When the titration reaction's stoichiometry is not a 1:1 ratio, then the potential at the equivalence point is a weighted average of the analyte's and the titrant's standard state potentials where the weighting factors are the number of electrons lost or gained; thus

$$E_{eq.pt.} = \frac{2E^\circ_{Sn^{4+}/Sn^{2+}} + E^\circ_{Ce^{4+}/Ce^{3+}}}{3} = \frac{(2)(0.154\ V) + 1.72V}{3} = 0.68\ V$$

(c) When the titration reaction's stoichiometry is not a 1:1 ratio, then the potential at the equivalence point is a weighted average of the analyte's and the titrant's standard state potentials where the weighting factors are the number of electrons lost or gained. In addition, as the thus half-reaction for the reduction of MnO_4^- to Mn^{2+} includes H^+, the equivalence point's potential is a function of the solution's pH. As shown in Example 9.10, the equivalence point potential for this titration is

$$E_{eq.pt.} = \frac{E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}}}{6} - 0.07888pH =$$

$$\frac{0.771\ V + (5)(1.51V)}{6} = 1.31\ V$$

45. (a) With an equivalence point potential of 0.73 V, diphenylamine, which has a standard state potential of 0.75 V, is an appropriate indicator.

(b) With an equivalence point potential of 0.68 V, diphenylamine, which has a standard state potential of 0.75 V, is an appropriate indicator.

(c) With an equivalence point potential of 1.31 V, tris(5-nitro-1,10-phenanthroline)iron, which has a standard state potential of 1.25 V, is an appropriate indicator.

46. (a) The procedure requires that we remove any excess Sn^{2+} so that it does not react with the titrant and cause a determinate error in the analysis for iron. To remove Sn^{2+}, the procedure uses Hg^{2+} to oxidize it to Sn^{4+}, with the Hg^{2+} forming a precipitate of Hg_2Cl_2. If we do not observe a precipitate, then excess Sn^{2+} is not present, which means we failed to reduce all the analyte from Fe^{3+} to Fe^{2+}. If a gray precipitate forms, then too much Sn^{2+} is present, reducing Hg^{2+} to Hg instead of to Hg_2Cl_2. This is a problem because it means we did may not have oxidize all the Sn^{2+}.

(b) No. The first addition of Sn^{2+} is used simply to speed up the dissolution of the ore.

(c) No. In the next step the Fe^{3+} is reduced back to Fe^{2+}.

47. We use volumetric glassware when we need to know the exact volume as part of a calculation. Of the volumes highlighted in the procedure, we need to know only two with any certainty: the volume of sample taken ("A 50-mL portion of the resulting solution...") and the volume of Fe^{2+} added in excess ("...50 mL of a standard solution of Fe^{2+}...").

48. (a) Because the titrant, $KMnO_4$, reacts with the stabilizer, we use more titrant than expected and report a concentration of H_2O_2 that is greater than expected.

(b) The simplest approach is to prepare and analyze a reagent blank by replacing the 25 mL of sample with 25 mL of distilled water that has been treated to remove any traces of dissolved organic matter. We then subtract he volume of titrant used to analyze the reagent blank from the volume of titrant used to analyze the sample.

(c) Because the concentration of H_2O_2 is 5× greater, the volume of $KMnO_4$ used in the titration will increase by a factor of five as well. To ensure that the titration's end point does not exceed the buret's maximum volume, we must either change the way the sample is prepared to reduce the concentration of H_2O_2 by a factor of five, or use a more concentrated solution of $KMnO_4$ as the titrant. For example, to change the concentration of H_2O_2, we can take a 5-mL sample in place of a 25-mL sample.

For a redox titration, we can determine the reaction's stoichiometry by considering the changes in oxidation states experienced by the analyte and by the titrant without working out the balanced reaction. Of course, we can write the balanced reaction as well, which, in this case, is

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightleftharpoons$$
$$5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$
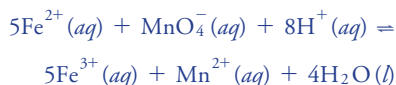
49. In the titration reaction, each iron loses one electron as it is oxidized from Fe^{2+} to Fe^{3+}, and each manganese gains five electrons as it is reduced from MnO_4^- to Mn^{2+}. The stoichiometry of the reaction, therefore, requires that five moles of Fe^{2+} react with each mole of MnO_4^-; thus, there are

$$0.04127 \, L \times \frac{0.02500 \, mol \, MnO_4^-}{L} \times$$
$$\frac{5 \, mol \, Fe^{2+}}{mol \, MnO_4^-} = 5.159 \times 10^{-3} \, mol \, Fe^{2+}$$

in the sample as analyzed. The concentration of Fe_2O_3 in the original sample is

$$5.159 \times 10^{-3} \, mol \, Fe^{2+} \times \frac{1 \, mol \, Fe_2O_3}{2 \, mol \, Fe^{2+}}$$
$$\times \frac{159.69 \, g \, Fe_2O_3}{mol \, Fe_2O_3} = 0.4119 \, g \, Fe_2O_3$$

$$\frac{0.4119 \, g \, Fe_2O_3}{0.4185 \, g \, sample} \times 100 = 98.42\%w/w \, Fe_2O_3$$

50. In the titration reaction, each manganese in the analyte loses two electrons as it is oxidized from Mn^{2+} to MnO_2, and each manganese in the titrant gains three electrons as it is reduced from MnO_4^- to MnO_2. The stoichiometry of the reaction, therefore, requires that three moles of Mn^{2+} react with two moles of MnO_4^-; thus, there are

$$0.03488 \, L \times \frac{0.03358 \, mol \, MnO_4^-}{L} \times$$
$$\frac{3 \, mol \, Mn^{2+}}{2 \, mol \, MnO_4^-} \times \frac{54.938 \, g \, Mn^{2+}}{mol \, Mn^{2+}} = 0.09652 \, g \, Mn^{2+}$$

in the sample as analyzed. The concentration of Mn^{2+} in the original sample is

$$\frac{0.09652 \, g \, Mn^{2+}}{0.5165 \, g \, sample} \times 100 = 18.69\%w/w \, Mn^{2+}$$

51. In this indirect titration, iron, in the form of Fe^{3+}, reacts with the analyte, uranium, and then, in the form of Fe^{2+}, with the titrant, $K_2Cr_2O_7$. In its reaction with the analyte, iron gains one electron as it is reduced from Fe^{3+} to Fe^{2+}, and uranium loses two electrons as it is oxidized from U^{4+} to U^{6+}; thus, each mole of U^{4+} produces two moles of Fe^{2+}. In its reaction with the titrant, iron loses one electron as it is oxidized from Fe^{2+} to Fe^{3+} and each chromium gains three electrons as it is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}; thus, the stoichiometry of the titration reaction requires that six moles of Fe^{2+} reacts with each mole of $Cr_2O_7^{2-}$. The titration with $K_2Cr_2O_7$ shows us that the moles of Fe^{2+} formed using the Walden reductor is

$$0.01052 \text{ L} \times \frac{0.00987 \text{ mol K}_2\text{Cr}_2\text{O}_7}{\text{L}} \times$$

$$\frac{6 \text{ mol Fe}^{2+}}{\text{mol K}_2\text{Cr}_2\text{O}_7} = 6.23 \times 10^{-4} \text{ mol Fe}^{2+}$$

which means the original sample contained

$$6.23 \times 10^{-4} \text{ mol Fe}^{2+} \times \frac{1 \text{ mol U}^{4+}}{2 \text{ mol Fe}^{2+}} = 3.12 \times 10^{-4} \text{ mol U}^{4+}$$

The concentration of uranium in the original sample, therefore is

$$\frac{3.12 \times 10^{-4} \text{ mol U}^{4+} \times \dfrac{238.08 \text{ g U}^{4+}}{\text{mol U}^{4+}}}{0.315 \text{ g sample}} \times 100 = 23.6\%\text{w/w U}^{4+}$$

52. In this back-titration, iron, in the form of Fe^{2+}, reacts with the analyte, chromium, and then with the titrant, $K_2Cr_2O_7$. In its reaction with the analyte, iron loses one electron as it is oxidized from Fe^{2+} to Fe^{3+} and each chromium gains three electrons as it is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}; thus, six moles of Fe^{2+} reacts with each mole of $Cr_2O_7^{2-}$. In its reaction with the titrant, iron loses one electron as it is oxidized from Fe^{2+} to Fe^{3+} and each chromium gains three electrons as it is reduced from $Cr_2O_7^{2-}$ to Cr^{3+}; thus, the stoichiometry of the titration reaction requires that each mole of Fe^{2+} reacts with six moles of $Cr_2O_7^{2-}$. The total moles of Fe^{2+} added to the original sample is

$$0.500 \text{ g Fe(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} \times$$

$$\frac{1 \text{ mol Fe}^{2+}}{392.12 \text{ g Fe(NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}} = 1.28 \times 10^{-3} \text{ mol Fe}^{2+}$$

Of this iron, the moles that react with the titrant, $K_2Cr_2O_7$ are

$$0.01829 \text{ L} \times \frac{0.00389 \text{ mol K}_2\text{Cr}_2\text{O}_7}{\text{L}} \times$$

$$\frac{6 \text{ mol Fe}^{2+}}{\text{mol K}_2\text{Cr}_2\text{O}_7} = 4.27 \times 10^{-4} \text{ mol Fe}^{2+}$$

which leaves $1.28 \times 10^{-3} - 4.27 \times 10^{-4} = 8.53 \times 10^{-4}$ moles of Fe^{2+} to react with chromium in the original sample; thus, the mass of chromium in the original sample is

$$8.53 \times 10^{-4} \text{ mol Fe}^{2+} \times \frac{1 \text{ mol Cr}_2\text{O}_7^{2-}}{6 \text{ mol Fe}^{2+}}$$

$$\times \frac{2 \text{ mol Cr}}{\text{mol Cr}_2\text{O}_7^{2-}} \times \frac{51.996 \text{ g Cr}}{\text{mol Cr}} = 0.0149 \text{ g Cr}$$

and the thickness of chromium is

$$\text{thickness} = \frac{\text{volume}}{\text{area}} =$$

$$\frac{0.0149 \text{ g} \times \dfrac{1 \text{ mL}}{7.20 \text{ g}} \times \dfrac{1 \text{ cm}^3}{\text{mL}}}{30.0 \text{ cm}^2} = 6.90 \times 10^{-5} \text{ cm}$$

53. In this indirect titration, the analyte, CO, reacts with I_2O_5 to form CO_2 and I_2. In this reaction, carbon loses two electrons as its oxidation state changes from $+2$ to $+4$, and each iodine gains five electrons as its oxidation state changes from $+5$ to 0; thus, ten moles of CO produced two moles of I_2. The I_2 formed is converted to I_3^-, which then is titrated with $S_2O_3^{2-}$, forming I^- and $S_4O_6^{2-}$. In the titration reaction, each iodine gains the equivalent of 2/3rd of an electron as its oxidation state changes from $-1/3$ to -1, and each sulfur loses the equivalent of 1/2 of an electron as its changes its oxidation state from $+2$ to $+2.5$; thus, each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$.

Beginning with the moles of $S_2O_3^{2-}$ used in the titration

$$0.00717 \text{ L } S_2O_3^- \times \frac{0.00329 \text{ mol } S_2O_3^{2-}}{L} = 2.36 \times 10^{-5} \text{ mol } S_2O_3^{2-}$$

we use stoichiometry to find the mass of CO in the original sample

$$2.36 \times 10^{-5} \text{ mol } S_2O_3^{2-} \times \frac{1 \text{ mol } I_3^-}{2 \text{ mol } S_2O_3^{2-}} \times$$

$$\frac{1 \text{ mol } I_2}{\text{mol } I_3^-} \times \frac{1 \text{ mol } I_2O_5}{\text{mol } I_2} = 1.18 \times 10^{-5} \text{ mol } I_2O_5$$

$$1.18 \times 10^{-5} \text{ mol } I_2O_5 \times \frac{10 \text{ mol CO}}{2 \text{ mol } I_2O_5} = 5.90 \times 10^{-5} \text{ mol CO}$$

$$5.90 \times 10^{-5} \text{ mol CO} \times \frac{28.01 \text{ g CO}}{\text{mol CO}} = 1.65 \times 10^{-3} \text{ g CO}$$

The mass of air taken is

$$4.79 \text{ L} \times \frac{1000 \text{ mL}}{L} \times \frac{1.23 \times 10^{-3} \text{ g}}{\text{mL}} = 5.89 \text{ g}$$

which makes the concentration of CO in the air

$$\frac{1.65 \times 10^{-3} \text{ g CO} \times \frac{10^6 \text{ µg}}{g}}{5.89 \text{ g air}} = 2.80 \times 10^2 \text{ ppm CO}$$

54. In the Winkler method, Mn^{2+} reacts with O_2 to form MnO_2 with manganese changing its oxidation state from $+2$ to $+4$, and each oxygen changing its oxidation state from 0 to -2; thus, each mole of O_2 reacts with two moles of Mn^{2+}. Subsequently, MnO_2 reacts with I^-, forming Mn^{2+} and I_3^- with manganese changing its oxidation state from $+4$ to $+2$, and each iodine changing its oxidation state from -1 to the equivalent of $-1/3$; thus three moles of I^- react with each mole of MnO_2. Finally, as we saw in Problem 53, in the titration of I_3^- with $S_2O_3^{2-}$, each mole of I_3^- reacts with two moles of $S_2O_3^{2-}$.

Beginning with the moles of $S_2O_3^{2-}$ used in the titration

$$0.00890 \text{ L } S_2O_3^- \times \frac{0.00870 \text{ mol } S_2O_3^{2-}}{L} = 7.74 \times 10^{-5} \text{ mol } S_2O_3^{2-}$$

we use stoichiometry to find the mass of O_2 in the original sample

$$7.74 \times 10^{-5} \text{ mol } S_2O_3^{2-} \times \frac{1 \text{ mol } I_3^-}{2 \text{ mol } S_2O_3^{2-}} \times \frac{3 \text{ mol } I^-}{\text{mol } I_3^-}$$

$$\times \frac{1 \text{ mol } MnO_2}{3 \text{ mol } I^-} \times \frac{1 \text{ mol } O_2}{2 \text{ mol } MnO_2} = 1.94 \times 10^{-5} \text{ mol } O_2$$

$$1.94 \times 10^{-5} \text{ mol } O_2 \times \frac{31.998 \text{ g } O_2}{\text{mol } O_2} = 6.21 \times 10^{-4} \text{ g } O_2$$

The concentration of O_2 in the original sample, therefore, is

$$\frac{6.21 \times 10^{-4} \text{ g } O_2 \times \dfrac{10^6 \text{ μg}}{\text{g}}}{100.0 \text{ mL}} = 6.21 \text{ ppm } O_2$$

55. The titration of KI with $AgNO_3$ is an example of a precipitation titration. The titration's equivalence point is reached when

$$n_I = M_I V_I = M_{Ag} V_{Ag} = n_{Ag}$$

where n is the moles of I^- or of Ag^+; thus

$$V_{eq.pt.} = V_{Ag} = \frac{M_I V_I}{M_{Ag}} = \frac{(0.0250 \text{ M})(50.0 \text{ mL})}{(0.0500 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, the concentration of I^- is determined by the amount of excess I^-, and the concentration of Ag^+ is determined by the solubility of AgI in the presence of excess I^-. For example, after adding 10.0 mL of $AgNO_3$, we find that

$$[I^-] = \frac{M_I V_I - M_{Ag} V_{Ag}}{V_I + V_{Ag}}$$

$$[I^-] = \frac{(0.0250 \text{ M})(50.0 \text{ mL}) - (0.0500 \text{ M})(10.0 \text{ ml})}{50.0 \text{ mL} + 10.0 \text{ mL}}$$

$$[I^-] = 0.0125 \text{ M}$$

$$[Ag^+] = \frac{K_{sp,AgI}}{[I^-]} = \frac{8.32 \times 10^{-17}}{0.0125} = 6.66 \times 10^{-15} \text{ M}$$

which gives pI as 1.90 and pAg as 14.18. After the equivalence point, the concentration of Ag^+ is determined by the amount of excess Ag^+, and the concentration of I^- is determined by the solubility of AgI in the presence of excess Ag^+. For example, after adding 35.0 mL of $AgNO_3$, we find that

$$[Ag^+] = \frac{M_{Ag} V_{Ag} - M_I V_I}{V_{Ag} + V_I}$$

$$[Ag^+] = \frac{(0.0500 \text{ M})(35.0 \text{ mL}) - (0.0250 \text{ M})(50.0 \text{ ml})}{35.0 \text{ mL} + 50.0 \text{ mL}}$$

$$[Ag^+] = 5.88 \times 10^{-3} \text{ M}$$

$$[I^-] = \frac{K_{sp,AgI}}{[Ag^+]} = \frac{8.32 \times 10^{-17}}{5.88 \times 10^{-3}} = 1.41 \times 10^{-14} \text{ M}$$
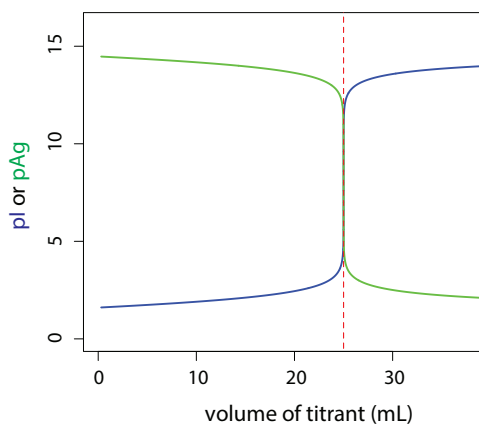
Figure SM9.23 The titration curve for 0.0250 M KI using 0.0500 M $AgNO_3$ as the titrant. The titration curve shown in **blue** is recorded by following the concentration of I^- and the titration curve shown in green is recorded by following the concentration of Ag^+. The **red** dashed line marks the volume of titrant at the equivalence point.

which gives pI as 13.85 and pAg as 2.23. Figure SM9.23 shows the full titration curve.

56. The titration of KI and KSCN with $AgNO_3$ is an example of a precipitation titration. Because AgI is less soluble than AgSCN, the titration's first equivalence point is reached when

$$n_I = M_I V_I = M_{Ag} V_{Ag} = n_{Ag}$$

where n is the moles of I^- or of Ag^+; thus

$$V_{eq.pt.1} = V_{Ag} = \frac{M_I V_I}{M_{Ag}} = \frac{(0.0500 \text{ M}) (25.0 \text{ mL})}{(0.0500 \text{ M})} = 25.0 \text{ mL}$$

Before the equivalence point, the concentration of Ag^+ is determined by the solubility of AgI in the presence of excess I^-. For example, after adding 10.0 mL of $AgNO_3$, we find that

$$[I^-] = \frac{M_I V_I - M_{Ag} V_{Ag}}{V_I + V_{Ag}}$$

$$[I^-] = \frac{(0.0500 \text{ M}) (25.0 \text{ mL}) - (0.0500 \text{ M}) (10.0 \text{ ml})}{25.0 \text{ mL} + 10.0 \text{ mL}}$$

$$[I^-] = 0.0214 \text{ M}$$

$$[Ag^+] = \frac{K_{sp,AgI}}{[I^-]} = \frac{8.32 \times 10^{-17}}{0.0214} = 3.89 \times 10^{-15} \text{ M}$$

which gives pAg as 14.41.

The titration's second equivalence point is reached when

$$n_I + n_{SCN} = M_I V_I + M_{SCN} V_{SCN} = M_{Ag} V_{Ag} = n_{Ag}$$

or after adding

$$V_{eq.pt.2} = V_{Ag} = \frac{M_I V_I + M_{SCN} V_{SCN}}{M_{Ag}} =$$

$$\frac{(0.0500 \text{ M}) (25.0 \text{ mL}) + (0.0500 \text{ M}) (25.0 \text{ mL})}{(0.0500 \text{ M})} = 50.0 \text{ mL}$$

of titrant. Between the two equivalence points, the concentration of Ag^+ is determined by the solubility of AgSCN in the presence of excess SCN^-. For example, after adding a total of 35.0 mL of $AgNO_3$, 10.0 mL of which react with SCN^-, we find that

$$[SCN^-] = \frac{M_{SCN} V_{SCN} - M_{Ag} (V_{Ag} - 25.0 \text{ ml})}{V_{SCN} + V_{Ag}}$$

$$[SCN^-] = \frac{(0.0500 \text{ M}) (25.0 \text{ mL}) - (0.0500 \text{ M}) (35.0 - 25.0 \text{ ml})}{25.0 \text{ mL} + 35.0 \text{ mL}}$$

$$[SCN^-] = 0.0125 \text{ M}$$

$$[Ag^+] = \frac{K_{sp,AgSCN}}{[I^-]} = \frac{1.1 \times 10^{-12}}{0.0125} = 8.8 \times 10^{-11} \text{ M}$$

which gives pAg as 10.05.

Finally, after the second equivalence point, the concentration of Ag^+ is determined by the amount of excess Ag^+. For example, after adding 60.0 mL of $AgNO_3$, we find that
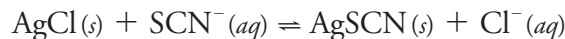
$$[Ag^+] = \frac{M_{Ag}V_{Ag} - M_I V_I - M_{SCN}V_{SCN}}{V_{Ag} + V_I}$$

$$[Ag^+] = \frac{\left\{\begin{array}{c}(0.0500\ M)(60.0\ mL) - (0.0500\ M)(25.0\ ml) \\ - (0.0500\ M)(25.0\ ml)\end{array}\right\}}{60.0\ mL + 25.0\ mL}$$

$$[Ag^+] = 5.88 \times 10^{-3}\ M$$

which gives pAg as 2.23. Figure SM9.24 shows the full titration curve.

57. (a) Because AgCl is more soluble than AgSCN, the SCN^- titrant displaces Cl^- from AgCl; that is, the equilibrium reaction

$$AgCl\,(s) + SCN^-\,(aq) \rightleftharpoons AgSCN\,(s) + Cl^-\,(aq)$$

favors the products.

(b) Because additional titrant is used, the apparent amount of unreacted Ag^+ is greater than the actual amount of unreacted Ag^+. In turn, this leads us to underestimate the amount of Cl^- in the sample, a negative determinate error.

(c) After we add the Ag^+ and allow AgCl to precipitate, we can filter the sample to remove the AgCl. We can then take a known volume of the filtrate and determine the concentration of excess Ag^+ in the filtrate.

(d) No. The K_{sp} for AgSCN of 1.1×10^{-12} is greater than the K_{sp} for AgBr of 5.0×10^{-13}; thus AgBr is the less soluble compound.

58. Before the equivalence point, the concentration of CrO_4^{2-} in solution is controlled by the solubility of $PbCrO_4$ and is, therefore, very small. What little CrO_4^{2-} is present reacts with the HNO_3, resulting in a steady but small increase in pH. Once the equivalence point is reached, the concentration of CrO_4^{2-} is determined by the volume of excess titrant, which quickly neutralizes the remaining HNO_3, causing the pH to change abruptly to basic levels. Figure SM9.25 shows the expected titration curve.

59. The volume of $AgNO_3$ reacting with KBr is the difference between the volume used to titrate the sample (25.13 mL) and the volume used to titrate the blank (0.65 mL), or 24.48 mL. The concentration of KBr in the sample is

To sketch an approximate titration curve, calculate any two points before the first equivalence point, any two points between the two equivalence points, and any two points after the second equivalence point. Use the lines passing through each pair of points and the vertical lines at the equivalence point volumes to sketch the titration curve.
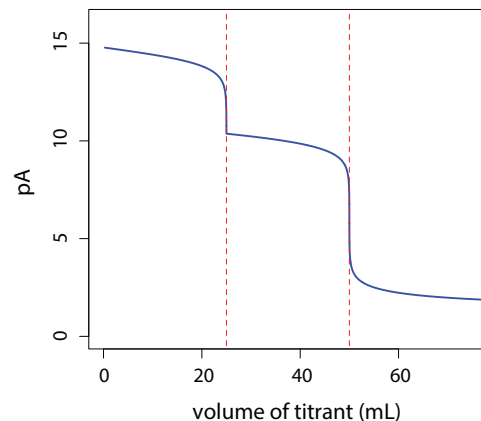
Figure SM9.24 The titration curve for the titration of a mixture of 0.0500 M KI and 0.0500 M KSCN using 0.0500 M $AgNO_3$ as the titrant. The titration curve shown in **blue** is recorded by following the concentration of Ag^+. The **red** dashed lines mark the volume of titrant at the equivalence points.
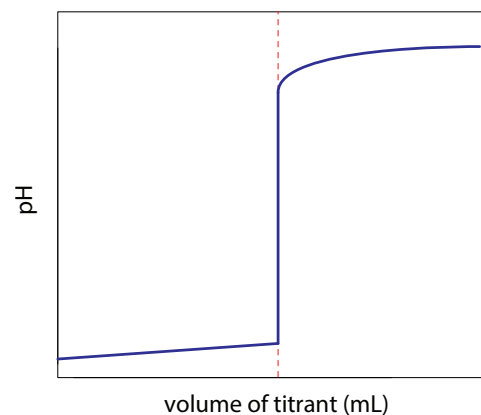
Figure SM9.25 The titration curve for Pb^{2+} using $KCrO_4$ as the titrant. The titration curve shown in **blue** is recorded by following the solution's pH. The **red** dashed line marks the volume of titrant at the equivalence point.

$$0.02448 \text{ L} \times \frac{0.04614 \text{ mol AgNO}_3}{\text{L}} \times$$

$$\frac{1 \text{ mol KBr}}{\text{mol AgNO}_3} \times \frac{119.00 \text{ g KBr}}{\text{mol KBr}} = 0.1344 \text{ g KBr}$$

$$\frac{0.1344 \text{ g KBr}}{0.5131 \text{ g sample}} \times 100 = 26.19\%\text{w/w KBr}$$

60. The total moles of $AgNO_3$ used in this analysis is

$$0.05000 \text{ L} \times \frac{0.06911 \text{ mol AgNO}_3}{\text{L}} = 3.456 \times 10^{-3} \text{ mol AgNO}_3$$

Of this, the moles reacting with the titrant is

$$0.02736 \text{ L} \times \frac{0.05781 \text{ mol KSCN}}{\text{L}} \times$$

$$\frac{1 \text{ mol AgNO}_3}{\text{mol KSCN}} = 1.582 \times 10^{-3} \text{ mol AgNO}_3$$

which leaves $3.456 \times 10^{-3} - 1.582 \times 10^{-3} = 1.874 \times 10^{-3}$ moles to react with the Na_2CO_3 in the original sample. The concentration of Na_2CO_3 in the original sample, therefore, is

$$1.874 \times 10^{-3} \text{ mol AgNO}_3 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{2 \text{ mol AgNO}_3} \times$$

$$\frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} = 0.09931 \text{ g Na}_2\text{CO}_3$$

$$\frac{0.09931 \text{ g Na}_2\text{CO}_3}{0.1093 \text{ g sample}} \times 100 = 90.9\%\text{w/w Na}_2\text{CO}_3$$

61. The total moles of Cl^- in the sample is determined by the moles of $AgNO_3$ used in the titration; thus

$$0.01946 \text{ L} \times \frac{0.07916 \text{ mol AgNO}_3}{\text{L}} \times$$

$$\frac{1 \text{ mol Cl}^-}{\text{mole AgNO}_3} = 1.540 \times 10^{-3} \text{ mol Cl}^-$$

The total moles of Cl^- in the sample also is equal to

$$1.540 \times 10^{-3} \text{ mol Cl}^- = 2 \times \text{mol BaCl}_2 + \text{mol NaCl}$$

Substituting in g/FW for mol $BaCl_2$ and for mol NaCl, and recognizing that the mass of NaCl is 0.1036 g – mass of $BaCl_2$ gives

$$1.540 \times 10^{-3} \text{ mol Cl}^- = \frac{2 \times \text{g BaCl}_2}{208.23 \text{ g/mol}} + \frac{0.1036 \text{ g} - \text{g BaCl}_2}{58.44 \text{ g/mol}}$$

Solving gives the mass of $BaCl_2$ as 0.03095 g; thus, the concentration of $BaCl_2$ in the original sample is

$$\frac{0.03095 \text{ g BaCl}_2}{0.1036 \text{ g sample}} \times 100 = 29.97\%\text{w/w BaCl}_2$$

Chapter 10

1. The following five equations provide the relationships between the four variables included in this problem

$$E = h\nu \quad E = \frac{hc}{\lambda} \quad \nu\lambda = c \quad \bar{\nu} = \frac{1}{\lambda} \quad E = hc\bar{\nu}$$

For the first row, given a wavelength of 4.50×10^{-9} m, we have

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{4.50 \times 10^{-9} \text{ m}} = 6.67 \times 10^{16} \text{ s}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{4.50 \times 10^{-9} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 2.22 \times 10^6 \text{ cm}^{-1}$$

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})}{4.50 \times 10^9 \text{ m}} = 4.42 \times 10^{-17} \text{ J}$$

For the second row, given a frequency of 1.33×10^{15} s^{-1}, we have

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m/s}}{1.33 \times 10^{15} \text{ s}^{-1}} = 2.26 \times 10^{-7} \text{ m}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.26 \times 10^{-7} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 4.42 \times 10^4 \text{ cm}^{-1}$$

$$E = h\nu = (6.626 \times 10^{-34} \text{ Js})(1.33 \times 10^{15} \text{ s}^{-1}) = 8.81 \times 10^{-19} \text{ J}$$

For the third row, given a wavenumber of 3215 cm^{-1}, we have

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{3215 \text{ cm}^{-1}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 3.11 \times 10^{-6} \text{ m}$$

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{3.11 \times 10^{-6} \text{ m}} = 9.65 \times 10^{13} \text{ s}^{-1}$$

$$E = h\nu = (6.626 \times 10^{-34} \text{ Js})(9.65 \times 10^{13} \text{ s}^{-1}) = 6.39 \times 10^{-20} \text{ J}$$

For the fourth row, given an energy of 7.20×10^{-19} J, we have

$$\lambda = \frac{hc}{E} = \frac{(6.626 \times 10^{-34} \text{ Js})(3.00 \times 10^8 \text{ m/s})}{7.20 \times 10^{-19} \text{ J}} = 2.76 \times 10^{-7} \text{ m}$$

$$\nu = \frac{E}{h} = \frac{7.20 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} = 1.09 \times 10^{15} \text{ s}^{-1}$$

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.76 \times 10^{-7} \text{ m}} \times \frac{1 \text{ m}}{100 \text{ cm}} = 3.62 \times 10^4 \text{ cm}^{-1}$$

2. The following two equations provide the relationships between the five variables included in this problem

$$A = \varepsilon b C \quad A = -\log T$$

For the first row we find that

$$A = \varepsilon b C = (1120 \text{ M}^{-1}\text{cm}^{-1})(1.00 \text{ cm})(1.40 \times 10^{-4} \text{ M}) = 0.157$$

$$T = 10^{-A} = 10^{-0.157} = 0.697 \text{ or } 69.7\% T$$

For the second row we find that

$$C = \frac{A}{\varepsilon b} = \frac{0.563}{(750 \ M^{-1} \ cm^{-1})(1.00 \ cm)} = 7.51 \times 10^{-4} \ M$$

$$T = 10^{-A} = 10^{-0.563} = 0.274 \ or \ 27.4\% \, T$$

For the third row we find that

$$b = \frac{A}{\varepsilon C} = \frac{0.225}{(440 \ M^{-1} \ cm^{-1})(2.56 \times 10^{-4} \ M)} = 2.00 \ cm$$

$$T = 10^{-A} = 10^{-0.225} = 0.596 \ or \ 59.6\% \, T$$

For the fourth row we find that

$$\varepsilon = \frac{A}{bC} = \frac{0.167}{(5.00 \ cm)(1.55 \times 10^{-3} \ M)} = 21.5 \ M^{-1} \ cm^{-1}$$

$$T = 10^{-A} = 10^{-0.167} = 0.681 \ or \ 68.1\% \, T$$

For the fifth row we find that

$$A = -\log T = -\log(0.333) = 0.478$$

$$C = \frac{A}{\varepsilon b} = \frac{0.478}{(565 \ M^{-1} \ cm^{-1})(1.00 \ cm)} = 8.46 \times 10^{-4} \ M$$

For the sixth row we find that

$$A = -\log T = -\log(0.212) = 0.674$$

$$b = \frac{A}{\varepsilon C} = \frac{0.674}{(1550 \ M^{-1} \ cm^{-1})(4.35 \times 10^{-3} \ M)} = 0.100 \ cm$$

For the seventh row we find that

$$A = -\log T = -\log(0.813) = 0.0899$$

$$\varepsilon = \frac{A}{bC} = \frac{0.0899}{(10.00 \ cm)(1.20 \times 10^{-4} \ M)} = 74.9 \ M^{-1} \ cm^{-1}$$

3. To find the new %T, we first calculate the solution's absorbance as it is a linear function of concentration; thus

$$A = -\log T = -\log(0.350) = 0.456$$

Diluting 25.0 mL of solution to 50.0 mL cuts in half the analyte's concentration and, therefore, its absorbance; thus, the absorbance is 0.228 and the transmittance is

$$T = 10^{-A} = 10^{-0.228} = 0.592 \ or \ 59.2\% \, T$$

4. To find the new %T, we first calculate the solution's absorbance as it is a linear function of pathlength; thus

$$A = -\log T = -\log(0.850) = 0.0706$$

Increasing the pathlength by a factor of 10 increases the absorbance by a factor of 10 as well; thus, the absorbance is 0.706 and the transmittance is

$$T = 10^{-A} = 10^{-0.706} = 0.197 \text{ or } 19.7\% T$$

5. To calculate the expected molar absorptivity, ε, first we calculate the molar concentration of $K_2Cr_2O_7$

$$\frac{60.06 \text{ mg } K_2Cr_2O_7}{L} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times$$

$$\frac{1 \text{ mol } K_2Cr_2O_7}{294.18 \text{ g } K_2Cr_2O_7} = 2.042 \times 10^{-4} \text{ M } K_2Cr_2O_7$$

and then the expected molar absorptivity

$$\varepsilon = \frac{A}{bC} = \frac{0.640}{(1.00 \text{ cm})(2.042 \times 10^{-4} \text{ M})} = 3134 \text{ M}^{-1} \text{ cm}^{-1}$$

6. For a mixture of HA and A^-, Beer's law requires that

$$A = \varepsilon_{HA} b C_{HA} + \varepsilon_A b C_A$$

where ε_{HA} and C_{HA} are the molar absorptivity and the concentration of the analyte's weak acid form, HA, and ε_A and C_A are the molar absorptivity and the concentration of the its weak base form, A^-.

(a) When $\varepsilon_{HA} = \varepsilon_A = 2000 \text{ M}^{-1} \text{ cm}^{-1}$, Beer's law becomes

$$A = (2000 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})(C_{HA} + C_A) = 2000 \text{ M}^{-1} C_{total}$$

where $C_{total} = C_{HA} + C_A$; thus, when C_{total} is 1.0×10^{-5}, the absorbance is

$$A = (2000 \text{ M}^{-1})(1.0 \times 10^{-5} \text{ M}) = 0.020$$

The remaining absorbance values are calculated in the same way and gathered here is this table

C_{total} (M)	Absorbance
1.0×10^{-5}	0.020
3.0×10^{-5}	0.060
5.0×10^{-5}	0.100
7.0×10^{-5}	0.140
9.0×10^{-5}	0.180
11.0×10^{-5}	0.220
13.0×10^{-5}	0.260

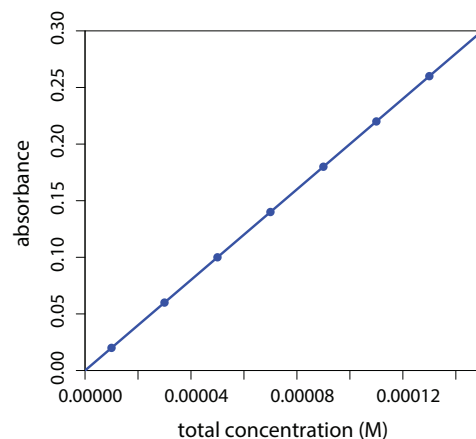Figure SM10.1 shows the resulting calibration curve, which is linear and shows no deviations from ideal behavior.

Figure SM10.1 Beer's law calibration curve for the weak acid in Problem 6a where $\varepsilon_{HA} = \varepsilon_A = 2000 \text{ M}^{-1} \text{ cm}^{-1}$. The **blue** dots are the calculated absorbance values; the **blue** line is from a linear regression on the data.

(b) When $\varepsilon_{HA} = 2000$ M^{-1} cm^{-1} and $\varepsilon_A = 500$ M^{-1} cm^{-1}, Beer's law becomes

$$A = (2000 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}^{-1}) C_{HA}$$
$$+ (500 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}^{-1}) C_A$$

$$A = (2000 \text{ M}^{-1}) C_{HA} + (500 \text{ M}^{-1}) C_A$$

To find C_{HA} and C_A, we take advantage of the acid dissociation reaction for HA

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$
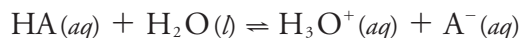
for which the equilibrium constant is

$$K_a = 2.0 \times 10^{-5} = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+] C_A}{C_{HA}} = \frac{(x)(x)}{C_{total} - x}$$

Given C_{total}, we can solve this equation for x; for example, when C_{total} is 1.0×10^{-5}, x is 7.32×10^{-6}. The concentrations of HA and A$^-$, therefore, are

$$C_{HA} = C_{total} - x = 1.0 \times 10^{-5} \text{ M} -$$
$$7.32 \times 10^{6} \text{ M} = 2.68 \times 10^{-6} \text{ M}$$

$$C_A = x = 7.32 \times 10^{6} \text{ M}$$

and the absorbance is

$$A = (2000 \text{ M}^{-1})(2.68 \times 10^{-6} \text{ M}) +$$
$$(500 \text{ M}^{-1})(7.32 \times 10^{-6} \text{ M}) = 0.009$$

The remaining absorbance values are calculated in the same way and gathered here is this table

C_{total} (M)	C_{HA} (M)	C_A (M)	Absorbance
1.0×10^{-5}	2.68×10^{-6}	7.32×10^{-6}	0.009
3.0×10^{-5}	1.35×10^{-5}	1.65×10^{-5}	0.035
5.0×10^{-5}	2.68×10^{-5}	2.32×10^{-5}	0.065
7.0×10^{-5}	4.17×10^{-5}	2.83×10^{-5}	0.098
9.0×10^{-5}	5.64×10^{-5}	3.36×10^{-5}	0.130
11.0×10^{-5}	7.20×10^{-5}	3.80×10^{-5}	0.163
13.0×10^{-5}	8.80×10^{-5}	4.20×10^{-5}	0.197

Figure SM10.2 shows the resulting calibration curve, in **red**, along with the calibration curve from part (a), in **blue**, for comparison. Two features of the data for part (b) show evidence of a chemical limitation to Beer's law: first, the regression line's y-intercept deviates from its expected value of zero; and second, the fit of the individual data points to the regression line shows evidence of curvature, with the regression

The solution of this equation is left to you, although you should recognize that you can rewrite the K_a expression in the form of a quadratic equation and solve for the chemically significant root. See Chapter 6G to review methods for solving equilibrium problems.

As expected, the absorbance is less for a solution where C_{total} is 1.0×10^{-5} when ε_A is 500 M^{-1} cm^{-1} than when ε_A is 2000 M^{-1} cm^{-1}.
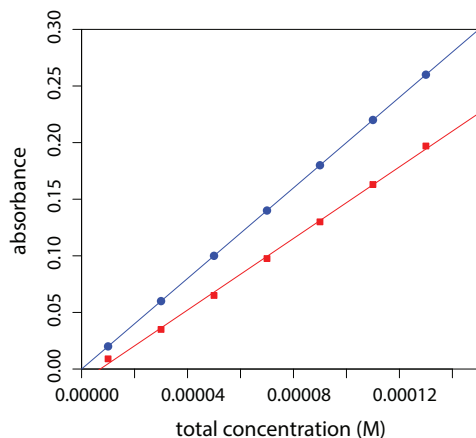

Figure SM10.2 Beer's law calibration curves for the weak acid in Problem 6a and 6b: for the data in **blue**, $\varepsilon_{HA} = \varepsilon_A = 2000$ M^{-1} cm^{-1}, and for the data in **red**, $\varepsilon_{HA} = 2000$ M^{-1} cm^{-1} and $\varepsilon_A = 500$ M^{-1} cm^{-1}. For both sets of data, the symbols are the calculated absorbance values and the line is from a linear regression on the data.

line underestimating slightly the absorbance values for the largest and the smallest values of C_{total}. The source of this error is clear when we look more closely at how C_{HA} and C_A change as a function of C_{total}. For example, when C_{total} is 1.0×10^{-5}, 73% of the weak acid is present as A^-; however, when C_{total} is 9.0×10^{-5}, only 37% of the weak acid is present as A^-. Because HA and A^- absorb to different extents, increasing C_{total} by a factor of $9\times$ does not increase the absorbance by a factor of $9\times$ (that is, from 0.009 to 0.081), because the relative contribution of the more strongly absorbing HA increases and the relative contribution of the more weakly absorbing A^- decreases.

(c) One way to resolve the chemical limitation in part (b) is to buffer the solution, as the relative concentration of HA and A^- in a buffer is fixed. The pH of an HA/A^- buffer is given by the Henderson-Hasselbalch equation

$$pH = pK_a + \log\frac{[A^-]}{[HA]} = 4.70 + \log\frac{C_A}{C_{HA}}$$

Substituting in a pH of 4.50 and $C_{total} - C_{HA}$ for C_A

$$4.50 = 4.70 + \log\frac{C_{total} - C_{HA}}{C_{HA}}$$

and solving for C_{HA} gives

$$-0.20 = \log\frac{C_{total} - C_{HA}}{C_{HA}}$$

$$0.631 = \frac{C_{total} - C_{HA}}{C_{HA}}$$

$$C_{HA} = \frac{C_{total}}{1.631}$$

Given C_{total}, we can calculate C_{HA}, C_A, and the absorbance; for example, when C_{total} is 1.0×10^{-5}, we find

$$C_{HA} = \frac{1.0 \times 10^{-5}\ M}{1.631} = 6.31 \times 10^{-6}\ M$$

$$C_A = 1.0 \times 10^{-5}\ M - 6.13 \times 10^{-6}\ M = 3.87 \times 10^{-6}\ M$$

$$A = (2000\ M^{-1})(6.31 \times 10^{-6}\ M) +$$
$$(500\ M^{-1})(3.87 \times 10^{-6}\ M) = 0.015$$

The remaining absorbance values are calculated in the same way and gathered here is this table

C_{total} (M)	C_{HA} (M)	C_A (M)	Absorbance
1.0×10^{-5}	6.13×10^{-6}	3.87×10^{-6}	0.015
3.0×10^{-5}	1.84×10^{-5}	1.16×10^{-5}	0.043
5.0×10^{-5}	3.07×10^{-5}	1.93×10^{-5}	0.071

Here is another way to understand the problem. When C_{total} is 1.0×10^{-5}, the average molar absorptivity is

$$\varepsilon = \frac{0.009}{(1.00\ cm^{-1})(1.0 \times 10^{-5})}$$

$$\varepsilon = 900\ M^{-1}cm^{-1}$$

When C_{total} is 9.0×10^{-5}, however, the average molar absorptivity is

$$\varepsilon = \frac{0.130}{(1.00\ cm^{-1})(9.0 \times 10^{-5})}$$

$$\varepsilon = 1440\ M^{-1}cm^{-1}$$

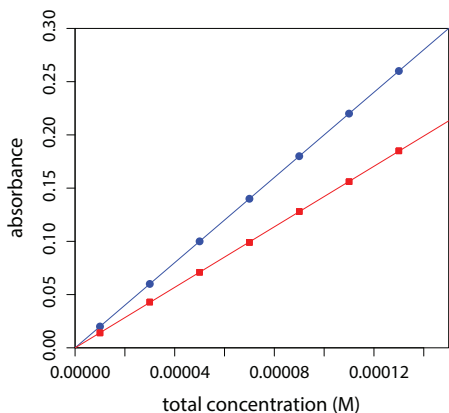See Chapter 6H to review buffers, in general, and the Henderson-Hasselbalch equation, more specifically.

Figure SM10.3 Beer's law calibration curves for the weak acid in Problem 6a and 6c: for the data in **blue**, $\varepsilon_{HA} = \varepsilon_A = 2000$ M^{-1} cm^{-1}, and for the data in **red**, $\varepsilon_{HA} = 2000$ M^{-1} cm^{-1} and $\varepsilon_A = 500$ M^{-1} cm^{-1}, and the solutions are buffered to a pH of 4.50. For both sets of data, the symbols are the calculated absorbance values and the line is from a linear regression on the data.

C_{total} (M)	C_{HA} (M)	C_A (M)	Absorbance
7.0×10^{-5}	4.29×10^{-5}	2.71×10^{-5}	0.099
9.0×10^{-5}	5.52×10^{-5}	3.48×10^{-5}	0.128
11.0×10^{-5}	6.74×10^{-5}	4.26×10^{-5}	0.156
13.0×10^{-5}	7.97×10^{-5}	5.03×10^{-5}	0.185

Figure SM10.3 shows the resulting calibration curve, in **red**, along with the calibration curve from part (a), in **blue**, for comparison. Although the absorbance for each standard is smaller than for the original data—because $\varepsilon_A = 500$ M^{-1} cm^{-1} instead of 2000 M^{-1} cm^{-1} as for the original data—there is no evidence of a chemical limitation to Beer's law: more specifically, the regression line's y-intercept does not deviate from its expected value of zero, and the fit of the individual data points to the regression line shows no evidence of curvature.

7. (a) Let's begin with the equation

$$A = -\log\frac{P_T' + P_T''}{P_0' + P_0''}$$

and then expand the logarithmic function on the equation's right side

$$A = \log(P_0' + P_0'') - \log(P_T' + P_T'')$$

Next, we need to find a relationship between P_T and P_0 (for any wavelength). To do this, we start with Beer's law

$$A = -\log\frac{P_T}{P_0} = \varepsilon bC$$

and then solve for P_T in terms of P_0

$$\log\frac{P_T}{P_0} = -\varepsilon bC$$

$$\frac{P_T}{P_0} = 10^{-\varepsilon bC}$$

$$P_T = P_0 \times 10^{-\varepsilon bC}$$

Substituting this general relationship back into our wavelength-specific equation for absorbance, we obtain

$$A = \log(P_0' + P_0'') - \log(P_0' \times 10^{-\varepsilon'bC} + P_0'' \times 10^{-\varepsilon''bC})$$

If $\varepsilon' = \varepsilon'' = \varepsilon$, then this equation becomes

$$A = \log(P_0' + P_0'') - \log(P_0' \times 10^{-\varepsilon bC} + P_0'' \times 10^{-\varepsilon bC})$$

$$A = \log(P_0' + P_0'') - \log\{(P_0' + P_0'') \times 10^{-\varepsilon bC}\}$$

$$A = \log(P_0' + P_0'') - \log(P_0' + P_0'') - \log(10^{-\varepsilon bC})$$

$$A = -\log(10^{-\varepsilon bC})$$

which we simplify to arrive at the simple form of Beer's law

$$A = \varepsilon b C$$

(b) To calculate the absorbance, we begin with this equation from part (a)

$$A = \log(P_0' + P_0'') - \log(P_0' \times 10^{-\varepsilon'bC} + P_0'' \times 10^{-\varepsilon''bC})$$

which, given that $P_0' = P_0'' = 1$, we can simplify to

$$A = \log(2) - \log(10^{-\varepsilon'bC} + 10^{-\varepsilon''bC})$$
$$A = 0.301 - \log(10^{-\varepsilon'bC} + 10^{-\varepsilon''bC})$$

To see how the values of ε' and ε'' affect the absorbance, we calculate the absorbance for different concentrations of analyte; if the concentration is 1×10^{-4} M and the pathlength is 1.00 cm, then the absorbance is

$$A = 0.301 - \log\left(\begin{array}{c} 10^{-(1000\,M^{-1}\,cm^{-1})(1.00\,cm)(1.0\times10^{-4}\,M)} + \\ 10^{-(1000\,M^{-1}\,cm^{-1})(1.00\,cm)(1.0\times10^{-4}\,M)} \end{array} \right) = 0.100$$

when $\varepsilon' = \varepsilon'' = 1000\ M^{-1}\ cm^{-1}$ and is

$$A = 0.301 - \log\left(\begin{array}{c} 10^{-(1900\,M^{-1}\,cm^{-1})(1.00\,cm)(1.0\times10^{-4}\,M)} + \\ 10^{-(100\,M^{-1}\,cm^{-1})(1.00\,cm)(1.0\times10^{-4}\,M)} \end{array} \right) = 0.091$$

when $\varepsilon' = 1900\ M^{-1}\ cm^{-1}$ and $\varepsilon'' = 100\ M^{-1}\ cm^{-1}$. Additional values for other concentrations are gathered here

concentration (M)	absorbance when $\varepsilon' = 1000\ M^{-1}\ cm^{-1}$ $\varepsilon'' = 1000\ M^{-1}\ cm^{-1}$	absorbance when $\varepsilon' = 1900\ M^{-1}\ cm^{-1}$ $\varepsilon'' = 100\ M^{-1}\ cm^{-1}$
2.0×10^{-5}	0.020	0.020
4.0×10^{-5}	0.040	0.039
6.0×10^{-5}	0.060	0.057
8.0×10^{-5}	0.080	0.074
1.0×10^{-4}	0.100	0.091

with the resulting calibration curves shown in Figure SM10.4. Note that the relative difference between the two sets of data becomes increasingly larger at higher concentrations, suggesting that the calibration curve when $\varepsilon' = 1900\ M^{-1}\ cm^{-1}$ and $\varepsilon'' = 100\ M^{-1}\ cm^{-1}$ is not a straight-line; this is even easier to see when extended to even greater concentrations, as seen in Figure SM10.5.

8.   The equation that relates P_0, P_T, and A to each other is

$$A = -\log\frac{P_T}{P_0}$$

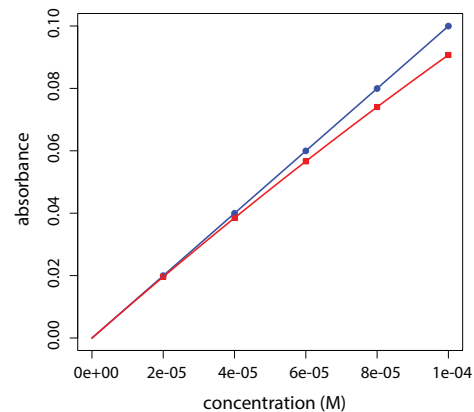Letting $P_0 = 100$ and solving for P_T

Figure SM10.4 Beer's law calibration curves when light is absorbed at two wavelengths: for the data in **blue**, $\varepsilon' = \varepsilon'' = 1000\ M^{-1}\ cm^{-1}$, and for the data in **red**, $\varepsilon' = 1900\ M^{-1}\ cm^{-1}$ and $\varepsilon'' = 100\ M^{-1}$ cm^{-1}. Figure SM 10.5 shows the same data over a broader range of concentrations.
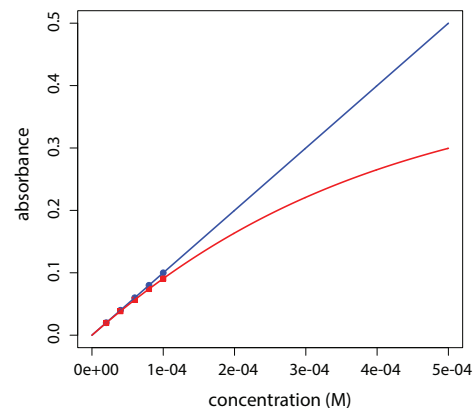

Figure SM10.5 Beer's law calibration curves when light is absorbed at two wavelengths: for the data in **blue**, $\varepsilon' = \varepsilon'' = 1000\ M^{-1}\ cm^{-1}$, and for the data in **red**, $\varepsilon' = 1900\ M^{-1}\ cm^{-1}$ and $\varepsilon'' = 100\ M^{-1}$ cm^{-1}. The individual data points are identical to those in Figure SM 10.4.
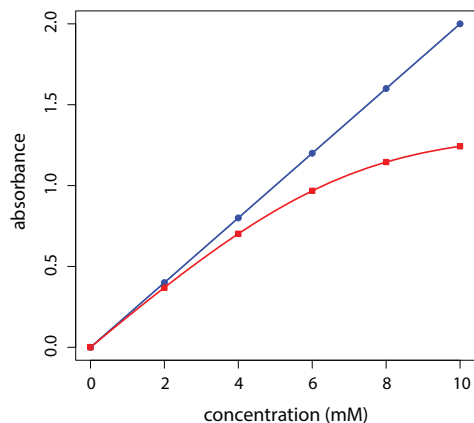
Figure SM10.6 Beer's law calibration curves in the absence of stray light (**blue**), and in the presence of stray light (**red**) when P_{stray} is 5% of P_0.

$$P_T = 100 \times 10^{-A}$$

allows us to calculate P_T for any absorbance; thus, when the absorbance is 0.40, P_T is 39.8 in the absence of stray light ($P_{stray} = 0$). When stray light is present at 5% of P_0 (a P_{stray} of 5) the absorbance is

$$A = \log\frac{P_0 + P_{stray}}{P_T + P_{stray}} = \log\frac{100 + 5}{39.8 + 5} = 0.37$$

Results for all samples are summarized in the following table

concentration (mM)	absorbance ($P_{stray} = 0$)	P_T	absorbance ($P_{stray} = 5$)
0.0	0.00	100.	0.00
2.0	0.40	39.8	0.37
4.0	0.80	15.8	0.70
6.0	1.20	6.31	0.97
8.0	1.60	2.51	1.15
10.0	2.00	1.00	1.24

and the resulting calibration curves are shown in Figure SM10.6; note that there is substantial curvature when P_{stray} is 5% of P_0.

9. Yes. The new cuvette likely will have a slightly different pathlength and slightly different optical properties than did the original cuvette. The importance of the first difference is obvious because absorbance, A, is proportional to the cuvette's pathlength, b.

$$A = \varepsilon bC$$

The importance of the second difference is less obvious; however, because absorbance, A, is related logarithmically to transmittance, T, and transmittance is inversely proportional to the amount of light that reaches the detector in the absence of analyte, P_0

$$A = -\log T = -\log\frac{P_T}{P_0}$$

any difference between the optical properties of the two cuvettes introduces a source of determinate error.

10. This method for manganese relies on the direct oxidation of Mn^{2+}, which is colorless, to MnO_4^-, which is purple. The only critical requirement is that each sample and standard has sufficient time for the oxidation reaction to go to completion: as long as this is true, we can prepare the samples and standards at different times and do not need to reproduce the exact reaction conditions.

The method for glucose, on the other hand, relies on an indirect analysis in which glucose effects the partial reduction of $Fe(CN)_6^{3-}$, which is yellow, to $Fe(CN)_6^{4-}$, which is colorless. The extent of this

reaction depends on the reaction's kinetics, which means that maintaining a constant reaction time and reaction temperature for all samples and standards is critical.

11. (a) A blank should contain all reagents except the analyte; thus, the blank for this procedure should include 5 mL of thioglycolic acid, 2 mL of 20% w/v ammonium citrate, and 5 mL of 0.22 M NH_3 diluted to 50 mL in a volumetric flask.

(b) No effect. By including ammonium citrate and thioglycolic acid in the blank, we account for the contribution of any trace impurity of iron.

(c) The choice to use a sample that contains approximately 0.1 g of Fe^{3+} ensures that the sample, as prepared, has a concentration of Fe^{3+} that falls within the range of concentrations of the external standards. To see that this is true, note that bringing 100 mg of Fe^{3+} to volume in a 1–L volumetric flask gives a solution that is 100 ppm Fe^{3+}. Diluting a 1-mL portion of this solution to 50 mL gives a final concentration of 2 ppm Fe^{3+}.

(d) Because we underestimate the 100-mL volumetric flask's true volume, the actual concentration of the 100-ppm Fe^{3+} standard is greater than 100 ppm. We use this standard to prepare all subsequent standards; thus, in turn, we underreport their concentrations. As we see in Figure SM10.7, if we use the resulting calibration curve, we will underreport the concentration of Fe^{3+} in our samples.

12. Let's assume our sample is 50% w/w Fe as this is in the middle of the expected range of concentrations. The concentration of iron in the 1-L volumetric flask, and thus the concentration of iron in the 5-mL volumetric pipet, is

$$\frac{0.5 \text{ g sample} \times \dfrac{50 \text{ g Fe}}{100 \text{ g sample}} \times \dfrac{1000 \text{ mg}}{\text{g}}}{1.0 \text{ L}} = 250 \text{ mg/L Fe}$$

We can dilute the 5-mL sample of this solution in one of many possible volumetric flasks, which give us a range of possible concentrations to consider; thus

volumetric flask	mg Fe/L	volumetric flask	mg Fe/L
10 mL	125	250 mL	5
25 mL	50	500 mL	2.5
50 mL	25	1000 mL	1.25
100 mL	12.5		

Our standard solutions of iron have concentrations that range from 5-20 mg/L. To avoid the need to extrapolate the calibration curve to a higher concentration of iron, which increases uncertainty, we do not
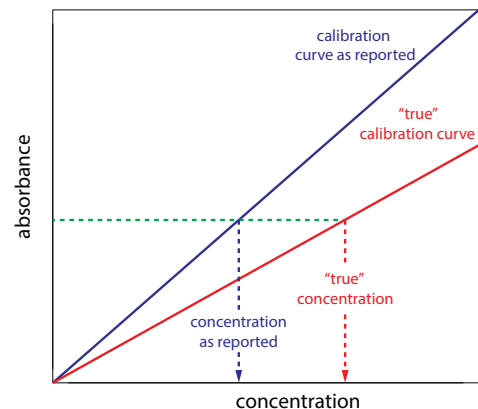
Figure SM10.7 Illustration showing how underestimating the concentration of a standard results in underreporting the concentration of analyte in the sample: text and lines in **blue** are data and results as reported; text and lines in **red** show the "true" results; and the dashed **green** line shows the sample's absorbance.

See Chapter 5D to review linear regression and the affect of an extrapolation on the uncertainty in a regression line's slope and y-intercept.

want to use the 10-mL, 25-mL, or 50-mL volumetric flasks. The best option is the 100-mL volumetric flask as this ensures that the samples have concentrations of iron that fall near the center of the calibration curve where the uncertainty in the calibration curve is at its smallest.

13. (a) If the cola is colored, then it will contribute to the measured absorbance and interfere with the analysis. Because the ingredients for commercial colas are proprietary, it is not possible to prepare a blank that corrects for this absorbance.

(b) One approach is to include a step in the procedure in which we either extract the analyte, PO_4^{3-}, from the sample, or extract from the sample those constituents responsible for the color.

(c) The presence of gas bubbles in the optical path shortens the pathlength through the sample, which introduces a systematic error; bubbles also scatter light, which introduces additional random error into the analysis.

(d) A suitable blank will consist of 2 mL of the ascorbic acid reducing solution diluted to volume in a 5-mL volumetric flask.

(e) Substituting the sample's absorbance into the equation for the calibration curve gives the concentration of P_2O_5 as 0.8125 ppm. The concentration of P in the sample as analyzed is

$$\frac{0.8125 \text{ mg } P_2O_5}{L} \times \frac{61.95 \text{ g P}}{141.94 \text{ g } P_2O_5} = 0.3546 \text{ mg P/L}$$

or 0.3546 ppm P. The concentration of P in the original sample is

$$0.3546 \text{ ppm P} \times \frac{5.00 \text{ mL}}{250 \text{ μL}} \times \frac{1000 \text{ μL}}{\text{mL}} \times \frac{50.00 \text{ mL}}{2.50 \text{ mL}} = 142 \text{ mg P/L}$$

14. (a) Using Beer's law for copper at a wavelength of 732.0 nm

$$A = 0.338 = \varepsilon bC = (95.2 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{Cu}$$

we find that the concentration of Cu^{2+} is 3.55×10^{-3} M.

(b) For a binary mixture of copper and cobalt, we must solve the following pair of simultaneous equations derived from Beer's law

$$0.453 = (2.11 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{Co}$$
$$+ (95.2 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{Cu}$$

$$0.107 = (15.8 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{Co}$$
$$+ (2.32 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{Cu}$$

Multiplying through the second equation by 2.11/15.8 and then subtracting the second equation from the first equation gives

$$0.4387 = (94.89 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{Cu}$$

for which we find that the concentration of Cu^{2+} is 4.62×10^{-3} M. Substituting this concentration back into either of the first two equations gives the concentration of Co^{2+} as 6.24×10^{-3} M.

(c) For a ternary mixture of copper, cobalt, and nickel we must solve the following three simultaneous equations derived from Beer's law

$$0.423 = (2.11 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Co}$$
$$+ (95.2 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Cu}$$
$$+ (3.03 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Ni}$$

$$0.184 = (15.8 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Co}$$
$$+ (2.32 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Cu}$$
$$+ (1.79 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Ni}$$

$$0.291 = (3.11 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Co}$$
$$+ (7.73 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Cu}$$
$$+ (13.5 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Ni}$$

Multiplying through the first equation by 15.8/2.11 and then subtracting the first equation from the second equation gives

$$-2.9835 = -(710.55 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Cu}$$
$$- (20.899 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Ni}$$

Multiplying through the third equation by 15.8/3.11 and then subtracting the second equation from the third equation gives

$$-1.2944 = -(36.951 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Cu}$$
$$- (66.795 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Ni}$$

With two equations and two unknowns, we solve these equations using the same general approach; thus, multiplying through the second of these equations by 710.55/36.951 and subtracting from the first equation leaves us with

$$21.907 = (1263.54 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})\, C_{Ni}$$

for which the concentration of Ni^{2+} is 1.73×10^{-2} M. Substituting back gives the concentration of Cu^{2+} as 3.69×10^{-3} M and the concentration of Co^{2+} as 9.14×10^{-3} M.

15. For the standard solution of phenol we have

$$A = 0.424 = abC = a(1.00 \text{ cm})(4.00 \text{ ppm})$$

where a is phenol's absorptivity (which we use here in place of the molar absorptivity, ε, because concentration is expressed in ppm instead of M). Solving for a gives its value as $0.106 \text{ ppm}^{-1} \text{ cm}^{-1}$. Using this value of a, we find that the concentration of phenol in the sample as analyzed is
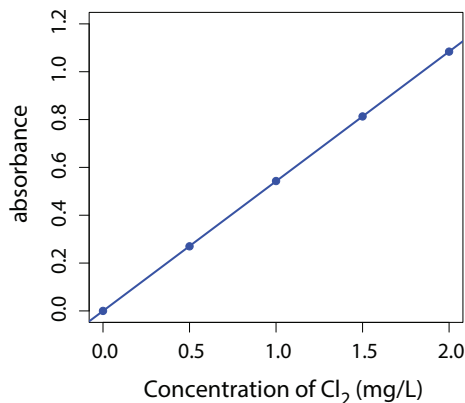
Figure SM10.8 Calibration data and calibration curve for Problem 17. The **blue** dots give the absorbance values for the blank and for the standards, and the **blue** regression line is the best fit to the data.
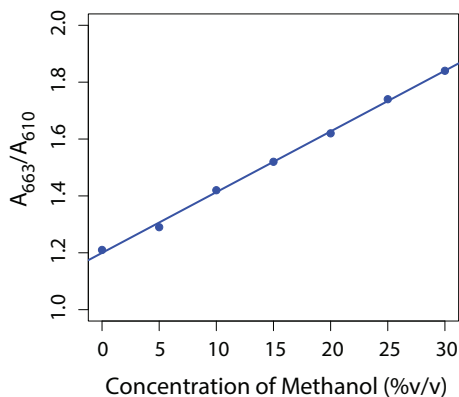

Figure SM10.9 Calibration data and calibration curve for Problem 18. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

$$C_{phenol} = \frac{A}{ab} = \frac{0.394}{(0.106 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm})} = 3.72 \text{ ppm}$$

Because we diluted the original sample by a factor of $2\times$, the concentration of phenol in the original sample is 7.44 ppm.

16. Substituting the absorbance into the equation for the calibration curve gives the concentration of Fe^{2+} as 1.16×10^{-5} M, or

$$\frac{1.16 \times 10^{-5} \text{ mol Fe}^{2+}}{L} \times \frac{55.845 \text{ g Fe}^{2+}}{\text{mol Fe}^{2+}}$$

$$\times \frac{1000 \text{ mg}}{g} = 0.648 \text{ mg Fe}^{2+}/L$$

17. Figure SM10.8 shows the calibration curve for the four standards and the blank, the calibration equation for which is

$$A = -2.0 \times 10^{-4} + (0.5422 \text{ mg}^{-1}\text{L}) \times C_{Cl_2}$$

Substituting the sample's absorbance into the calibration equation gives the concentration of Cl_2 as 0.209 mg Cl_2/L.

18. Figure SM10.9 shows the calibration curve for the seven standards, the calibration equation for which is

$$\frac{A_{663}}{A_{610}} = 1.200 + (2.136 \times 10^{-2} \text{ %v/v}^{-1}) C_{methanol}$$

For the sample, we have $A_{663}/A_{610} = 1.07/0.75 = 1.427$, which, when substituted back into the calibration equation gives the concentration of methanol in the sample as 10.6% v/v.

19. The spectrophotometric determination of serum barbiturates uses the absorbance at a pH of 10 as a means of correcting the absorbance at a pH of 13 for contributions from the sample's matrix; thus, the corrected absorbance for any standard or sample is

$$A_{barb} = A_{pH13} - \frac{V_{samp} + V_{NH_4Cl}}{V_{samp}} \times A_{pH10}$$

Using the data for the standard, we find a corrected absorbance of

$$A_{barb} = 0.295 - \frac{3.00 \text{ mL} + 0.50 \text{ mL}}{3.00 \text{ mL}} \times 0.002 = 0.293$$

Substituting this absorbance into Beer's law

$$0.293 = a(1.00 \text{ cm})(3.0 \text{ mg}/100 \text{ mL})$$

gives an absorptivity, a, of 9.77 mL cm^{-1} mg^{-1} for barbital. The corrected absorbance for the sample is

$$A_{barb} = 0.115 - \frac{3.00 \text{ mL} + 0.50 \text{ mL}}{3.00 \text{ mL}} \times 0.023 = 0.0882$$

which gives the concentration of barbital as

$$C_{barb} = \frac{A_{barb}}{ab} =$$

$$\frac{0.0882}{(9.77 \text{ mL cm}^{-1} \text{ mg}^{-1})(1.00 \text{ cm})} = 9.0 \times 10^{-3} \text{ mg/mL}$$

or 0.90 mg/100 mL.

20. The concentration of aspirin, C_{asp}, is determined using the absorbance at 277 nm where it is the only analyte that absorbs; thus

$$0.600 = (0.00682 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{asp}$$

which gives C_{asp} as 87.98 ppm in the sample as analyzed. To find the amount of aspirin in the analgesic tablet, we account for the sample preparation

$$87.98 \text{ ppm} \times \frac{100.0 \text{ mL}}{20.00 \text{ mL}} \times 0.5000 \text{ L} = 220 \text{ mg aspirin}$$

To find the concentrations of caffeine, C_{caf}, and of phenacetin, C_{phen}, we must solve the following pair of simultaneous equations for the absorbance at 250 nm and at 275 nm where they are the only analytes that absorb

$$0.466 = (0.0131 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{caf}$$
$$+ (0.0702 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{phen}$$

$$0.164 = (0.0485 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{caf}$$
$$+ (0.0159 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) C_{phen}$$

Multiplying through the second equation by 0.0131/0.0485 and then subtracting the second equation from the first equation gives

$$0.4217 = (0.06591 \text{ ppm}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}^{-1}) C_{phen}$$

for which we find that the concentration of phenacetin is 6.40 ppm. Substituting this concentration back into either of the first two equations gives the concentration of caffeine as 1.29 ppm. These are their respective concentrations as analyzed; the amount of each in the analgesic tablet is

$$6.40 \text{ ppm} \times \frac{200.0 \text{ mL}}{2.00 \text{ mL}} \times 0.2500 \text{ L} = 160 \text{ mg phenacetin}$$

$$1.29 \text{ ppm} \times \frac{200.0 \text{ mL}}{2.00 \text{ mL}} \times 0.2500 \text{ L} = 32 \text{ mg caffeine}$$

21. The concentration of SO_2 in the standard as analyzed is

$$15.00 \text{ ppm SO}_2 \times \frac{1.00 \text{ mL}}{25.00 \text{ mL}} = 0.600 \text{ ppm SO}_2$$

Substituting this concentration into Beer's law

$$0.181 = a(1.00 \text{ cm})(0.600 \text{ ppm SO}_2)$$

we find that the absorptivity, a, of SO_2 is 0.302 ppm^{-1} cm^{-1}. Next, we calculate the concentration of SO_2 in the sample as analyzed, finding that it is

$$C_{SO_2} = \frac{A}{bC} =$$

$$\frac{0.485}{(1.00 \text{ cm})(0.302 \text{ ppm}^{-1} \text{ cm}^{-1})} = 1.61 \text{ ppm } SO_2$$

This is, of course, the concentration of SO_2 in solution; to find its concentration in the sample of air, we determine the micrograms of SO_2 in the sample

$$\frac{1.61 \text{ mg } SO_2}{L} \times \frac{1000 \text{ μg}}{\text{mg}} \times 0.02500 \text{ L} = 40.2 \text{ μg } SO_2$$

the mass of the air collected

$$\frac{1.6 \text{ L}}{\text{min}} \times 75 \text{ min} \times \frac{1.18 \text{ g air}}{L} = 142 \text{ g air}$$

and the concentration

$$\frac{40.2 \text{ μg } SO_2}{142 \text{ g air}} = 0.28 \text{ ppm } SO_2$$

22. To find the amount of carbon monoxide in a sample, we first calculate the partial pressure of CO using the equation for the calibration curve, and then calculate the %CO relative to the total pressure; for example, the partial pressure of CO in the first sample is

$$P_{CO} = \frac{0.1146 + 1.1 \times 10^{-4}}{9.9 \times 10^{-4} \text{ torr}^{-1}} = 116 \text{ torr}$$

which makes the %CO in the sample

$$\frac{116 \text{ torr}}{595 \text{ torr}} \times 100 = 19.5\%$$

The results for all five samples are gathered here

absorbance	P_{CO} (torr)	P_{total} (torr)	%CO
0.1146	116	595	19.5
0.0642	65.0	354	18.4
0.0591	59.8	332	18.0
0.0412	41.7	233	17.9
0.0254	25.8	143	18.0

The mean and the standard deviation for the five samples are 18.4% CO and 0.666 %CO, respectively, which gives us a 95% confidence interval of

$$\mu = \overline{X} \pm \frac{ts}{\sqrt{n}} = 18.4 \pm \frac{(2.776)(0.666)}{\sqrt{5}} = 18.4 \pm 0.8\% \text{ CO}$$

23. For this internal standardization, the calibration curve plots the analyte's absorbance relative to the internal standard's absorbance (A_{1494}/A_{2064}) on the y-axis versus the mass of polystyrene on the x-axis. Figure SM10.10 shows the resulting calibration data and calibration curve for which the calibration equation is

$$\frac{A_{1494\ cm^{-1}}}{A_{2064\ cm^{-1}}} = 6.97 \times 10^{-3} + (1.456\ g^{-1})\,m_{polystyrene}$$

To determine the concentration of polystyrene in a sample, we first use the sample's absorbance at 1494 cm^{-1} and at 2064 cm^{-1} to calculate the mass of polystyrene in the sample, and then calculate the %w/w polystyrene relative to the sample's mass; thus, for the first replicate we have

$$m_{polystyrene} = \frac{\dfrac{0.2729}{0.3582} - 6.97 \times 10^{-3}}{1.456\ g^{-1}} = 0.5185\ g$$

$$\frac{0.5185\ g\ polystyrene}{0.8006\ g\ sample} \times 100 = 64.76\%\ w/w\ polystyrene$$

The results for all three replicates are 64.76%, 62.50%, and 65.00% with a mean of 64.09% and a standard deviation of 1.38%. To determine if there is evidence of a determinate error, we use a t-test of the following null and alternative hypotheses

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

The test statistic is

$$t_{exp} = \frac{|\mu - \overline{X}|\sqrt{n}}{s} = \frac{|67 - 64.09|\sqrt{3}}{1.38} = 3.65$$

which is smaller than the critical value for $t(0.05,2)$ of 4.303; thus, we do not have evidence of a determinate error at $\alpha = 0.05$.

24. The optimum wavelengths are those where the ratio of $\varepsilon_{Cu}/\varepsilon_{Ba}$ has its maximum and its minimum value. As we see in Figure SM10.11, the optimum wavelengths are at approximately 613 nm and at 658 nm.

25. (a) Figure SM10.12 shows a plot that displays A_{mix}/A_{Ti} on the y-axis and A_V/A_{Ti} on the x-axis. A linear regression analysis of the calibration data gives a calibration equation of

$$\frac{A_{mix}}{A_{Ti}} = 0.4993 + 0.6069 \times \frac{A_V}{A_{Ti}}$$

with the y-intercept equivalent to $(C_{Ti})_{sample}/(C_{Ti})_{standard}$ and with the slope equivalent to $(C_V)_{sample}/(C_V)_{standard}$; thus

$$(C_{Ti})_{sample} = 63.1\ ppm \times 0.4993 = 31.5\ ppm\ Ti(IV)$$

$$(C_V)_{sample} = 96.4\ ppm \times 0.6069 = 58.5\ ppm\ V(V)$$
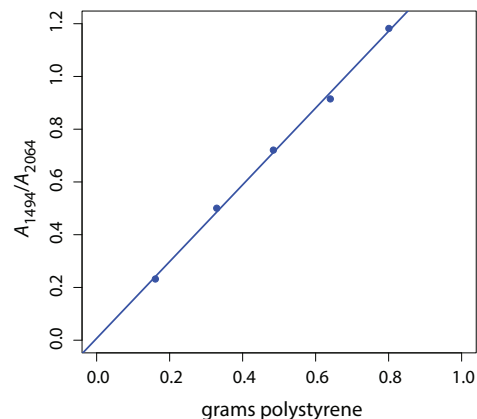
Figure SM10.10 Internal standards calibration curve for the data in Problem 23. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

To review the t-test, see Chapter 4F.
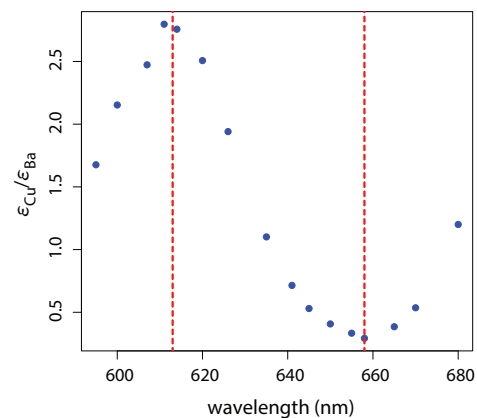
Figure SM10.11 Plot showing the relative absorptivity of copper and barium. The points in **blue** are the data from Problem 24; the dashed **red** lines show the wavelengths where the difference in their relative absorptivities are at their greatest.

Figure SM10.12 Calibration data and calibration curve for Problem 25a. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

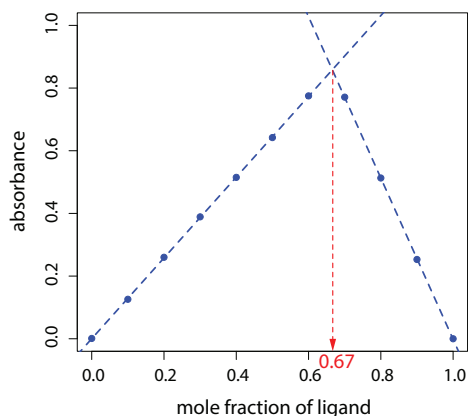Figure SM10.13 Calibration data and calibration curve for Problem 25b. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

Figure SM10.14 Continuous variations plot for the data (**blue** dots) in Problem 26. The intersection of the data's left branch and its right branch, as shown by the dashed **blue** lines and the dashed **red** line, gives the mole fraction of ligand in the complex.
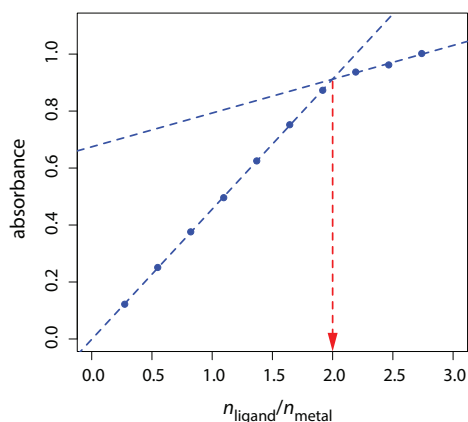

Figure SM10.15 Mole-ratio plot for the data (**blue** dots) in Problem 27. The intersection of the data's left branch and its right branch, as shown by the dashed **blue** lines and the dashed **red** line, gives the ratio of ligand-to-metal in the complex.
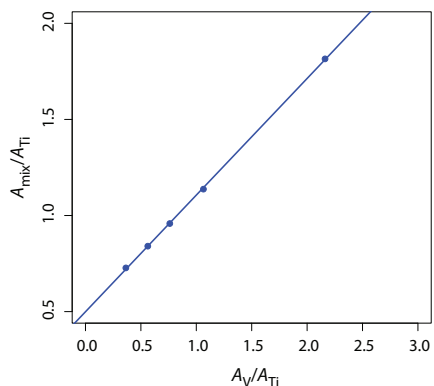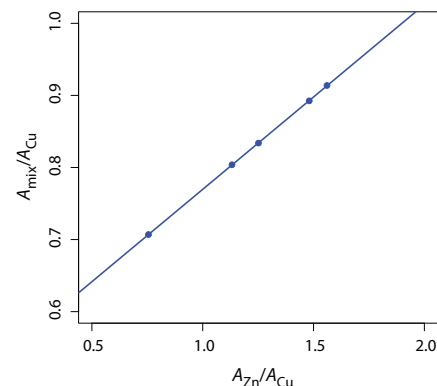
(b) To correct the absorbance values for the contribution of PAR, we subtract its absorbance at each wavelength from the absorbance of each standard and from the absorbance of the mixture; for example, at a wavelength of 480 nm, the corrected absorbance values are 0.487 for Cu^{2+}, 0.760 for Zn^{2+}, and 0.445 for the mixture. Figure SM10.13 shows a plot that displays A_{mix}/A_{Cu} on the y-axis and A_{Zn}/A_{Cu} on the x-axis. A linear regression analysis of the calibration data gives a calibration equation of

$$\frac{A_{mix}}{A_{Cu}} = 0.5134 + 0.2563 \times \frac{A_{Zn}}{A_{Cu}}$$

with the y-intercept equivalent to $(C_{Cu})_{sample}/(C_{Cu})_{standard}$ and with the slope equivalent to $(C_{Zn})_{sample}/(C_{Zn})_{standard}$; thus

$$(C_{Cu})_{sample} = 1.00 \text{ ppm} \times 0.5134 = 0.51 \text{ ppm Cu}^{2+}$$

$$(C_{Zn})_{sample} = 1.00 \text{ ppm} \times 0.2563 = 0.26 \text{ ppm Zn}^{2+}$$

26. Figure SM10.14 shows the continuous variations plot for the data, in which the x-axis is defined by the mole fraction of ligand in each sample. The intersection of the plot's left branch and its right branch is at $X_L = 0.67$; thus, the metal-ligand complex's stoichiometry is

$$\frac{n_{ligand}}{n_{metal}} = \frac{X_L}{1 - X_L} = \frac{0.67}{0.33} = 2$$

and the complex is ML_2.

27. Figure SM10.15 shows the mole-ratio plot for the data, in which the x-axis is defined by the ratio of ligand-to-metal in each sample. The intersection of the two linear branches is at a mole ratio of 2; thus, the metal-ligand complex's stoichiometry is ML_2.
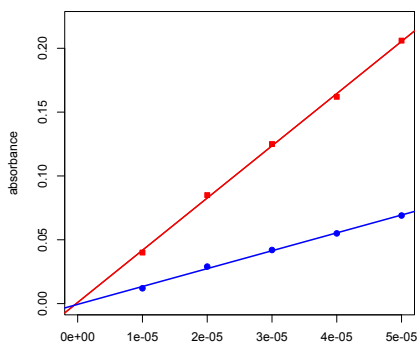
Figure SM10.16 Slope-ratio plot for the data (**blue** dots) in Problem 28. The **red** data points and line are for the metal, and the **blue** data points and line are for the ligand.
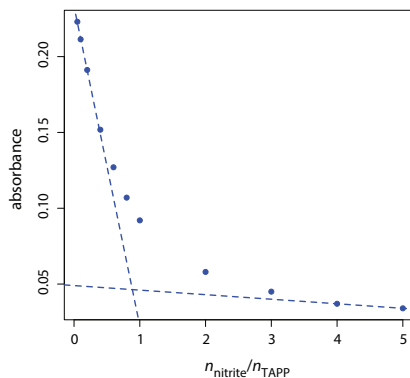

Figure SM10.17 Mole-ratio plot for the data (**blue** dots) in Problem 28. The intersection of the data's left branch and its right branch, as shown by the two dashed **blue** lines, gives the ratio of ligand-to-metal in the complex.

28. Figure SM10.16 shows the slope-ratio plot for the data, in which the x-axis is the concentration of metal or the concentration of ligand. The slope for the metal's data is 1400 M^{-1} and the slope for the ligand's data is 4090 M^{-1}; thus,

$$\frac{n_{\text{metal}}}{n_{\text{ligand}}} = \frac{\text{slope for metal}}{\text{slope for ligand}} = \frac{4090 \text{ M}^{-1}}{1400 \text{ M}^{-1}} = 2.92 \approx 3$$

The metal-ligand complex's stoichiometry, therefore, is ML_3.

29. As shown in Figure SM10.17, the data are best treated using a mole-ratio plot of absorbance versus the ratio of moles NO_2^--to-moles TAPP. The intersection of the two line segments suggests that the stoichiometry is 1:1.

30. The relationship between the three absorbance values, the solution's pH, and the indicator's pK_a is

$$pK_a = pH - \log\frac{A - A_{\text{HIn}}}{A_{\text{In}} - A}$$

Substituting known values gives the indicator's pK_a as

$$pK_a = 4.17 - \log\frac{0.439 - 0.673}{0.118 - 0.439} = 4.31$$

31. Looking at the table, we note that the absorbance is the same for solutions with pH levels of 1.53 and 2.20, which tells us that A_{HIn} is 0.010. We also note that the absorbance is the same for solutions with pH levels of 7.20 and 7.78, which tells us that A_{In} is 0.317. Using these values, we calculate

$$\log\frac{A - A_{\text{HIn}}}{A_{\text{In}} - A}$$

We have sufficient information here to place some limits on the indicator's pK_a. A ladder diagram for any weak acid suggests that we will find its weak acid form, HA, as the only significant species when $pH < pK_a - 1$, and that we will find its weak base form, A^-, as the only significant species when $pH > pK_a + 1$; thus, we expect that the indicator's pK_a is greater than 3.20 and less than 6.20.
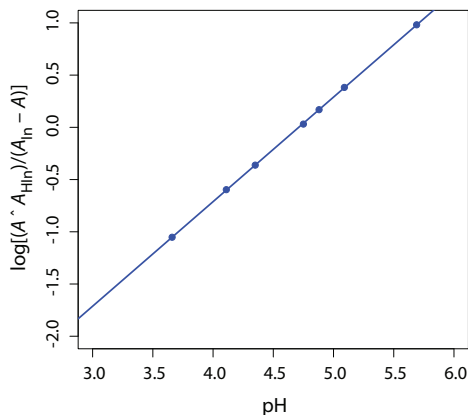
Figure SM10.18 Plot of the data from Problem 31. The **blue** dots are the individual values from the table and the **blue** line is the result of a linear regression of this data.

for the pH levels where both HIn and In$^-$ are present, gathering together the results in the following table and in Figure SM10.18.

pH	$\log\left(\dfrac{A - A_{\text{HIn}}}{A_{\text{In}} - A}\right)$
3.66	−1.052
4.11	−0.597
4.35	−0.362
4.75	0.031
4.88	0.169
5.09	0.382
5.69	0.982

A regression analysis of the data in Figure SM10.18 gives a slope of −4.716, or a pK_a for the indicator of 4.72.

32. (a) First, we need to convert the limits for the analyte's %T to limits for its absorbance; thus

$$A = -\log T = -\log(0.15) = 0.82$$

$$A = -\log T = -\log(0.85) = 0.071$$

Next, we convert these limits for the analyte's absorbance to limits for its concentration; thus

$$C = \frac{A}{\varepsilon b} = \frac{0.82}{(1138\ \text{M}^{-1}\ \text{cm}^{-1})(1.00\ \text{cm})} = 7.2 \times 10^{-4}\ \text{M}$$

$$C = \frac{A}{\varepsilon b} = \frac{0.071}{(1138\ \text{M}^{-1}\ \text{cm}^{-1})(1.00\ \text{cm})} = 6.2 \times 10^{-5}\ \text{M}$$

or between 6.2×10^{-5} M and 7.2×10^{-4} M.

(b) A sample that is 10 μM in analyte has a concentration that is 1.0×10^{-5} M, which is less than our lower limit. To increase the absorbance we can try concentrating the analyte or we can use a sample cell that has a longer pathlength. A sample that is 0.1 mM in analyte has a concentration of 1.0×10^{-4} M; as this falls within our limits, we can analyze the sample as is. A sample that is 1.0 mM in analyte has a concentration of 1.0×10^{-3} M, which is more than our upper limit. To decrease the absorbance, we can dilute the sample or we can use a sample cell that has a shorter pathlength.

33. (a) The sample's absorbance is

$$A = \varepsilon bC =$$
$$(1.0 \times 10^{4}\ \text{M}^{-1}\text{cm}^{-1})(1.00\ \text{cm})(2.0 \times 10^{-4}\ \text{M}) = 2.0$$

or a transmittance, T, of $10^{-A} = 10^{-2.0} = 0.01$. From Table 10.8, we know that the relative uncertainty in concentration is

$$\frac{s_C}{C} = \frac{0.434 s_T}{T \log T} = \frac{(0.434)(\pm 0.002)}{(0.01)\log(0.01)} = \pm 0.043$$

or 4%.

(b) If we use a blank that is 1.0×10^{-4} M in analyte, then the analyte's apparent concentration is 2.0×10^{-4} M $- 1.0 \times 10^{-4}$ M, or 1.0×10^{-4} M. In this case the sample's absorbance is

$$A = \varepsilon b C =$$

$$(1.0 \times 10^4 \, M^{-1} cm^{-1})(1.00 \, cm)(1.0 \times 10^{-4} \, M) = 1.0$$

or a transmittance, T, of $10^{-A} = 10^{-1.0} = 0.1$. From Table 10.8, we know that the relative uncertainty in concentration is

$$\frac{s_C}{C} = \frac{0.434 s_T}{T \log T} = \frac{(0.434)(\pm 0.002)}{(0.1)\log(0.1)} = \pm 0.00868$$

or 0.9%.

34. Figure SM10.19 shows the calibration data and the calibration curve, the equation for which is

$$A = -1.186 \times 10^{-2} + (2.854 \times 10^{-5} \, ppm^{-1}) \times C_P$$

Substituting the sample's absorbance into the calibration equation and solving for C_P gives

$$C_P = \frac{0.135 + 1.186 \times 10^{-2}}{2.854 \times 10^{-5} \, ppm^{-1}} = 5146 \, ppm \, P$$

Converting the concentration of P in the sample into an equivalent mass of Na_2HPO_4

$$\frac{5146 \, mg \, P}{L} \times \frac{1 \, g}{1000 \, mg} \times 0.1000 \, L \times$$

$$\frac{141.96 \, g \, Na_2HPO_4}{30.974 \, g \, P} = 2.359 \, g \, Na_2HPO_4$$

The sample's purity, therefore, is

$$\frac{2.359 \, g \, Na_2HPO_4}{2.469 \, g \, sample} \times 100 = 95.5\% \, pure$$

35. (a) Figure SM10.20 shows the calibration data and the calibration curve for the analysis of copper, for which the calibration curve's equation is

$$A = 2.429 \times 10^{-3} + (7.104 \times 10^{-2} \, mg^{-1} \, L) \times C_{Cu}$$

Substituting the sample's absorbance into the calibration equation and solving for C_{Cu} gives

$$C_{Cu} = \frac{0.027 - 2.429 \times 10^{-3}}{7.104 \times 10^{-2} \, mg^{-1} L} = 0.346 \, mg \, Cu/L$$

Figure SM10.19 Calibration data and calibration curve for Problem 34. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

Figure SM10.20 Calibration data and calibration curve for Problem 35a. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.

Figure SM10.21 Calibration data and calibration curve for Problem 35b. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.
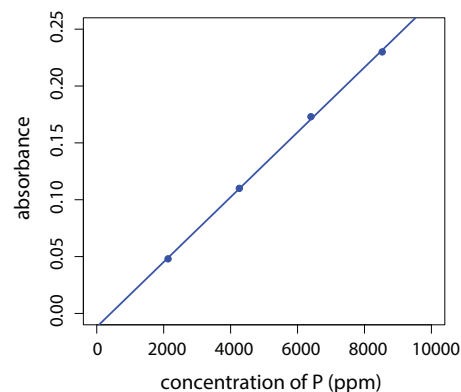

Figure SM10.22 Calibration data and calibration curve for Problem 36. The **blue** dots give the absorbance values for the standards, and the **blue** regression line is the best fit to the data.
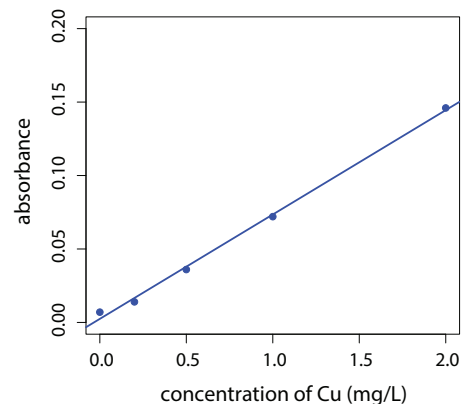
Accounting for the sample's preparation gives the concentration of copper in the original sample as

$$\frac{0.346 \text{ mg Cu}}{L} \times \frac{500.0 \text{ mL}}{200.0 \text{ mL}} = 0.865 \text{ mg Cu/L}$$

(b) Figure SM10.21 shows the calibration data and the calibration curve for the analysis of chromium, for which the calibration curve's equation is

$$A = 4.750 \times 10^{-2} + (0.1435 \text{ mg}^{-1} \text{ L}) \times C_{Cr}$$

For a standard addition, the concentration of chromium is the absolute value of the x-intercept; thus, setting the absorbance to zero and solving

$$\frac{0 - 4.750 \times 10^{-2}}{0.1435 \text{ mg}^{-1} \text{L}} = -0.331 \text{ mg Cr/L}$$

gives C_{Cr} as 0.331 mg/L for the sample as analyzed. Accounting for the sample's preparation gives the concentration of chromium in the original sample as

$$\frac{0.331 \text{ mg Cr}}{L} \times \frac{50.0 \text{ mL}}{200.0 \text{ mL}} = 0.0828 \text{ mg Cr/L}$$

36. The concentration of Mn^{2+} added to the sample in the three standard additions are 0.00, 1.25, and 2.50 ppb, respectively. Figure SM10.22 shows the calibration data and the calibration curve, for which the calibration equation is

$$A = 0.224 + (0.0552 \text{ ppb}^{-1}) C_{Mn}$$

For a standard addition, the concentration of chromium is the absolute value of the x-intercept; thus, setting the absorbance to zero and solving

$$\frac{0 - 0.224}{0.0552 \text{ ppb}^{-1}} = -4.06 \text{ ppb Mn}$$

gives C_{Mn} as 4.06 ppb for the sample as analyzed. Accounting for the sample's preparation gives the concentration of Mn^{2+} in the original sample as

$$\frac{\left(4.06 \text{ ppb Mn}^{2+} \times \frac{5.0 \, \mu L}{2.5 \mu L} \times \frac{100.0 \text{ mL}}{1.000 \text{ mL}} \times 0.05000 \text{ L} \right)}{1.00 \text{ L seawater}} = 40.6 \text{ ppb Mn}^{2+}$$

37. Figure SM10.23 shows the calibration data and the calibration curve for the analysis of sodium, for which the calibration curve's equation is

$$I = 0.7810 + (44.99 \text{ mg}^{-1} \text{ L}) \times C_{Na}$$

Substituting the sample's emission into the calibration equation and solving for C_{Na} gives

$$C_{Na} = \frac{238 - 0.7810}{44.99 \text{ mg}^{-1} \text{L}} = 5.273 \text{ mg Na/L}$$

Accounting for the sample's preparation gives the concentration of sodium in the original sample as

$$\frac{\frac{5.273 \text{ mg Na}}{L} \times 0.0500 \text{ mL} \times \frac{1000 \, \mu g}{mg}}{4.0264 \text{ g sample}} = 65.5 \, \mu g \text{ Na/g sample}$$

38. Substituting the sample's emission intensity into the equation for the calibration curve gives

$$\frac{5.72 + 0.03}{1.594 \text{ mg}^{-1} \text{L}} = 3.607 \text{ mg Fe}^{3+}/L$$

Accounting for the sample's preparation gives the concentration of iron in the original sample as

$$\frac{\frac{3.607 \text{ mg Fe}^{3+}}{L} \times 0.05000 \text{ L} \times \frac{1000 \, \mu g}{mg}}{0.5113 \text{ g sample}} = 353 \, \mu g \text{ Fe}^{3+}/g \text{ sample}$$

39. For a single external standard, we have

$$I = k[1,3\text{–dihydroxynapthalene}]$$

$$4.85 = k(5.00 \times 10^{-5} \text{ M})$$

$$k = 9.70 \times 10^{4}$$

Figure SM10.23 Calibration data and calibration curve for Problem 37. The **blue** dots give the emission values for the standards, and the **blue** regression line is the best fit to the data.
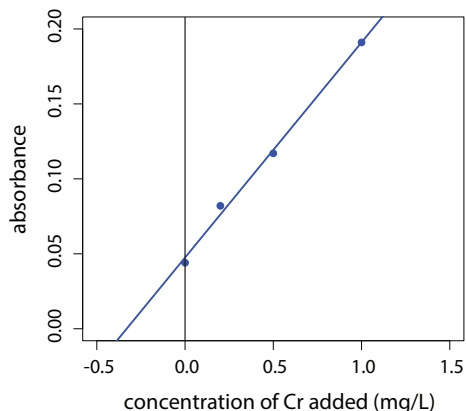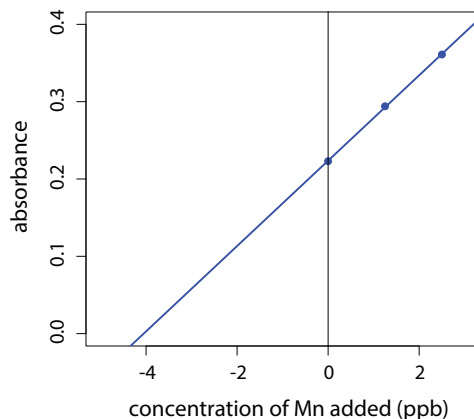
Figure SM10.24 Calibration data and calibration curve for Problem 40. The **blue** dots give the emission values for the standards, and the **blue** regression line is the best fit to the data.
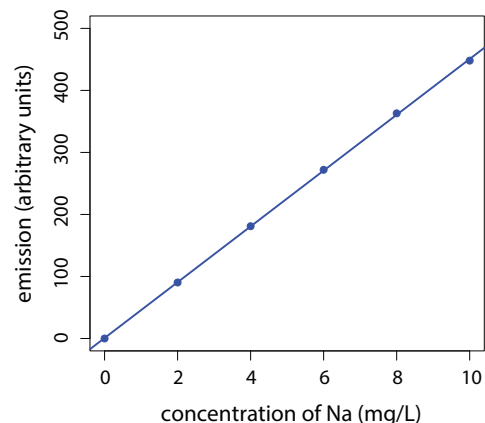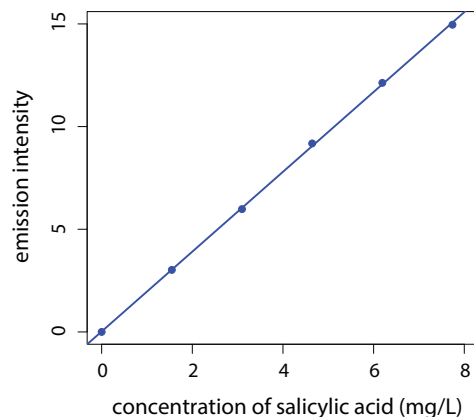

Figure SM10.25 Calibration data and calibration curve for Problem 41. The **blue** dots give the emission values for the standards, and the **blue** regression line is the best fit to the data.

The concentration of 1,3-dihydroxynapthalene in the sample, therefore, is

$$[1,3\text{–dihydroxynapthalene}] = \frac{I}{k} =$$

$$\frac{3.74}{9.70 \times 10^4 \text{ M}^{-1}} = 3.86 \times 10^{-5} \text{ M}$$

40. Figure SM10.24 shows the calibration data and the calibration curve for the analysis of benzo[a]pyrene, for which the calibration curve's equation is

$$I = 3.503 \times 10^{-2} + (1.024 \times 10^{-5} \text{ M}^{-1}) \times C_{\text{benzo[a]pyrene}}$$

Substituting the sample's emission into the calibration equation and solving for $C_{\text{benzo[a]pyrene}}$ gives

$$C_{\text{benzo[a]pyrene}} = \frac{4.97 - 3.503 \times 10^{-2}}{1.024 \times 10^5 \text{ M}^{-1}} = 4.82 \times 10^{-5} \text{ M}$$

41. The stock solution of salicylic acid, SA, has a concentration of 77.4 mg/L, which makes the concentration of SA in the standards 0.00, 1.55, 3.87, 4.64, 6.19, and 7.74 mg/L. Figure SM10.25 shows the calibration data and the calibration curve for the analysis of SA, for which the calibration curve's equation is

$$I = 1.847 \times 10^{-2} + (1.945 \text{ mg}^{-1}\text{L}) \times C_{\text{SA}}$$

Substituting the sample's emission into the calibration equation and solving for C_{SA} gives

$$C_{\text{SA}} = \frac{8.69 - 1.847 \times 10^{-2}}{1.945 \text{mg}^{-1}\text{ L}} = 4.458 \text{ mg/L}$$

Accounting for the sample's preparation gives the concentration of acetylsalicylic acid, ASA, in the original sample as

$$\dfrac{\left(\begin{array}{c}\dfrac{4.458\ \text{mg SA}}{\text{L}} \times \dfrac{180.16\ \text{g ASA}}{122.12\ \text{g SA}} \times \\[2mm] \dfrac{100.0\ \text{mL}}{10.0\ \text{mL}} \times 1.000\ \text{L} \times \dfrac{1.000\ \text{g}}{1000\ \text{mg}}\end{array}\right)}{0.1013\ \text{g sample}} \times 100 = 64.9\%\ \text{w/w ASA}$$

42. Figure SM10.26 shows the calibration data and the calibration curve, for which the calibration equation is

$$I = 326.5 + (133.25\ \text{nM}^{-1})\, C_{Se(IV)}$$

For a standard addition, the concentration of Se(IV) is the absolute value of the x-intercept; thus,

$$\dfrac{0 - 326.5}{133.25\ \text{nM}^{-1}} = -2.45\ \text{nM Se(IV)}$$

gives $C_{Se(IV)}$ as 2.45 nM.

43. Substituting the sample's emission intensity into the calibration curve's equation gives

$$C = \dfrac{44.70 + 4.66}{9907.63\ \text{g}^{-1}\text{L}} = 4.98 \times 10^{-3}\ \text{g/L}$$

Accounting for the sample's preparation gives the concentration of fibrinogin in the plasma as

$$\dfrac{\dfrac{4.98 \times 10^{-3}\ \text{g}}{\text{L}} \times \dfrac{250.0\ \text{mL}}{1.000\ \text{mL}} \times 10.00\ \text{mL}}{9.00\ \text{mL plasma}} = 1.38\ \text{g fibrinogen/L}$$
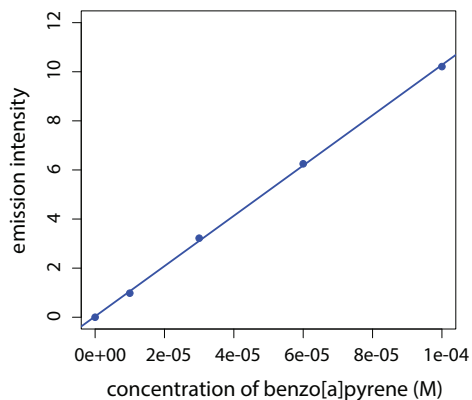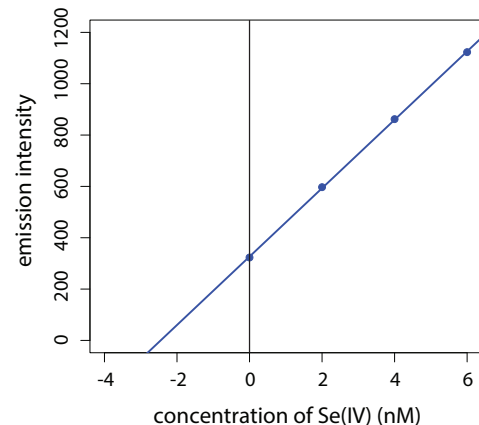

Figure SM10.26 Calibration data and calibration curve for Problem 42. The **blue** dots give the emission values for the standards, and the **blue** regression line is the best fit to the data.

Chapter 11

1. By convention, we describe an electrochemical cell from left-to-right and from anode-to-cathode; thus

   (a) The anode is the Pt electrode where the oxidation reaction

   $$Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + e^-$$

   takes place; the cathode is the Ag electrode with the reduction reaction

   $$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$$
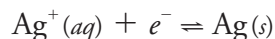
   (b) The anode is the Ag electrode where the oxidation reaction

   $$Ag(s) + Br^-(aq) \rightleftharpoons AgBr(s) + e^-$$
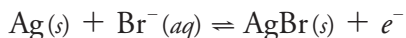
   takes place; the cathode is the Cd electrode with the reduction reaction

   $$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$$
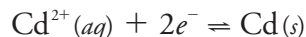
   (c) The anode is the Pb electrode where the oxidation reaction

   $$Pb(s) + SO_4^{2-}(aq) \rightleftharpoons PbSO_4(s) + 2e^-$$
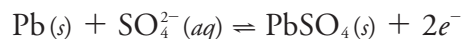
   takes place; the cathode is the PbO_2 electrode with the reduction reaction

   $$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$$
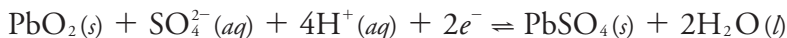
2. (a) The potential is

   $$E = \left(E^\circ_{Ag^+/Ag} - 0.05916\log\frac{1}{a_{Ag^+}} \right) -$$
   $$\left(E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \right)$$

   $$E = 0.7996 - 0.05916\log\frac{1}{0.1} - 0.771 + 0.05916\log\frac{0.015}{0.045}$$

   $$E = -0.059 \text{ V}$$

   (b) The potential is

   $$E = \left(E^\circ_{Cd^{2+}/Cd} - \frac{0.05916}{2}\log\frac{1}{a_{Cd^{2+}}} \right) -$$
   $$\left(E^\circ_{AgBr/Ag} - 0.05916\log a_{Br^-} \right)$$

   $$E = -0.4030 - \frac{0.05916}{2}\log\frac{1}{0.05} - 0.071 + 0.05916\log(1.0)$$

   $$E = -0.512 \text{ V}$$

   (c) The potential is

$$E = \left(E^\circ_{\text{PbO}_2/\text{PbSO}_4} - \frac{0.05916}{2}\log\frac{1}{a_{\text{SO}_4^{2-}}\, a_{\text{H}^+}^4} \right) -$$

$$\left(E^\circ_{\text{PbSO}_4/\text{Pb}} - \frac{0.05916}{2}\log a_{\text{SO}_4^{2-}} \right)$$

$$E = 1.690 - \frac{0.05916}{2}\log\frac{1}{(2.0)(2.0)^4} +$$

$$0.356 + \frac{0.05916}{2}\log(1.5)$$

$$E = +2.10 \text{ V}$$

3. The Nernst equation for the electrochemical cell is

$$E = \left(E^\circ_{\text{I}_2/\text{I}^-} - \frac{0.05916}{2}\log a_{\text{I}^-}^2 \right) - \left(E^\circ_{\text{AgCl/Ag}} - 0.05916\log a_{\text{Cl}^-} \right)$$

Substituting in known values and solving

$$0.294 = 0.5355 - \frac{0.05916}{2}\log(x)^2$$

$$- 0.2223 + 0.05916\log(0.1)$$

$$0.03996 = -\frac{0.05916}{2}\log(x)^2 = -0.05916\log(x)$$

$$-0.6755 = \log(x)$$

gives the activity of I^- as 0.211.

4. In an acidic solution, zinc dissolves as a result of the following oxidation–reduction reaction

$$\text{Zn}\,(s) + 2\text{H}^+\,(aq) \rightleftharpoons \text{H}_2\,(g) + \text{Zn}^{2+}\,(aq)$$
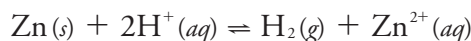
for which the standard state potential is

$$E^\circ = E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} = 0.000 \text{ V} - (-0.7618 \text{ V}) = 0.7618 \text{ V}$$

Because the reaction's potential is positive, we know that the reaction is thermodynamically favorable under standard state conditions. In principle, we expect that any metal with a positive oxidation potential will show similar behavior.

5. To find the selectivity coefficient, we plot potential on the y-axis and the concentration of salicylate, expressed logarithmically, on the x-axis; Figure SM11.1 shows the resulting plot, which consists of two linear regions. For smaller concentrations of salicylate, the electrode's potential is nearly constant as it responds to the concentration of benzoate in solution. For larger concentrations of salicylate, the electrode's potential is determined by the concentration of salicylate.

The intersection of the two linear regions gives the concentration of salicylate, log[salicylate] = –3 or 1.0×10^{-3} M salicylate, that yields a potential equal to that for a solution of 0.1 M benzoate; the selectivity coefficient, therefore, is

$$K_{A,I} = \frac{[\text{salicylate}]}{[\text{benzoate}]^{z_A/z_I}} = \frac{1.0 \times 10^{-3}}{(0.1)^{-1/-1}} = 0.010$$

To maintain an error of less than 1%, we require that

$$K_{A,I} \times [\text{benzoate}] \leq 0.01 \times [\text{salicylate}]$$

$$(0.01) \times [\text{benzoate}] \leq (0.01)(1 \times 10^{-5}\ \text{M})$$

$$[\text{benzoate}] \leq 1.0 \times 10^{-5}\ \text{M}$$

6. Cocaine is a weak base alkaloid with a pK_a of 8.64 for its conjugate weak acid. Below a pH of 8, cocaine exists primarily in it protonated weak acid form, to which the electrode's membrane is sensitive. Above a pH of 9, cocaine exists primarily in its unprotonated weak base form; apparently the electrode's membrane is not sensitive to this form of cocaine, which explains why the potential declines sharply when the pH exceeds 8.

7. The potential of the pH electrode is

$$E_{\text{cell}} = K + 0.05916 \log a_{\text{H}_3\text{O}^+}$$

The inner solution of the ammonia electrode, as shown in Table 11.4, contains a fixed concentration of NH_4^+, for which the acid dissociation constant is

$$K_a = \frac{a_{\text{H}_3\text{O}^+} a_{\text{NH}_3}}{a_{\text{NH}_4^+}}$$

Solving the K_a expression for $a_{\text{H}_3\text{O}^+}$ and substituting back into the equation for the pH electrode's potential gives

$$E_{\text{cell}} = K + 0.05916 \log \frac{K_a a_{\text{NH}_4^+}}{a_{\text{NH}_3}}$$

$$E_{\text{cell}} = K + 0.05916 \log (K_a a_{\text{NH}_4^+}) + 0.05916 \log \frac{1}{a_{\text{NH}_3}}$$

$$E_{\text{cell}} = K' - 0.05916 \log a_{\text{NH}_3}$$

where

$$K' = K + 0.05916 \log (K_a a_{\text{NH}_4^+})$$

In the solution between the two membranes, the activity of NH_3 depends on the activity of NH_4^+, which, in turn, depends on the activity of urea in the outer solution; thus

$$E_{\text{cell}} = K'' - 0.05916 \log a_{\text{urea}}$$

where K'' includes the equilibrium constants for the reactions in the outer solution and the pH of the outer solution.

8. The potential of the pH electrode is

$$E_{\text{cell}} = K' + 0.05916 \log a_{\text{H}_3\text{O}^+} = K' - 0.05916 \times \text{pH}$$
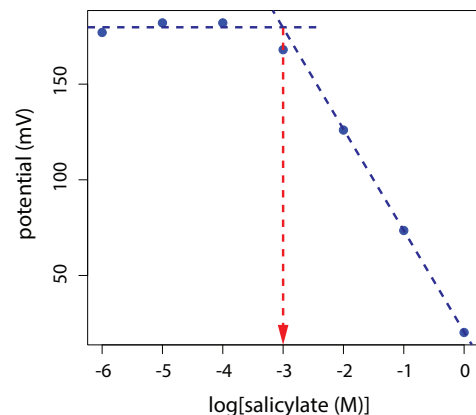
Figure SM11.1 Potential versus concentration data for a salicylate ion-selective electrode in the presence of 0.1 M benzoate. The **blue** dots are the data from Problem 5 and the **blue** dashed lines show the regions where the ISE's potential is determined by the concentration of benzoate or of salicylate. The **red** dashed line shows the concentration of salicylate that yields the same potential as does 0.1 M benzoate.

Solving this equation for pH and substituting into equation 11.15 gives

$$pH = \frac{K' - E_{cell}}{0.05916} = Ka_{urea}$$

which we rearrange to give

$$E_{cell} = K' - 0.05916Ka_{urea}$$

What is interesting about this result is that the potential is a linear function of urea's activity when using the membrane electrode in Figure 11.21, but a logarithmic function of urea's activity when using the membrane electrode in Figure 11.20. The potential is a linear function of urea's activity for the membrane electrode in Figure 11.21 because it is related to the kinetics of the enzymatic reaction and the presence within the membrane of a buffer that can maintain a constant buffering strength; see, Ruzicka, J.; Hansen, E. H.; Ghose, A. K.; Mottola, H. A. *Anal. Chem.* **1979**, *51*, 199–203 for further details.

9. We start with the potential of an electrochemical cell that includes a Ag_2S membrane electrode, with the cell's potential defined in terms of the activity of Ag^+

$$E_{cell} = K + 0.05916 \log a_{Ag^+}$$

Next, we use the complexation reaction between Ag^+ and CN^-

$$Ag^+(aq) + 2CN^-(aq) \rightleftharpoons Ag(CN)_2^-(aq)$$
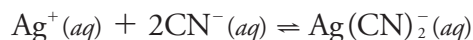
and its overall formation constant

$$\beta_2 = \frac{a_{Ag(CN)_2^-}}{a_{Ag^+} a_{CN^-}^2}$$

to rewrite the electrochemical cell's potential in terms of the activity of CN^-

$$E_{cell} = K + 0.05916 \log \frac{a_{Ag(CN)_2^-}}{\beta_2 (a_{CN^-})^2} = K' - 0.05916 \log (a_{CN^-})^2$$

where K' includes K, β_2, and the activity of $Ag(CN)_2^-$, all of which are constant. Finally, we use the acid-base reaction for HCN

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$
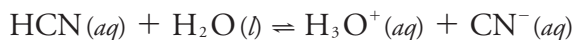
and its acid dissociation constant

$$K_a = \frac{a_{H_3O^+} a_{CN^-}}{a_{HCN}}$$

to rewrite the electrochemical cell's potential in terms of the activity of HCN

$$E_{cell} = K' - 0.05916 \log \frac{(K_a)^2 (a_{HCN})^2}{(a_{H_3O^+})^2}$$

$$E_{cell} = K'' - 2 \times 0.05916 \log a_{HCN}$$

where K'' includes K', K_a, and the activity of H_3O^+, all of which are constant. Our final equation suggests that a 10-fold increase in the activity of HCN will decrease the potential by 0.118 V, or 118 mV. If you examine Figure 2 of US Patent 3859191, you will see that the actual change in potential is approximately −125 mV per 10-fold change in molar concentration, which is in reasonable agreement with our derivation.

10. (a) Figure SM11.2 shows a plot of the data, which is linear for all but the first point and the last point; thus, the linear range is

$$-5.00 \le \log[\text{penicillin}] \le -2.70$$

or

$$1.0 \times 10^{-5} \text{ M} \le [\text{pencillin}] \le 2.0 \times 10^{-3} \text{ M}$$

(b) A linear regression using the data within the calibration curve's linear range gives a calibration equation of

$$E = 331.4 \text{ mV} + 47.76 \text{ mV} \times \log[\text{pencillin}]$$

(c) Substituting the sample's potential into the calibration equation gives log[penicillin] as −3.97 and the concentration of penicillin as 1.1×10^{-4} M.

11. Figure SM11.3 shows the calibration data—note that the x-axis is $\log[K^+]$, not $[K^+]$—and the resulting calibration curve, the equation for which is

$$E = 67.56 + 42.36 \times \log[K^+]$$

Substituting the sample's potential into the calibration curve's equation gives $\log[K^+]$ as −0.389 and $[K^+]$ as 0.41 mM. This is the concentration in the sample as analyzed; because the original serum sample was diluted by a factor of 10× (1.00 mL to 10.00 mL), the concentration of K^+ in the original sample is 4.1 mM.

12. Figure SM11.4 shows a plot of the pH electrode's potential on the y-axis versus pH on the x-axis, along with the calibration curve, the equation for which the equation is

$$E = 427.4 \text{ mV} - (65.46 \text{ mV}) \times \text{pH}$$

Substituting into the calibration equation the measured potential for each sample gives the following results:

tomato juice: pH of 4.0

tap water: pH of 6.9

coffee: pH of 4.7
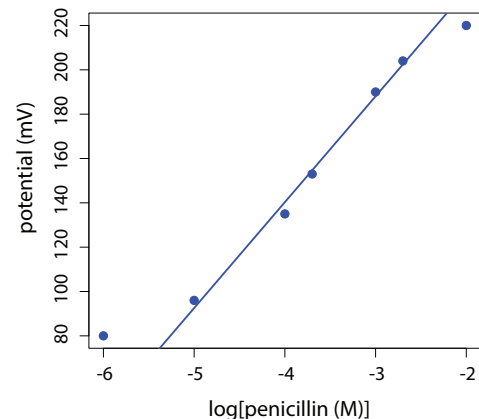
Figure SM11.2 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 10. The calibration curve is restricted to log[penicillin] values between −2.70 and −5.00.
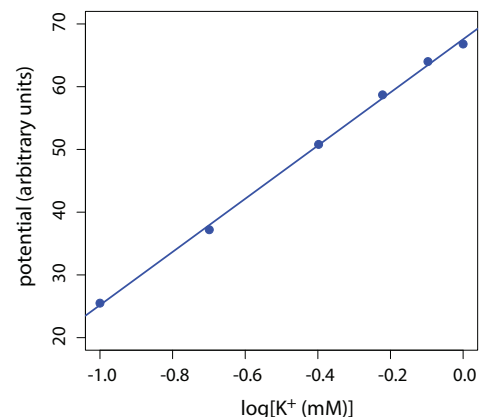
Figure SM11.3 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 11.
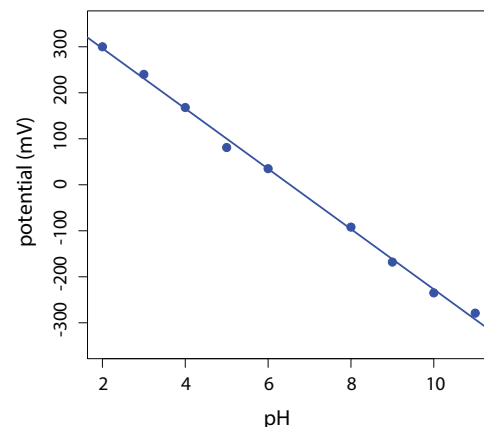
Figure SM11.4 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 12.

13. The following two equations apply to this standard addition
$$0.102 = K - 0.05916\log[NO_2^-]$$

$$0.089 = K - 0.05916\log\left\{\begin{array}{l}[NO_2^-] \times \dfrac{25.00\ \text{mL}}{26.00\ \text{mL}} + \\[2mm] \dfrac{200.0\ \text{mg NO}_2^-}{L} \times \dfrac{1.00\ \text{mL}}{26.00\ \text{mL}}\end{array}\right\}$$

Subtracting the second equation from the first equation and cleaning up the terms inside the second equation's brackets, leaves us with

$$0.013 = 0.05916\log\left\{\begin{array}{l}0.9615\,[NO_2^-] + \\[1mm] \dfrac{7.692\ \text{mg NO}_2^-}{L}\end{array}\right\} - 0.05916\log[NO_2^-]$$

Finally, solving for $[NO_2^-]$ gives

$$0.013 = 0.05916\log\left\{\dfrac{0.9615\,[NO_2^-] + \dfrac{7.692\ \text{mg NO}_2^-}{L}}{[NO_2^-]}\right\}$$

$$1.659 = \dfrac{0.9615\,[NO_2^-] + \dfrac{7.692\ \text{mg NO}_2^-}{L}}{[NO_2^-]}$$

$$1.659\,[NO_2^-] = 0.9615\,[NO_2^-] + \dfrac{7.692\ \text{mg NO}_2^-}{L}$$

$$0.6795\,[NO_2^-] = \dfrac{7.692\ \text{mg NO}_2^-}{L}$$

$$[NO_2^-] = \dfrac{11.0\ \text{mg NO}_2^-}{L}$$

14. To determine the concentration of F^- in either the sample of tap water or the sample of toothpaste, we must find an appropriate way to plot the standard additions data. We begin with the Nernst equation

$$E = K - 0.05916\log\left\{C_{samp} \times \dfrac{V_{samp}}{V_{tot}} + C_{std} \times \dfrac{V_{std}}{V_{tot}}\right\}$$

where C_{samp} is the concentration of F^- in the original sample, V_{samp} is the volume of the original sample, C_{std} is the concentration of F^- in the standard, V_{std} is the volume of standard, and V_{tot} is the sum of V_{samp} and V_{std}. Rearranging and dividing through by -0.05916 gives

$$\dfrac{K - E}{0.05916} = \log\left\{C_{samp} \times \dfrac{V_{samp}}{V_{tot}} + C_{std} \times \dfrac{V_{std}}{V_{tot}}\right\}$$

Taking the inverse log of both sides of the equation gives

$$10^{\frac{K-E}{0.05916}} = \left\{C_{samp} \times \dfrac{V_{samp}}{V_{tot}} + C_{std} \times \dfrac{V_{std}}{V_{tot}}\right\}$$

Expanding the term on the equation's left

$$10^{\frac{K}{0.05916}} \times 10^{\frac{-E}{0.05916}} = \left\{C_{samp} \times \dfrac{V_{samp}}{V_{tot}} + C_{std} \times \dfrac{V_{std}}{V_{tot}}\right\}$$

and rearranging leaves us with

$$10^{\frac{-E}{0.05916}} = 10^{\frac{-K}{0.05916}}\left\{C_{samp} \times \frac{V_{samp}}{V_{tot}} + C_{std} \times \frac{V_{std}}{V_{tot}}\right\}$$

$$10^{\frac{-E}{0.05916}} = \frac{10^{\frac{-K}{0.05916}} C_{samp} V_{samp}}{V_{tot}} + \frac{10^{\frac{-K}{0.05916}} C_{std} V_{std}}{V_{tot}}$$

$$V_{tot} 10^{\frac{-E}{0.05916}} = 10^{\frac{-K}{0.05916}} C_{samp} V_{samp} + 10^{\frac{-K}{0.05916}} C_{std} V_{std}$$

This last equation is the one we seek as it shows us that a plot of $V_{tot} \times 10^{-E/0.05916}$ versus V_{std} is a straight-line with a slope, b_1, that is equal to

$$b_1 = C_{std} \times 10^{-K/0.05916}$$

and a y-intercept, b_0, that is equal to

$$b_0 = C_{samp} V_{samp} \times 10^{-K/0.05916}$$

Dividing the equation for b_0 by the equation for b_1 and rearranging gives us a way to determine the concentration of F^- in our original sample

$$C_{samp} = \frac{b_0 C_{std}}{b_1 V_{samp}}$$

Now we can turn our attention to the two sets of data.

(a) To analyze the data for the sample of tap water, we first calculate the average potential for each standard addition and then calculate the y-axis values, $V_{tot} \times 10^{-E/0.05916}$, expressing volume in liters. Figure SM11.5a shows the calibration data and the calibration curve, for which the calibration equation is

$$V_{tot} 10^{\frac{-E}{0.05916}} = 1.115\,L + 4068\,V_{std}$$

Substituting into the equation for C_{samp} gives the concentration of F^- as analyzed as 0.548 ppm, or as 1.10 ppm in the tap water sample.

(b) To analyze the data for the sample of toothpaste, we first calculate the average potential for each standard addition and then calculate the y-axis values, $V_{tot} \times 10^{-E/0.05916}$, expressing volume in liters. Figure SM11.5b shows the calibration data and the calibration curve, for which the calibration equation is

$$V_{tot} 10^{\frac{-E}{0.05916}} = 0.1513\,L + 364.9\,V_{std}$$

Substituting into the equation for C_{samp} gives the concentration of F^- as 2.073 ppm in the sample as analyzed. Accounting for the sample's preparation gives the concentration of F^- in the toothpaste as

$$\frac{2.073\text{ mg F}^-/\text{L} \times 0.1000\text{ L} \times \dfrac{1\text{ g}}{1000\text{ mg}}}{0.3619\text{ g sample}} \times 100 = 0.0573\%\text{w/w F}^-$$
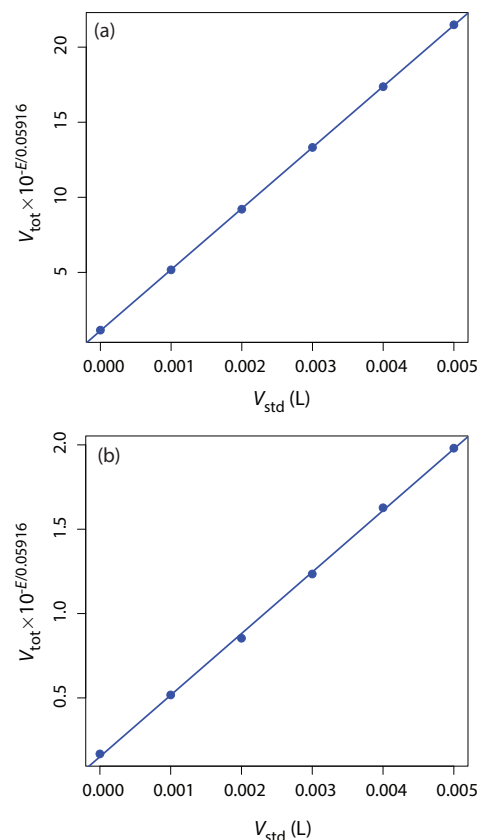
Figure SM11.5 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 14: (a) tap water, and (b) toothpaste.

15. When using external standards, we want to ensure that the matrix of the standards matches the matrix of the samples; thus, we should add sufficient NaCl to each standard solution of KI to match that of the samples. When using internal standards, we prepare a single sample of iodized salt and then spike it with known volumes of a standard solution of KI; there is no need to add NaCl to the standard solution of KI as adding a small volume of the standard to a larger volume of sample will not change significantly the sample's matrix.

16. We can decrease the time needed to oxidize or reduce all the analyte in a sample by (a) increasing the working electrode's surface area, which allows more of the analyte to undergo oxidation or reduction in any unit of time; by (b) using a smaller volume of sample, which means there is less analyte to oxidize or reduce; or by (c) increasing the rate at which we stir the sample as this brings the analyte to the working electrode more quickly and removes more quickly the products of the analyte's oxidation or reduction reaction.

For (c), remember that an oxidation or a reduction reaction takes place at the electrode's surface only.

17. The reduction of picric acid to triaminophenol, involves 18 electrons; thus, using Faraday's law, the moles of picric acid in the sample as analyzed is

$$N_A = \frac{Q}{nF} = \frac{21.67\ C}{\dfrac{18\ mol\ e^-}{mol} \times \dfrac{96485\ C}{mol\ e^-}} = 1.248 \times 10^{-5}\ mol$$

After accounting for the sample's preparation, we find that the original sample's purity is

$$\frac{1.248 \times 10^{-5}\,mol \times \dfrac{1000.0\ mL}{10.00\ mL} \times \dfrac{229.10\ g}{mol}}{0.2917\ g\ sample} \times 100 = 98.0\%\,pure$$

18. For a coulometric titration, the moles of analyte, N_A, the applied current, i, and the end point time, t_e, are related by the equation

$$it_e = nFN_A$$

where n is the number of electrons in the oxidation-reduction reaction, which, for the coulometric titration of H_2S by I_3^-, is 2 (see Table 11.9 for the titrant's reaction). Solving for N_A, we find that the sample as analyzed contains

Remember that 1 C is equivalent to 1 A•s.

$$N_A = \frac{it_e}{nF} = \frac{(0.0846\ A)\,(386\ s)}{\dfrac{2\ mol\ e^-}{mol\ H_2S} \times \dfrac{96485\ C}{mol\ e^-}} = 1.692 \times 10^{-4}\ mol\ H_2S$$

After accounting for the sample's preparation, we find that the concentration of H_2S in the original sample is

$$\frac{1.692 \times 10^{-4}\ mol\ H_2S \times \dfrac{34.08\ g\ H_2S}{mol\ H_2S} \times \dfrac{10^6\ \mu g}{g}}{50.00\ mL} = \frac{115\ \mu g\ H_2S}{mL}$$

19. For this titration to work, the reaction's potential must be positive; thus, we know that under standard-state conditions

$$E^\circ_{rxn} = E^\circ_{I_3^-/I^-} - E^\circ_{H_3AsO_4/H_3AsO_3} = 0.536\ V - 0.559\ V = -0.023\ V$$

the reaction's potential is negative and unfavorable. Because the potential for the H_3AsO_4/H_3AsO_3 half-reaction

$$H_3AsO_4(aq) + 2H^+(aq) + 2e^- \rightleftharpoons H_3AsO_3(aq) + H_2O(l)$$
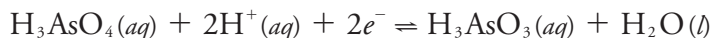
depends on pH

$$E_{H_3AsO_4/H_3AsO_3} = E^\circ_{H_3AsO_4/H_3AsO_3} - \frac{0.05916}{2}\log\frac{[H_3AsO_3]}{[H_3AsO_4][H^+]^2}$$

it seems likely that the reaction must be more favorable at less acidic pH levels. To demonstrate this, let's assume that the concentrations of H_3AsO_3 and of H_3AsO_4 are equal and at their standard state values so that we can explore the affect on the potential of non-standard state concentrations of H^+ only; under this condition, the potential for the reaction is

$$E^\circ_{rxn} = 0.536\ V - \left\{ 0.559\ V - \frac{0.05916}{2}\log\frac{1}{[H^+]^2} \right\}$$

$$E^\circ_{rxn} = -0.023\ V - 0.05916\log[H^+]$$

$$E^\circ_{rxn} = -0.023\ V + 0.05916pH$$

Setting E°_{rxn} to zero and solving for pH shows us that the reaction is favorable for any pH greater than 0.39. For example, the pH of 6 M HCl is approximately –0.8, which means the reaction is unfavorable in a strongly acidic solution. Maintaining a more neutral pH provides for a more positive potential; thus, at a pH of 3 the potential is 0.154 V, but at a pH of 7 the potential is 0.391 V.

20. First we calculate the moles of acrylonitrile in our sample, which is

$$0.594\ g \times \frac{1\ mol}{53.06\ g} \times \frac{1.00\ mL}{1000.0\ mL} = 1.119 \times 10^{-5}\ mol$$

Next, we use Faraday's law to calculate the number of electrons

$$n = \frac{C}{FN_A} = \frac{1.080\ C}{(96485\ C/mol\ e^-)(1.119 \times 10^{-5}\ mol\ acrylonitrile)}$$

$$n = 1.00\ mol\ e^-/mol\ acrylonitrile$$

21. (a) Let's begin with the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction

$$E = E^\circ_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]_{x=0}}{[Fe^{3+}]_{x=0}}$$

using the subscript $x=0$ to remind us that the potential is determined by the concentrations of Fe^{3+} and Fe^{2+} at the electrode's surface. For

the reduction at the cathode of Fe^{3+}, we know from equation 11.38 that the current is proportional to the difference between its concentration in bulk solution and its concentration at the electrode's surface

$$i = K_{Fe^{3+}}\{[Fe^{3+}]_{bulk} - [Fe^{3+}]_{x=0}\}$$

with a cathodic limiting current of

$$i_{l,c} = K_{Fe^{3+}}[Fe^{3+}]_{bulk}$$

Combining these two equations and solving for $[Fe^{3+}]_{bulk}$ gives

$$i = i_{l,c} - K_{Fe^{3+}}[Fe^{3+}]_{x=0}$$

$$[Fe^{3+}]_{x=0} = \frac{i_{l,c} - i}{K_{Fe^{3+}}}$$

The minus sign is included here because the cathodic current and the anodic current have opposite signs.

For the oxidation at the anode of Fe^{2+}, a similar treatment gives

$$i = -K_{Fe^{2+}}\{[Fe^{2+}]_{bulk} - [Fe^{2+}]_{x=0}\}$$

$$i_{l,a} = -K_{Fe^{2+}}[Fe^{2+}]_{bulk}$$

$$i = i_{l,a} + K_{Fe^{2+}}[Fe^{2+}]_{x=0}$$

$$[Fe^{2+}]_{x=0} = \frac{i - i_{l,a}}{K_{Fe^{2+}}}$$

Substituting back into the Nernst equation gives

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{\frac{i - i_{l,a}}{K_{Fe^{2+}}}}{\frac{i_{l,c} - i}{K_{Fe^{3+}}}}$$

which we rearrange to arrive at our final equation

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{i - i_{l,a}}{i_{l,c} - i}$$

(b) When the current, i, is zero, the equation for the potential is

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{-i_{l,a}}{i_{l,c}}$$

The cathodic and the anodic limiting currents, as we showed earlier, are related to the bulk concentrations of Fe^{3+} and of Fe^{2+}; thus

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} - 0.05916\log\frac{K_{Fe^{2+}}[Fe^{2+}]_{bulk}}{K_{Fe^{3+}}[Fe^{3+}]_{bulk}}$$

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{K_{Fe^{3+}}}{K_{Fe^{2+}}} -$$

$$0.05916\log\frac{K_{Fe^{2+}}}{K_{Fe^{3+}}} - 0.05916\log\frac{[Fe^{2+}]_{bulk}}{[Fe^{3+}]_{bulk}}$$

$$E = E^{\circ}_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]_{bulk}}{[Fe^{3+}]_{bulk}}$$

$$E = 0.771\,V - 0.05916\log\frac{0.050\,mM}{0.100\,mM} = 0.789\,V$$

22. Figure SM11.6 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = 0.1478\,\mu A + (0.01967\,\mu A/\mu g) \times m_S$$

where m_S is the μg S used to prepare a standard solution. Substituting in the sample's peak current gives a result of 82.5 μg S; as this is the mass of sulfur in the 1.000-mL sample, the concentration of sulfur in the sample is 82.5 $\mu g/mL$.

23. Figure SM11.7 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = 3.2\,\mu A + (62.10\,\mu A/M) \times C_{K_3Fe(CN)_6}$$

Substituting in the sample's limiting current gives the concentration of $K_3Fe(CN)_6$ as 7.10 mM as analyzed; the purity of the original sample, therefore, is

$$\frac{\dfrac{7.10 \times 10^{-3}\ \text{mol}}{L} \times 0.1000\ L \times \dfrac{329.25\ g}{\text{mol}}}{0.246\ g\ \text{sample}} \times 100 = 95.0\%\ \text{pure}$$

24. Letting C_{Sb} represent the concentration of antimony in the vial after soaking the swab in 5.00 mL of 4 M HCl, we have the following two equations for the sample and the standard addition

$$0.38 = k\left\{ C_{Sb} \times \frac{4.00\ \text{mL}}{4.10\ \text{mL}} \right\}$$

$$1.14 = k\left\{ C_{Sb} \times \frac{4.00\ \text{mL}}{4.20\ \text{mL}} + (5.00 \times 10^2\,\text{ppb}) \times \frac{0.100\ \text{mL}}{4.20\ \text{mL}} \right\}$$

Solving both equations for k and setting them equal to each other gives

$$\frac{0.38}{C_{Sb} \times \dfrac{4.00\ \text{mL}}{4.10\ \text{mL}}} = \frac{1.14}{C_{Sb} \times \dfrac{4.00\ \text{mL}}{4.20\ \text{mL}} + 11.90}$$

which we solve for C_{Sb}

$$0.3619 C_{Sb} + 4.522 = 1.112 C_{Sb}$$

$$0.7501 C_{Sb} = 4.522$$

$$C_{Sb} = 6.03\ \text{ppb Sb}$$

This is the concentration of antimony in the sample as analyzed. The mass of antimony recovered from the suspect's hand is

$$m_{Sb} = \frac{6.03\ \text{ng Sb}}{\text{mL}} \times 5.00\ \text{mL} = 30.2\ \text{ng Sb}$$

25. For the internal standard we have the following relationship between current and concentration
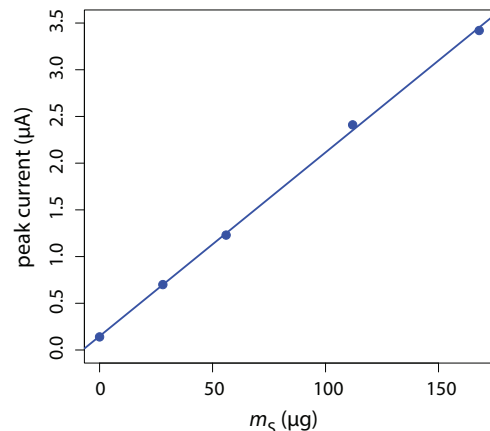
Figure SM11.6 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 22.
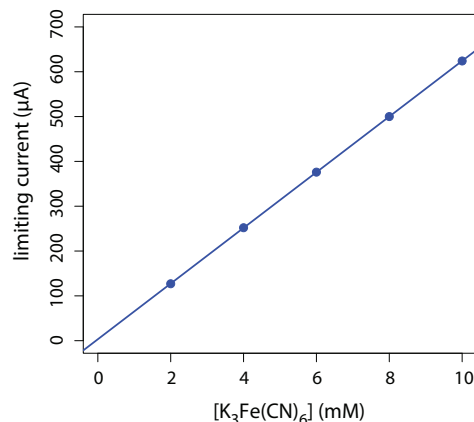
Figure SM11.7 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 23.

$$\frac{i_{Tl}}{i_{Zn}} = \frac{3.19\ \mu A}{5.71\ \mu A} = K \times \frac{C_{Tl}}{C_{Zn}} = K \times \frac{2.50 \times 10^{-5}\ M}{5.00 \times 10^{-5}\ M}$$

Solving for K gives its value as 1.117. For the sample, we have the following equation that relates current to concentration

$$\frac{20.2\ \mu A}{12.3\ \mu A} = 1.117 \times \frac{C_{Tl}}{5.00 \times 10^{-4}\ M \times \frac{25.00\ mL}{50.00\ mL}}$$

which gives the concentration of thallium as 3.68×10^{-4} M in the sample as analyzed; the concentration of thallium in the original sample, therefore, is

$$\frac{\left\{ \frac{3.68 \times 10^{-4}\ mol}{L} \times \frac{50.00\ mL}{25.00\ mL} \times 0.5000\ L \times \frac{204.38\ g}{mol} \right\}}{8.713\ g\ sample} \times 100 = 0.863\%w/w\ Tl$$

26. We begin by letting C_{AA} and C_C represent the concentration of ascorbic acid and the concentration of caffeine, respectively, in the 100-mL volumetric flask. For the analysis of ascorbic acid we have the following two equations for the sample and the standard addition

$$1.40 = k_{AA} \left\{ C_{AA} \times \frac{0.500\ mL}{20.50\ mL} \right\}$$

$$2.80 = k_{AA} \left\{ C_{AA} \times \frac{0.500\ mL}{21.00\ mL} + (250.0\ ppm) \times \frac{0.500\ mL}{21.00\ mL} \right\}$$

Solving both equations for k_{AA}, setting them equal to each other, and solving for C_{Sb} gives

$$\frac{1.40}{C_{AA} \times \frac{0.500\ mL}{20.50\ mL}} = \frac{2.80}{C_{AA} \times \frac{0.500\ mL}{21.00\ mL} + 5.952}$$

$$0.0333 C_{AA} + 8.333 = 0.0683 C_{AA}$$

$$0.035 C_{AA} = 8.333$$

$$C_{AA} = 238\ ppm$$

This is the concentration of ascorbic acid in the sample as analyzed; the mass of ascorbic acid in the original tablet is

$$\frac{238\ mg\ AA}{L} \times 0.1000\ L \times \frac{0.9183\ g}{0.5630\ g} = 38.8\ mg\ AA$$

For the analysis of caffeine we have the following two equations for the sample and the standard addition

$$3.88 = k_C \left\{ C_C \times \frac{0.500\ mL}{20.50\ mL} \right\}$$

$$8.02 = k_C \left\{ C_C \times \frac{0.500 \text{ mL}}{21.00 \text{ mL}} + (200.0 \text{ ppm}) \times \frac{0.500 \text{ mL}}{21.00 \text{ mL}} \right\}$$

Solving both equations for k_C, setting them equal to each other, and solving for C_C gives

$$\frac{3.88}{C_C \times \frac{0.500 \text{ mL}}{20.50 \text{ mL}}} = \frac{8.02}{C_C \times \frac{0.500 \text{ mL}}{21.00 \text{ mL}} + 4.762}$$

$$0.0924 C_C + 18.477 = 0.1956 C_C$$

$$0.1032 C_C = 18.477$$

$$C_C = 179 \text{ ppm}$$

This is the concentration of ascorbic acid in the sample as analyzed; the mass of ascorbic acid in the original tablet is

$$\frac{179 \text{ mg C}}{\text{L}} \times 0.1000 \text{ L} \times \frac{0.9183 \text{ g}}{0.5630 \text{ g}} = 29.2 \text{ mg C}$$

27. Figure SM11.8 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = -5.600 + (1.772 \text{ ppb}^{-1}) \times C_{Sn^{4+}}$$

Substituting in the sample's limiting current gives the concentration of Sn^{4+} as 75.5 ppb as analyzed; the concentration of Sn^{4+} in the original sample, therefore, is

$$75.5 \text{ ppb} \times \frac{1 \text{ ppm}}{1000 \text{ ppb}} \times \frac{30.00 \text{ mL}}{0.500 \text{ mL}} \times \frac{22.00 \text{ mL}}{2.00 \text{ mL}} = 49.8 \text{ ppm}$$

28. Figure SM11.9 shows the calibration data and the resulting calibration curve, the equation for which is

$$i = -0.490 + (8.615 \text{ mg}^{-1} \cdot 100 \text{ mL}) \times C_{glucose}$$

Substituting in the sample's current gives the concentration of glucose as 2.796 mg/100 mL as analyzed; the concentration of glucose in the original sample, therefore, is

$$\frac{2.796 \text{ mg}}{100 \text{ mL}} \times \frac{10.00 \text{ mL}}{2.00 \text{ mL}} = \frac{14.0 \text{ mg}}{100 \text{ mL}}$$

29. First, using the equation $i = kC$, we convert the peak currents and concentrations for each analyte at each potential into values of k, which we gather together in the following table (units: μg^{-1} mL)

| analyte	k at –0.385 V	k at –0.455 V	k at –0.557 V
Pb^{2+}	26.1	2.9	0
Tl^+	3.9	11.75	1.6
In^{3+}	0	0	57.25
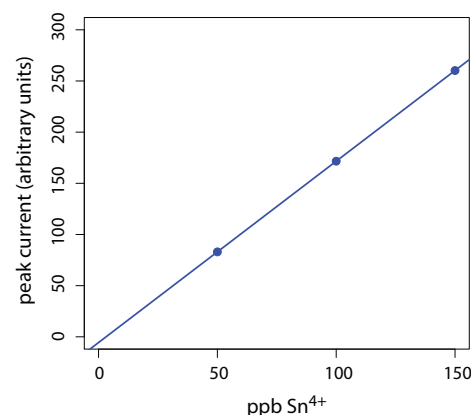
Figure SM11.8 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 27.
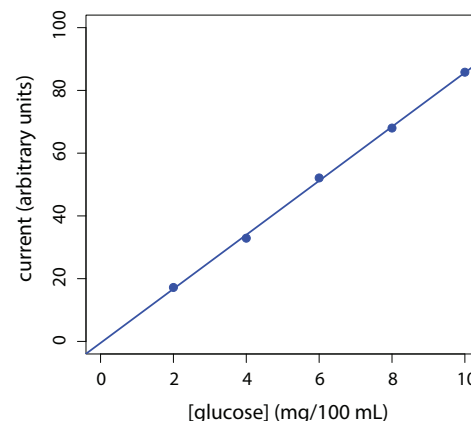
Figure SM11.9 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 28.

Because In^{3+} does not contribute to the current when the potential is –0.385 V or –0.455 V, we can use the sample's currents at these potentials to determine the concentration of Pb^{2+} and of Tl^+ by solving the following pair of simultaneous equations

$$60.6 = (26.1\,\mu g^{-1}\,mL)\,C_{Pb^{2+}} + (3.9\,\mu g^{-1}\,mL)\,C_{Tl^+}$$

$$28.8 = (2.9\,\mu g^{-1}\,mL)\,C_{Pb^{2+}} + (11.75\,\mu g^{-1}\,mL)\,C_{Tl^+}$$

Multiplying the second equation by 26.1/2.9 and subtracting it from the first equation leaves us with

$$-198.6 = -(101.85\,\mu g^{-1}\,mL)\,C_{Tl^+}$$

$$C_{Tl^+} = 1.95\,\mu g/mL \approx 2.0\,\mu g/mL$$

Substituting back into the first of the simultaneous equations a concentration for Tl^+ of 1.95 µg/mL gives the concentration of Pb^{2+} as

$$C_{Pb^{2+}} = \frac{60.6 - (3.9\,\mu g^{-1}\,mL)\,(1.95\,\mu g/mL)}{26.1\,\mu g^{-1}\,mL} = 2.03\,\mu g/mL$$

$$C_{Pb^{2+}} \approx 2.0\,\mu g/mL$$

At a potential of –0.557 V, the current is

$$54.1 = (57.25\,\mu g^{-1}\,mL)\,C_{In^{3+}} + (1.6\,\mu g^{-1}\,mL)\,C_{Tl^+}$$

Substituting in the concentration of Tl^+ and solving for the concentration of In^{3+} gives

$$C_{In^{3+}} = \frac{54.1 - (1.6\,\mu g^{-1}\,mL)\,(1.95\,\mu g/mL)}{57.25\,\mu g^{-1}\,mL} = 0.89\,\mu g/mL$$

30. Figure SM11.10 shows how the method's sensitivity changes as a function of pH. Superimposed on the x-axis is a ladder diagram for NH_4^+. The sudden drop in sensitivity above a pH of 8.3 corresponds to the conversion of NH_4^+ to NH_3; however, the increase in the sensitivity from a pH of 6.2 to a pH of 8.3 must be a function of the enzyme's properties as the concentration of NH_4^+ is the same over this range of pH values.

31. (a) The following relationships exist between the eight measurements (A – H) and the seven groups (I – VII) into which the trace metals are divided

    (A) ASV-labile metals after filtration: I + II + III

    (B) total metals after filtration: I + II + III + IV + V + VI + VII

    (C) ASV-labile metals after ion-exchange: II + III

    (D) total metals after ion-exchange: II + III + VI + VII

    (E) ASV-labile metals after UV: I + II + III + IV + VI

Figure SM11.10 The sensitivity of an amperometric biosensor for NH_4^+ over the pH range 6.2 to 9.3. Superimposed on the x-axis is a ladder diagram for NH_4^+, which shows its weak acid form in **blue** and its weak base form in **green**.

(F) total metals after UV: I + II + III + IV + V + VI + VII

(G) ASV-labile metals after ion-exchange and UV: III

(H) total metals after ion-exchange and UV: III + VII

Using these eight measurements, the following set of equations define each metal ion's total concentration, C_{tot}, and the concentration of the metal ion in each of the seven groups

$C_{tot} = (B + F)/2$

$I = A - C$

$II = C - G$

$III = G$

$IV = E - A - D + C + H - G$

$V = C_{tot} - E - H + G$

$VI = D - C - H + G$

$VII = H - G$

(b) For Cd^{2+}, we have

$C_{tot} = (0.28 + 0.28)/2 = 0.28$ ppb

$I = 0.24 - 0.21 = 0.03$ ppb

$II = 0.21 - 0.00 = 0.21$ ppb

$III = 0.00$ ppb

$IV = 0.26 - 0.24 - 0.26 + 0.21 + 0.02 - 0.00 = -0.01$ ppb

$V = 0.28 - 0.26 - 0.02 + 0.00 = 0$ ppb

$VI = 0.26 - 0.21 - 0.02 + 0.00 = 0.03$ ppb

$VII = 0.02 - 0.00 = 0.02$ ppb

and for Pb^{2+}, we have

$C_{tot} = (0.50 + 0.50)/2 = 0.50$ ppb

$I = 0.39 - 0.33 = 0.06$ ppb

$II = 0.33 - 0.00 = 0.33$ ppb

$III = 0.00$ ppb

$IV = 0.37 - 0.39 - 0.43 + 0.33 + 0.12 - 0.00 = 0.00$ ppb

$V = 0.50 - 0.37 - 0.12 + 0.00 = 0.01$ ppb

$VI = 0.43 - 0.33 - 0.12 + 0.00 = -0.02$ ppb

$VII = 0.12 - 0.00 = 0.12$ ppb

and for Cu^{2+}, we have

$C_{tot} = (0.40 + 0.43)/2 = 0.415$ ppb

$I = 0.26 - 0.17 = 0.09$ ppb

Be sure to convince yourself that these equations are correct. For example

$$A = I + II + III$$

and

$$C = II + III$$

which makes

$$A - C = I + II + III - II - III = I$$

$$\text{II} = 0.17 - 0.00 = 0.17 \text{ ppb}$$

$$\text{III} = 0.00 \text{ ppb}$$

$$\text{IV} = 0.33 - 0.26 - 0.24 + 0.17 + 0.10 - 0.00 = 0.10 \text{ ppb}$$

$$\text{V} = 0.415 - 0.33 - 0.10 + 0.00 = -0.015 \text{ ppb}$$

$$\text{VI} = 0.24 - 0.17 - 0.10 + 0.00 = -0.03 \text{ ppb}$$

$$\text{VII} = 0.10 - 0.00 = 0.10 \text{ ppb}$$

Several of the concentrations have negative values, which, of course, is not possible; these values, which range from –0.03 to –0.01 suggest that concentrations of ±0.03 are the result of random error in the measurement process.

Based on our results, it appears that Cd^{2+} is present primarily as strong, labile organic complexes or labile metals absorbed on organic solids (Group II); that Pb^{2+} is present primarily as free metal ions and weak, labile organic and inorganic complexes (Group I), as strong, labile organic complexes or labile metals absorbed on organic solids (Group II), and as strong nonlabile inorganic complexes or as non-labile metals absorbed on inorganic solids (Group VII); and that Cu^{2+} is present primarily as free metal ions and weak, labile organic and inorganic complexes (Group I), as strong, labile organic complexes or labile metals absorbed on organic solids (Group II), as weaker nonlabile organic complexes (Group IV), and as strong nonlabile inorganic complexes or as nonlabile metals absorbed on inorganic solids (Group VII).

32. Letting C_{Cu} represent the concentration of copper in seawater, we have the following two equations for the sample and the standard addition

$$26.1 = k\left\{C_{Cu} \times \frac{20.00 \text{ mL}}{25.00 \text{ mL}}\right\}$$

$$38.4 = k\left\{C_{Cu} \times \frac{20.00 \text{ mL}}{25.00 \text{ mL}} + (5.00 \text{ μM}) \times \frac{0.10 \text{ mL}}{25.00 \text{ mL}}\right\}$$

Solving both equations for k and setting them equal to each other

$$\frac{26.1}{C_{Cu} \times \dfrac{20.00 \text{ mL}}{25.00 \text{ mL}}} = \frac{38.4}{C_{Cu} \times \dfrac{20.00 \text{ mL}}{25.00 \text{ mL}} + 0.0200 \text{ μM}}$$

$$20.88 C_{Cu} + 0.522 \text{ μM} = 30.72 C_{Cu}$$

$$9.84 C_{Cu} = 0.522 \text{ μM}$$

gives the concentration of copper as 0.0530 μM. The concentration of Cu^{2+} in mg/L, therefore, is

$$\frac{0.053 \times 10^{-6} \text{ mol}}{L} \times \frac{63.546 \text{ g}}{\text{mol}} \times \frac{10^6 \text{ μg}}{\text{g}} = 3.37 \text{ μg/L}$$

33. Letting C_{thio} represent the concentration of the thioamide drug in the sample of urine, we have the following two equations for the sample and the standard addition

$$0.562 = k\left\{ C_{\text{thio}} \times \frac{2.00 \text{ mL}}{4.00 \text{ mL}} \right\}$$

$$0.837 = k\left\{ C_{\text{thio}} \times \frac{2.00 \text{ mL}}{4.10 \text{ mL}} + (5.00 \text{ μM}) \times \frac{0.10 \text{ mL}}{4.10 \text{ mL}} \right\}$$

Solving both equations for k and setting them equal to each other

$$\frac{0.562}{C_{\text{thio}} \times \frac{2.00 \text{ mL}}{4.00 \text{ mL}}} = \frac{0.837}{C_{\text{thio}} \times \frac{2.00 \text{ mL}}{4.10 \text{ mL}} + 0.1220 \text{ μM}}$$

$$0.2741 C_{\text{thio}} + 0.06856 \text{ μM} = 0.4185 C_{\text{thio}}$$

$$0.1444 C_{\text{thio}} = 0.06856 \text{ μM}$$

gives the drug's concentration as 0.47 μM.

34. Figure SM11.11 shows the calibration data and calibration curve, the equation for which is

$$i = 15.52 \text{ nA} + (4.47 \times 10^8 \text{ nA/M}) C_{V(V)}$$

For a standard addition, the concentration of V(V) is the absolute value of the x-intercept; thus,

$$\frac{0 - 15.52 \text{ nA}}{4.47 \times 10^8 \text{ nA/M}} = -3.5 \times 10^{-8}$$

35. A positive potential corresponds to a negative free energy; thus, the more positive the potential, the more thermodynamically favorable the reaction. In this case, because Cu^{2+} forms a strong complex with EDTA, CuY^{2-}, we expect that $E^{\circ}_{CuY^{2-}/Cu} < E^{\circ}_{Cu^{2+}/Cu} = +0.342 \text{ V}$.

36. Lead forms several stable hydroxy-complexes, such as $Pb(OH)_3^-$, that shift the reduction potential toward more negative values.

37. To show that the reduction of Pb^{2+} is reversible, we plot the potential on the y-axis versus $\log\{i/(i_l - i)\}$ on the x-axis, which should result in a straight-line with a slope of $-0.05916/n$ and a y-intercept of $E_{1/2}$. Figure SM11.12 shows the resulting data and regression line, the equation for which is

$$E = -0.390 - 0.02948 \log \frac{i}{i_l - i}$$

From the slope, we find that

$$-0.02948 = \frac{-0.05916}{n}$$

$$n = 2.01 \approx 2$$

which makes sense for the reduction of Pb^{2+}; thus, the straight-line and the slope suggest that the reduction of Pb^{2+} is reversible.
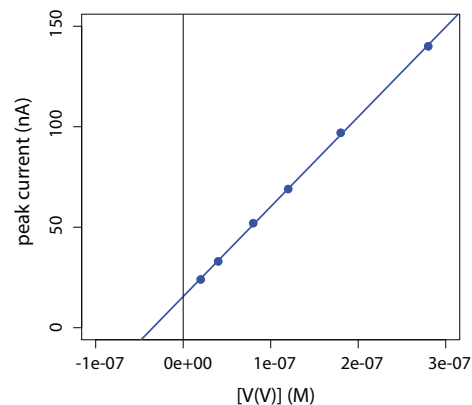
Figure SM11.11 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 34.
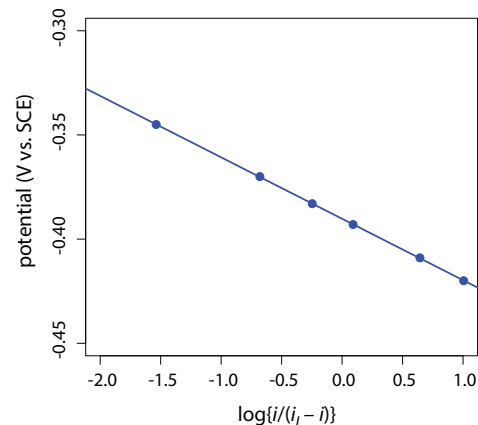
Figure SM11.12 Data (**blue** dots) and regression line (**blue** line) for Problem 37, which confirms that the reduction of Pb^{2+} is reversible.
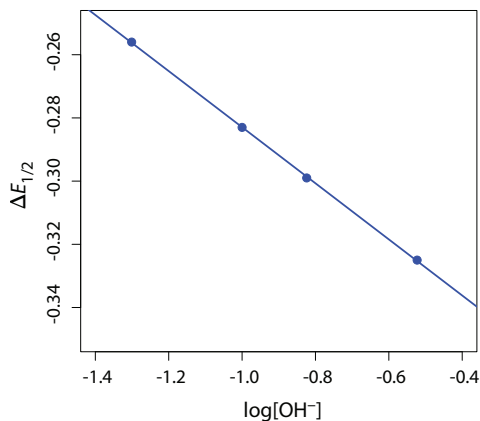
Figure SM11.13 Data (**blue** dots) and regression line (**blue** line) for Problem 37 used to determine the stoichiometry and the formation constant for a complex between Pb^{2+} and OH^-.
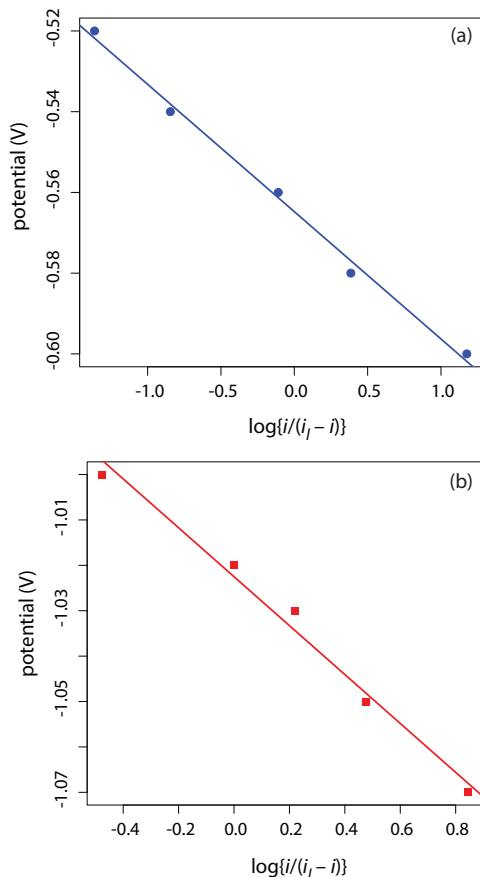
Figure SM11.14 Data and regression line for Problem 38: (a) reduction of Cd^{2+} and (b) reduction of Ni^{2+}.

The value of $E_{1/2}$ for the reduction of Pb^{2+} is equal to the y-intercept of the data in Figure SM11.12, or -0.390 V. To characterize the lead-hydroxy complex's stoichiometry and formation constant, we plot $\Delta E_{1/2}$ on the y-axis, where

$$\Delta E_{1/2} = (E_{1/2})_{complex} - (E_{1/2})_{no\ complex} = (E_{1/2})_{complex} + 0.390\ V$$

and $\log[OH^-]$ on the x-axis. Figure SM11.13 shows the resulting plot and regression line, the equation for which is

$$\Delta E_{1/2} = -0.3717 - 0.08878\log[OH^-]$$

Using the slope, we find that for the complex $Pb(OH)_p^{2-p}$

$$-0.08878 = -\frac{0.05916p}{n} = -\frac{0.05916p}{2}$$

the value of p is 3.0; thus, the complex is $Pb(OH)_3^-$. Using the y-intercept, we find that the complex's overall formation constant

$$-0.3717 = -\frac{0.05916}{n}\log\beta_3 = -\frac{0.05916}{2}\log\beta_3$$

is 3.68×10^{12}.

38. To evaluate each metal ion for its reversibility, we plot its potential on the y-axis versus $\log\{i/(i_l-i)\}$ on the x-axis, which should result in a straight-line with a slope of $-0.05916/n$ and a y-intercept of $E_{1/2}$. Figure SM11.14a shows the results for Cd^{2+} and Figure SM11.14b shows the results for Ni^{2+}. For Cd^{2+}, a regression analysis of the data yields on equation of

$$E = -0.565 - 0.0315\log\frac{i}{i_l-i}$$

From the slope, we find that

$$-0.0315 = \frac{-0.05916}{n}$$

$$n = 1.9 \approx 2$$

A two-electron reduction for Cd^{2+} is consistent with a reversible reduction reaction of

$$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(Hg)$$
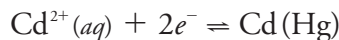
where $Cd(Hg)$ represents the formation of an amalgam of cadmium and mercury. For Ni^+, a regression analysis of the data yields on equation of

$$E = -1.02 - 0.0539\log\frac{i}{i_l-i}$$

From the slope, we find that

$$-0.0539 = \frac{-0.05916}{n}$$

$$n = 1.1$$

A one-electron reduction for Ni^{2+} is not consistent with its reduction reaction of

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(Hg)$$
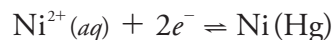
Presumably there is a slow rate of electron transfer that prevents the reduction from displaying electrochemical reversibility.

39. To evaluate electrochemical reversibility for cyclic voltammetry we examine values for ΔE_p, where $\Delta E_p = E_{p,a} - E_{p,c}$. For an electro-chemically reversible reaction, ΔE_p is independent of scan rate and equal to $0.05916/n$. For p-phenyldiamine, ΔE_p varies from 0.044 V at a scan rate of 2 mV/s to 0.117 V at a scan rate of 100 mV/s, all of which exceed the theoretical value of $0.05916/2 = 0.02953$ V; thus, the reaction is not electrochemically reversible. For each scan rate, the ratio of the cathodic peak current and the anodic peak currents are approximately 1.00, which means the reaction must be chemically reversible; thus, the lack of electrochemical reversibility presumably results from slow kinetics and not from a chemical reaction.

Chapter 12

1. (a) To calculate the number of theoretical plates we use equation 12.15; thus

$$N_A = 16 \times \left(\frac{t_{r,A}}{w_A}\right)^2 = 16 \times \left(\frac{8.04 \text{ min}}{0.15 \text{ min}}\right)^2 = 46000 \text{ plates}$$

$$N_B = 16 \times \left(\frac{t_{r,B}}{w_B}\right)^2 = 16 \times \left(\frac{8.26 \text{ min}}{0.15 \text{ min}}\right)^2 = 48500 \text{ plates}$$

$$N_C = 16 \times \left(\frac{t_{r,C}}{w_C}\right)^2 = 16 \times \left(\frac{8.43 \text{ min}}{0.16 \text{ min}}\right)^2 = 44400 \text{ plates}$$

The average number of theoretical plates is 46 300.

(b) The height of a theoretical plate, H, is equal to L/N where L is the length of the column and N is the number of theoretical plates. Using the average number of theoretical plates from part (a) gives the average height as

$$H = \frac{20 \text{ m} \times \dfrac{1000 \text{ mm}}{\text{m}}}{46300 \text{ plates}} = 0.43 \text{ mm/plate}$$

(c) Theoretical plates do not really exist; they are, instead, an artificial construct that is useful for modeling the variables that affect the width of a solute's peak and its resolution relative to other solutes. As we see from equation 12.15, the number of theoretical plates for a solute is defined in terms of its retention time and its peak width. Two solutes may have identical retention times but different peak widths because retention time is a function of the equilibrium between the concentration of solute in the mobile phase and the concentration of solute in the stationary phase, but peak width is a function, in part, of the kinetic effects that control how quickly the solute moves within the stationary phase and within the mobile phase.

2. Using equation 12.1, the resolution between solutes A and B is

$$R_{AB} = \frac{2(t_{r,B} - t_{r,A})}{w_A + w_B} = \frac{2(8.26 \text{ min} - 8.04 \text{ min})}{0.15 \text{ min} + 0.15 \text{ min}} = 1.47 \approx 1.5$$

and the resolution between solutes B and C is

$$R_{BC} = \frac{2(t_{r,C} - t_{r,B})}{w_B + w_C} = \frac{2(8.43 \text{ min} - 8.26 \text{ min})}{0.15 \text{ min} + 0.16 \text{ min}} = 1.10 \approx 1.1$$

To calculate selectivity factors or to calculate resolution using equation 12.19, we first must calculate each solute's retention factor using equation 12.8; thus

$$k_A = \frac{t_{r,A} - t_m}{t_m} = \frac{8.04 \text{ min} - 1.19 \text{ min}}{1.19 \text{ min}} = 5.756 \approx 5.76$$

$$k_B = \frac{t_{r,B} - t_m}{t_m} = \frac{8.26 \text{ min} - 1.19 \text{ min}}{1.19 \text{ min}} = 5.941 \approx 5.94$$

$$k_C = \frac{t_{r,C} - t_m}{t_m} = \frac{8.43 \text{ min} - 1.19 \text{ min}}{1.19 \text{ min}} = 6.084 \approx 6.08$$

With retention factors in hand, we calculate the selectivity factors using equation 12.9; thus

$$\alpha_{AB} = \frac{k_B}{k_A} = \frac{5.941}{5.765} = 1.032 \approx 1.03$$

$$\alpha_{BC} = \frac{k_C}{k_B} = \frac{6.084}{5.941} = 1.024 \approx 1.02$$

Finally, we use equation 12.19 to calculate resolution; thus

$$R_{AB} = \frac{\sqrt{N_B}}{4} \times \frac{\alpha - 1}{\alpha} \times \frac{k_B}{1 + k_B} =$$

$$\frac{\sqrt{48500}}{4} \times \frac{1.032 - 1}{1.032} \times \frac{5.941}{1 + 5.941} = 1.46 \approx 1.5$$

$$R_{BC} = \frac{\sqrt{N_C}}{4} \times \frac{\alpha - 1}{\alpha} \times \frac{k_C}{1 + k_C} =$$

$$\frac{\sqrt{44400}}{4} \times \frac{1.024 - 1}{1.024} \times \frac{6.084}{1 + 6.084} = 1.06 \approx 1.1$$

To improve the resolution between solute B and solute C, we might pursue the following: increase the number of theoretical plates; increase the resolution factor for solute C; and/or increase the column's relative selectivity for the two solutes. For the latter, we can seek to decrease the retention time for solute B, increase the retention time for solute C, or both.

3. Depending on your measurements, your answers may vary slightly from those given here: the solute's retention time, t_r, is 350 s, the retention time for the non-retained solutes, t_m, is 25 s, and the solute's peak width, w, is 22 s. Using these values gives the following additional results

$$t_r' = t_r - t_m = 350 \text{ s} - 25 \text{ s} = 325 \text{ s}$$

$$k = \frac{t_r - t_m}{t_m} = \frac{350 \text{ s} - 25 \text{ s}}{25 \text{ s}} = 13$$

$$N = 16 \times \left(\frac{t_r}{w}\right)^2 = 16 \times \left(\frac{350 \text{ s}}{22 \text{ s}}\right)^2 = 4050 \text{ plates}$$

$$H = \frac{L}{N} = \frac{2 \text{ m} \times \frac{1000 \text{ mm}}{\text{m}}}{4050 \text{ plates}} = 0.49 \text{ mm/plate}$$

4. Depending on your measurements, your answers may vary slightly from those given here: solute A's retention time, $t_{r,A}$, is 350 s and its peak width, w_A, is 19.8 s; solute B's retention time, $t_{r,B}$, is 370 s and its peak width, w_B, is 20.3 s. Using these values gives a resolution of

$$R_{AB} = \frac{2(t_{r,B} - t_{r,A})}{w_A + w_B} = \frac{2(370 \text{ s} - 350 \text{ s})}{19.8 \text{ s} + 20.3 \text{ s}} = 0.998 \approx 1.0$$

5. Increasing the length of the column increases the number of theoretical plates. Using equation 12.19, we see that

$$\frac{(R_{AB})_{new}}{(R_{AB})_{old}} = \frac{1.5}{1.0} = \frac{(\sqrt{N_B})_{new}}{(\sqrt{N_B})_{old}}$$

Rearranging and solving for the number of theoretical plates in the new, longer column gives

$$(\sqrt{N_B})_{new} = 1.5 \times (\sqrt{N_B})_{old}$$

$$(N_B)_{new} = 2.25 \times (N_B)_{old}$$

To increase the number of theoretical plates by a factor of 2.25× by adjusting the column's length only, requires a column that is 2.25× longer than the original column, or 4.5 m in length.

To increase the number of theoretical plates without increasing the column's length, we must decrease the height of a theoretical plate. First, let's calculate the number of theoretical plates for the second solute in Figure 12.68, as this is the number of theoretical plates that appears in equation 12.19; thus

$$N_B = 16 \times \left(\frac{t_{r,B}}{w_B}\right)^2 = 16 \times \left(\frac{370\ s}{20.3\ s}\right)^2 = 5315\ \text{plates}$$

To increase the number of theoretical plates by a factor of 2.25× requires a column that has 11 960 plates, or a height of

$$H = \frac{L}{N} = \frac{2\ m \times \dfrac{1000\ mm}{m}}{11960\ \text{plates}} = 0.167\ \text{mm/plate}$$

6. Using equation 12.19, we find that for the first row the resolution is

$$R_{AB} = \frac{\sqrt{100000}}{4} \times \frac{1.05 - 1}{1.05} \times \frac{0.5}{1 + 0.5} = 1.25$$

and for the second row, the retention factor for solute B is

$$1.50 = \frac{\sqrt{10000}}{4} \times \frac{1.10 - 1}{1.10} \times \frac{k_B}{1 + k_B}$$

$$1.50 = 2.273 \times \frac{k_B}{1 + k_B}$$

$$0.6599 + 0.6599k_B = k_B$$

$$k_B = 1.94$$

and for the third row, the selectivity ratio is

$$1.00 = \frac{\sqrt{10000}}{4} \times \frac{\alpha - 1}{\alpha} \times \frac{4}{1 + 4}$$

$$1.00 = 20 \times \frac{\alpha - 1}{\alpha}$$
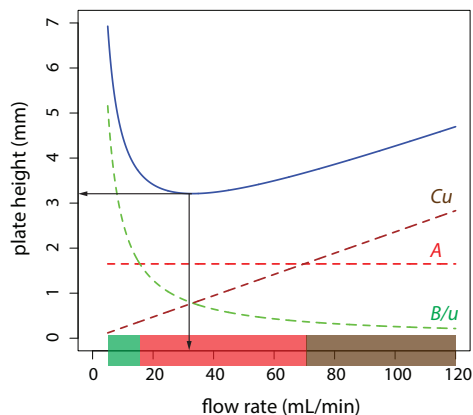
Figure SM12.1 The van Deemter plot for Problem 7a. The solid **blue** line shows the plate height as a function of flow rate using equation 12.26; the **red**, **green**, and **brown** dashed lines show, respectively, the contribution to the plate height of multiple paths (*A*), of longitudinal diffusion (*B*), and of mass transfer (*C*). The range of flow rates where each term is the limiting factor are shown along the *x*-axis; from left-to-right, they are *B*, *A*, and *C*. The arrows identify the optimum flow rate of 33 mL/min with a plate height of 3.20 mm.
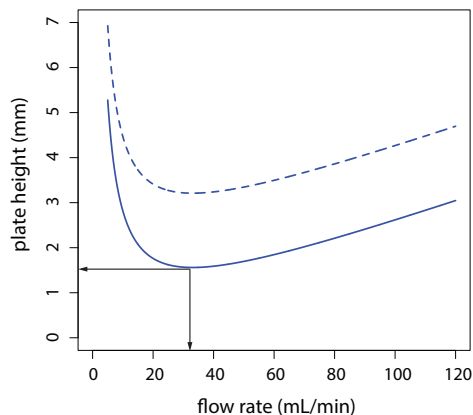
Figure SM12.2 The van Deemter plot for Problem 7d. The solid **blue** line shows the plate height as a function of flow rate for an open-tubular column and the dashed **blue** line is for the packed column in Problem 7a. The arrows identify the optimum flow rate of 33 mL/min with a plate height of 1.56 mm.

$$0.0500\alpha = \alpha - 1$$

$$\alpha = 1.05$$

and for the fourth row, the number of theoretical plates is

$$1.75 = \frac{\sqrt{N_B}}{4} \times \frac{1.05 - 1}{1.05} \times \frac{3.0}{1 + 3.0}$$

$$1.75 = 8.929 \times 10^{-3} \sqrt{N_B}$$

$$\sqrt{N_B} = 196.0$$

$$N_B = 38400 \text{ plates}$$

7. (a) Figure SM12.1 shows the van Deemter plot of plate height, *H*, as a function of the mobile phase's flow rate, *u*, with the individual contributions to plate height shown by the dashed lines and their combined contribution shown by the solid line.

(b) The *B* term (longitudinal diffusion) limits the plate height for flow rates less than 16 mL/min. The *A* term (multiple pathlengths) limits the plate height for flow rates between 16 mL/min and 71 mL/min. The *C* term (mass transfer) limits the plate height for flow rates greater than 71 mL/min.

(c) The optimum flow rate is 33 mL/min with a corresponding plate height of 3.20 mm.

(d) Figure SM12.2 shows the van Deemter plot for an open-tubular column along with the original packed column from part (a). The optimum flow rate remains unchanged at 33 mL/min, but the corresponding plate height is 1.56 mm.

(e) Using equation 12.10

$$\frac{N_{open}}{N_{packed}} = \frac{L/H_{open}}{L/H_{packed}} = \frac{H_{packed}}{H_{open}} = \frac{3.20 \text{ mm}}{1.56 \text{ mm}} = 2.05$$

we find that the open-tubular column has approximately $2\times$ as many theoretical plates as in the packed column.

8. (a) Figure SM12.3 shows the van Deemter plots for both the first row of data and for the last row of data. For the first row of data, the optimum reduced flow rate is 3.63, which corresponds to an actual flow rate of

$$u = \frac{\nu D_m}{d_p} = \frac{3.63 \times (6.23 \times 10^{-6} \text{ cm}^2\text{s}^{-1})}{(5.44 \times 10^{-6} \text{ m}) \times \frac{100 \text{ cm}}{\text{m}}} = 0.0416 \text{ cm/s}$$

and the optimum reduced plate height is 1.36, which corresponds to an actual plate height of

$$H = hd_p = 1.36 \times (5.44 \, \mu m) = 7.40 \, \mu m$$

For the last row of data, the optimum reduced flow rate is 3.25, which corresponds to an actual flow rate of

$$u = \frac{\nu D_m}{d_p} = \frac{3.25 \times (6.23 \times 10^{-6} \, cm^2 s^{-1})}{(5.44 \times 10^{-6} \, m) \times \dfrac{100 \, cm}{m}} = 0.0372 \, cm/s$$

and the optimum reduced plate height is 0.97, which corresponds to an actual plate height of

$$H = hd_p = 0.97 \times (5.44 \, \mu m) = 5.28 \, \mu m$$

(b) One of the most important contributions to the multiple paths term (A) in the van Deemter equation, is the difference in the stationary phase's packing efficiency near the column's walls relative to that near the column's center. The less compact packing found near the column's walls allows for a shorter pathlength through the column. Solute molecules that spend more time near the column's walls elute more quickly than solute molecules that spend more time near the column's center. The result of this difference, of course, is greater band broadening, fewer theoretical plates, and larger value for H. A column with an internal diameter of 12 µm packed with 5.44 µm diameter particles can fit only two particles side-by-side, which means it no longer makes sense to distinguish between the column's center and its walls; the result is a reduction in A.
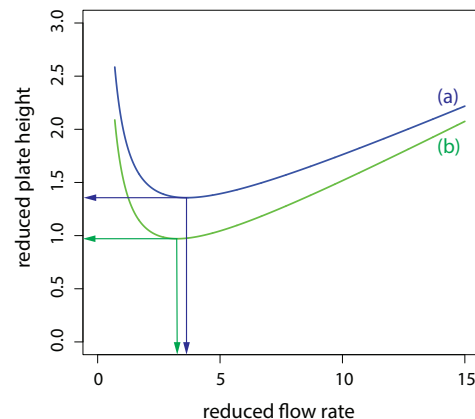
Figure SM12.3 The van Deemter plot for Problem 8a. The solid **blue** line shows results for the first row of data and the solid **green** line shows the results for the last row of data. The arrows identify the optimum reduced flow rate and the optimum reduced plate height for each set of data.

9. The order of elution in both cases is determined by the relative polarities of the solutes, which, from least polar-to-most polar are n-heptane, tetrahydrofuran, 2-butanone, and n-proponal. When using a more polar stationary phase, such as Carbowax, the more polar solutes are retained longer—and, thus, elute later—than the less polar solutes. The order of elution is reversed when using a less polar stationary phase, such as polydimethyl siloxane.

10. For a single standard we assume that $S = k_A C_A$, where S is the signal, k_A is the analyte's sensitivity, and C_A is the analyte's concentration. Given the data for the standard that contains all four trihalomethanes, we obtain the following values of k_A

$$k_{CHCl_3} = \frac{S}{C_{CHCl_3}} = \frac{1.35 \times 10^4}{1.30 \, ppb} = 1.038 \times 10^4 \, ppb^{-1}$$

$$k_{CHCl_2Br} = \frac{S}{C_{CHCl_2Br}} = \frac{6.12 \times 10^4}{0.90 \, ppb} = 6.800 \times 10^4 \, ppb^{-1}$$

$$k_{CHClBr_2} = \frac{S}{C_{CHClBr_2}} = \frac{1.71 \times 10^4}{4.00 \, ppb} = 4.275 \times 10^3 \, ppb^{-1}$$

$$k_{CHBr_3} = \frac{S}{C_{CHBr_3}} = \frac{1.52 \times 10^4}{1.20 \, ppb} = 1.267 \times 10^4 \, ppb^{-1}$$

Now that we know each analyte's sensitivity, we can calculate each analyte's concentration in the sample; thus

$$C_{CHCl_3} = \frac{S}{k_{CHCl_3}} = \frac{1.56 \times 10^4}{1.038 \times 10^4 \text{ ppb}^{-1}} = 1.50 \text{ ppb}$$

$$C_{CHCl_2Br} = \frac{S}{k_{CHCl_2Br}} = \frac{5.13 \times 10^4}{6.800 \times 10^4 \text{ ppb}^{-1}} = 0.754 \text{ ppb}$$

$$C_{CHClBr_2} = \frac{S}{k_{CHClBr_2}} = \frac{1.49 \times 10^4}{4.275 \times 10^3 \text{ ppb}^{-1}} = 3.49 \text{ ppb}$$

$$C_{CHClBr_3} = \frac{S}{k_{CHClBr_3}} = \frac{1.76 \times 10^4}{1.267 \times 10^4 \text{ ppb}^{-1}} = 1.39 \text{ ppb}$$
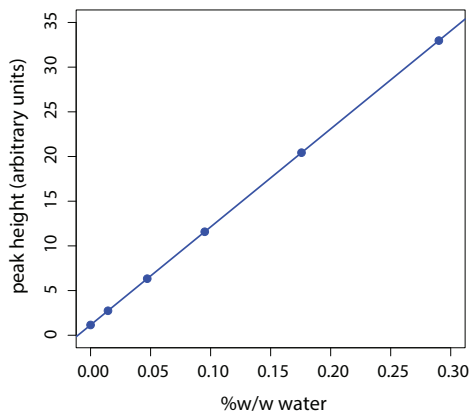
Figure SM12.4 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 11.

11. (a) Figure SM12.4 shows the calibration data and the calibration curve, for which the equation is

$$\text{peak height} = 1.151 + 109.7\%\text{w/w}^{-1} \times C_{water}$$

Substituting in the sample's peak height of 8.63 gives the concentration of water as 0.0682% w/w.

(b) Substituting in the sample's peak height of 13.66 gives the concentration of water as 0.114%w/w as analyzed. The concentration of water in the original sample is

$$\frac{\dfrac{0.114 \text{ g H}_2\text{O}}{100 \text{ g CH}_3\text{OH}} \times 4.489 \text{ g CH}_3\text{OH}}{0.175 \text{ g sample}} \times 100 = 2.92\%\text{w/w H}_2\text{O}$$

12. The two equations for this standard additions are

$$2.70 \times 10^5 = kC_{water}$$

$$1.06 \times 10^6 = k(C_{water} + 5.0 \text{ mg H}_2\text{O/g soil})$$

Solving the first equation for k and substituting into the second equation gives

$$1.06 \times 10^6 = \frac{2.70 \times 10^5}{C_{water}}(C_{water} + 5.0 \text{ mg H}_2\text{O/g soil})$$

which we solve for C_{water}

$$1.06 \times 10^6 = 2.70 \times 10^5 + \frac{1.35 \times 10^6 \text{ mg H}_2\text{O/g soil}}{C_{water}}$$

$$7.90 \times 10^5 = \frac{1.35 \times 10^6 \text{ mg H}_2\text{O/g soil}}{C_{water}}$$

$$C_{water} = \frac{1.35 \times 10^6 \text{ mg H}_2\text{O/g soil}}{7.90 \times 10^5} = 1.7 \text{ mg H}_2\text{O/g soil}$$
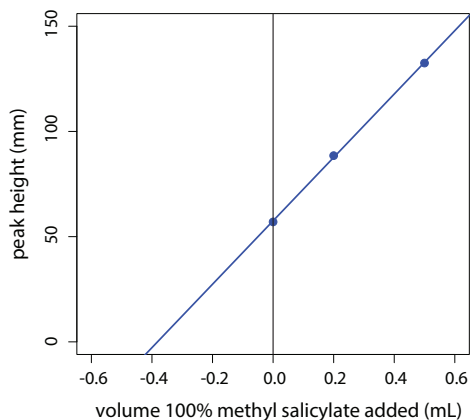
Figure SM12.5 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 13.

13. The three standard additions in this case are of pure methyl salicylate. Figure SM12.5 shows the calibration data and the calibration curve, plotting peak height on the *y*-axis versus the volume of methyl salic-

ylate added on the *x*-axis. A regression analysis gives the calibration equation as

$$\text{peak height} = 57.51 \text{ mm} + (150.66 \text{ mm/mL}) \times V_{\text{added}}$$

When we plot a standard addition in this way, the *y*-intercept is $k_A C_A V_o / V_f$, where k_A is the method's sensitivity for methyl salicylate, C_A is the concentration of methyl salicylate, V_o is the volume of sample taken (20.00 mL), and V_f is the sample's final volume after dilution (25.00 mL). The slope is $k_A C_{\text{std}} / V_f$, where C_{std} is the concentration of the standard solution of methyl salicylate (100%). Solving both the equation for the slope, b_1, and the equation for the *y*-intercept, b_0, for k, and setting the equations equal to each other gives

$$\frac{b_0 V_f}{C_A V_o} = k_A = \frac{b_1 V_f}{C_{\text{std}}}$$

Solving for C_A gives its value as

$$C_A = \frac{b_0 C_{\text{std}}}{b_1 V_o} = \frac{57.51 \text{ mm} \times 100\%}{150.66 \text{ mm/mL} \times 20.00 \text{ mL}} = 1.91\%$$

14. For the internal standard we have

$$\frac{S_A}{S_{\text{IS}}} = \frac{67.3}{19.8} = K \times \frac{C_A}{C_{\text{IS}}} = \frac{45.2 \text{ mg camphor}}{(2.00 \text{ mL}) \times (6.00 \text{ mg terpene/mL})}$$

which we solve for K, obtaining 0.902 mg camphor/mg terpene. Using this value for K and the data for the sample, we have

$$\frac{24.9}{13.5} = \frac{0.902 \text{ mg camphor}}{\text{mg terpene}} \times \frac{C_A}{2.00 \text{ mL} \times \dfrac{6.00 \text{ mg terpene}}{\text{mL}}}$$

which we solve for C_A, obtaining 24.54 mg camphor in the sample as analyzed. The concentration of camphor in the original sample is

$$\frac{24.45 \text{ mg camphor}}{53.6 \text{ mg sample}} \times 100 = 45.8\% \text{w/w camphor}$$

15. Figure SM12.6 shows the calibration data and the calibration curve, for which the equation is

$$\frac{A_{\text{analyte}}}{A_{\text{int std}}} = -0.01983 + (3.206 \times 10^{-3} \text{ ppb}^{-1})\, C_{\text{analyte}}$$

Substituting in the sample's peak area ratio of 0.108 gives the concentration of heptachlor epoxide as 39.87 ppb in the sample as analyzed. The concentration of heptachlor epoxide in the original sample of orange rind is

$$\frac{\dfrac{39.86 \text{ ng}}{\text{mL}} \times 10.00 \text{ mL}}{50.0 \text{ g sample}} = \frac{7.97 \text{ ng}}{\text{g}} = 7.97 \text{ ppb}$$
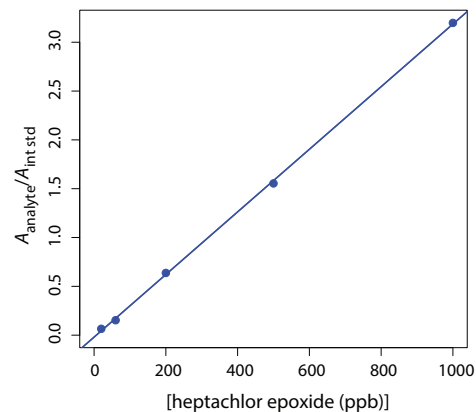
Figure SM12.6 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 15.

Recall that 1.00 ppb is equivalent to 1.00 ng/mL or to 1.00 ng/g.
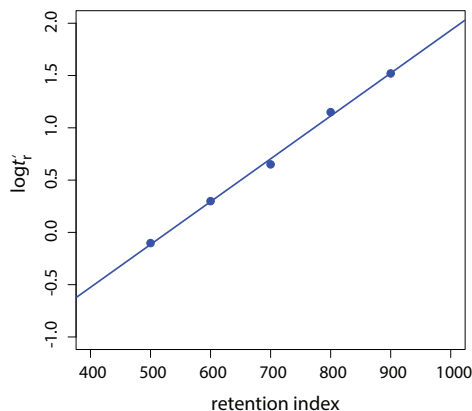
Figure SM12.7 Calibration data (**blue dots**) and calibration curve (**blue** line) for the data in Problem 17.
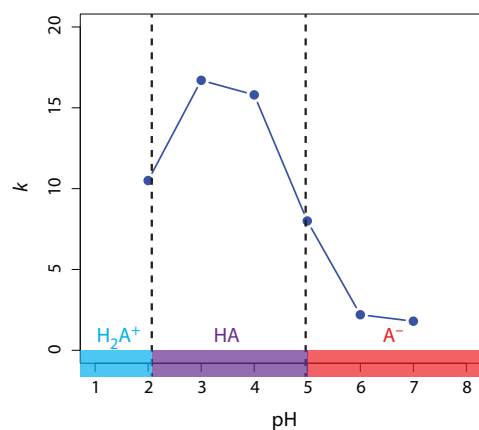
Figure SM12.8 Plot showing the effect of pH on the retention factor for 2-amino-benzoic acid. The x-axis also displays the ladder diagram for 2-aminobenzoic acid, which shows, in **blue**, that its full protonated form, H_2A^+, is the predominate species below a pH of 2.08, that shows, in **purple**, that its neutral form, HA, is the predominate species between a pH of 2.08 and a pH of 4.96, and that shows, in **red**, that its fully deprotonated form, A^-, is the predominate species above a pH of 4.96.

16. The retention indices for octane and for nonane are, by definition, 800 and 900, respectively. The retention index for toluene is calculated using equation 12.27; thus

$$I_{\text{toluene}} = 100 \times \frac{\log(17.73) - \log(15.98)}{\log(20.42) - \log(15.98)} + 800 = 842$$

17. Figure SM12.7 shows a plot of the data where the y-axis is the log of adjusted retention time and where the x-axis is the retention index (100×number of C atoms). A regression analysis of the data gives the calibration curve's equation as

$$\log t'_r = -2.163 + (4.096 \times 10^{-3})I$$

Substituting in the analyte's retention time of 9.36 min gives its retention index, I, as 765.

18. In a split injection, only a small portion of the sample enters the column, which results in peaks with smaller areas and smaller widths when compared to a splitless injection, where essentially all the sample enters the column. Because it takes longer for the sample to enter the column when using a splitless injection, retention times are longer and peak widths are broader.

19. Figure SM12.8 shows a plot of the retention factor for 2-amino-benzoic acid as a function of pH. Superimposed on the x-axis is a ladder diagram for 2-aminobenzoice acid, a diprotic weak acid with pK_a values of 2.08 and of 4.96. The neutral form of 2-aminobenzoic acid, HA, partitions into the stationary phase to a greater extent and, therefore, has a longer retention time and a larger retention factor than either its fully protonated form, H_2A^+, or its fully deprotonated form, A^-.

20. (a) For a reverse-phase separation, increasing the %v/v methanol in the mobile phase leads to a less polar mobile phase and to smaller retention times; the result is a decrease in each solute's retention factor.

    (b) The advantage to using a smaller concentration of methanol in the mobile phase is that the resolution between caffeine and salicylamide is better ($\alpha = 1.8$ when using 30%v/v methanol and $\alpha = 1.3$ when using 55% methanol); the disadvantage of using a smaller concentration of methanol is that the separation requires more time.

21. (a) The retention time for benzoic acid (pK_a of 4.2) shows a sharp decrease between a pH of 4.0 and 4.5 as its predominate form changes from a neutral weak acid, HA, to an anionic weak base, A^-, that is less strong retained by the stationary phase. The retention time for aspartame (reported pK_a values are in the range of 3.0–3.5 and 7.3–8.5) increases above a pH of 3.5 as its predominate form changes from H_2A^+ to HA, with the neutral form being more strong retained by the stationary phase. Caffeine is a neutral base throughout this

pH range; thus, the modest change in its retention times cannot be explained by its acid-base chemistry.

(b) Figure SM12.9 shows a plot of the retention times for each species as a function of pH. The two shaded areas show ranges of pH values where an adequate separation is likely (defined here as a difference in retention time of at least 1.0 min). For pH values between 3.5 and 4.1, the retention times for benzoic acid and aspartame are similar in value, with the two coeluting at a pH of approximately 3.9. Above a pH of 4.3, the retention times for benzoic acid and caffeine are similar in value with the two coeluting a pH of 4.4.

22. For a single standard we assume that $S = k_A C_A$, where S is the signal, k_A is the analyte's sensitivity, and C_A is the analyte's concentration. Given the data for the standard that contains all seven analytes, we obtain the following values of k_A

$$k_{\text{vit C}} = \frac{S}{C_{\text{vit C}}} = \frac{0.22}{170 \text{ ppm}} = 1.29 \times 10^{-3} \text{ ppm}^{-1}$$

$$k_{\text{niacin}} = \frac{S}{C_{\text{niacin}}} = \frac{1.35}{130 \text{ ppm}} = 1.04 \times 10^{-2} \text{ ppm}^{-1}$$

$$k_{\text{niacinamide}} = \frac{S}{C_{\text{niacinamide}}} = \frac{0.90}{120 \text{ ppm}} = 7.50 \times 10^{-3} \text{ ppm}^{-1}$$

$$k_{\text{pyridoxine}} = \frac{S}{C_{\text{pyridoxine}}} = \frac{1.37}{150 \text{ ppm}} = 9.13 \times 10^{-3} \text{ ppm}^{-1}$$

$$k_{\text{thiamine}} = \frac{S}{C_{\text{thiamine}}} = \frac{0.82}{60 \text{ ppm}} = 1.37 \times 10^{-2} \text{ ppm}^{-1}$$

$$k_{\text{folic acid}} = \frac{S}{C_{\text{folic acid}}} = \frac{0.36}{15 \text{ ppm}} = 2.40 \times 10^{-2} \text{ ppm}^{-1}$$

$$k_{\text{riboflavin}} = \frac{S}{C_{\text{riboflavin}}} = \frac{0.29}{10 \text{ ppm}} = 2.90 \times 10^{-2} \text{ ppm}^{-1}$$

Now that we know each analyte's sensitivity, we can calculate each analyte's concentration in the sample; thus

$$C_{\text{Vit C}} = \frac{S}{k_{\text{Vit C}}} = \frac{0.87}{1.29 \times 10^{-3} \text{ ppm}^{-1}} = 674 \text{ ppm}$$

$$C_{\text{niacin}} = \frac{S}{k_{\text{niacin}}} = \frac{0.00}{1.04 \times 10^{-2} \text{ ppm}^{-1}} = 0 \text{ ppm}$$

$$C_{\text{niacinamide}} = \frac{S}{k_{\text{niacinamide}}} = \frac{1.40}{7.50 \times 10^{-3} \text{ ppm}^{-1}} = 187 \text{ ppm}$$

$$C_{\text{pryidoxine}} = \frac{S}{k_{\text{pryidoxine}}} = \frac{0.22}{9.13 \times 10^{-3} \text{ ppm}^{-1}} = 24.1 \text{ ppm}$$

$$C_{\text{thiamine}} = \frac{S}{k_{\text{thiamine}}} = \frac{0.19}{1.37 \times 10^{-2} \text{ ppm}^{-1}} = 13.9 \text{ ppm}$$

Figure SM12.9 Plot showing the effect of pH on the retention times for benzoic acid (in **blue**), for aspartame (in **green**), and for caffeine (in **red**). The areas highlighted in **brown** show mobile phases where an adequate separation of all three compounds is possible.

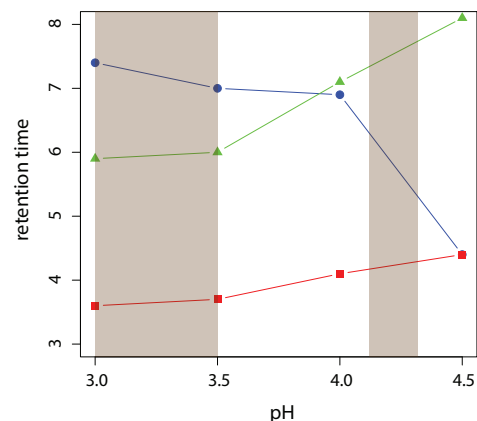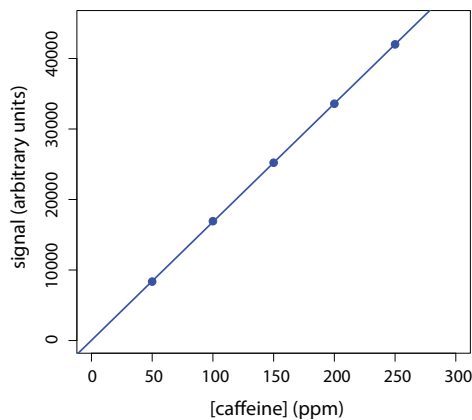**Figure SM12.10** Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 23.
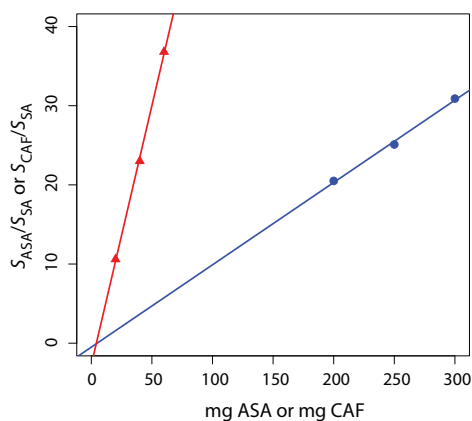
Figure SM12.11 Calibration data and calibration curve for the analytes in Problem 24: data and results for acetylsalicylic acid (ASA) shown in **blue**, and data and results for caffeine (CAF) shown in **red**.

$$C_{\text{folic acid}} = \frac{S}{k_{\text{folic acid}}} = \frac{0.11}{2.40 \times 10^{-2} \text{ ppm}^{-1}} = 4.58 \text{ ppm}$$

$$C_{\text{riboflavin}} = \frac{S}{k_{\text{riboflavin}}} = \frac{0.44}{2.90 \times 10^{-2} \text{ ppm}^{-1}} = 15.2 \text{ ppm}$$

These are the concentrations as analyzed. To prepare the tablet for analysis, we dissolved it in 100 mL of solvent (10 mL of 1% v/v NH_3 in dimethyl sulfoxide and 90 mL of 2% acetic acid); thus, we multiply each concentration by 0.100 L to arrive at the mass of each analyte in the original tablet: 67 mg of vitamin C; 0 mg of niacin; 19 mg of niacinamide; 2.4 mg of pyridoxine; 1.4 mg of thiamine; 0.46 mg of folic acid; and 1.5 mg of riboflavin.

23. Figure SM12.10 shows the calibration data and the calibration curve, for which the equation is

$$\text{signal} = 30.20 + (167.91 \text{ppm}^{-1})\, C_{\text{caffeine}}$$

Substituting in the sample's signal of 21 469 gives the concentration of caffeine as 127.7 ppm in the sample as analyzed. The amount of caffeine in the original sample, therefore, is

$$\frac{127.7 \text{ mg caffeine}}{L} \times \frac{10.00 \text{ mL}}{1.00 \text{ mL}} \times 0.02500 \text{ L} = 31.9 \text{ mg caffeine}$$

24. (a) Figure SM12.11 shows the calibration data and the calibration curves for both acetylsalicylic acid (ASA) and for caffeine (CAF), using salicylic acid (SA) as an internal standard. The calibration equation for acetylsalicylic acid is

$$\frac{S_{\text{ASA}}}{S_{\text{SA}}} = -0.5000 + (0.1040 \text{ mg}^{-1})\, m_{\text{ASA}}$$

and the calibration curve for caffeine is

$$\frac{S_{\text{CAF}}}{S_{\text{SA}}} = -2.733 + (0.6550 \text{ mg}^{-1})\, m_{\text{CAF}}$$

Substituting in the peak area ratio of 23.2 for ACA gives the amount of acetylsalicylic acid as 228 mg, and substituting in the peak area ratio of 17.9 for CAF gives the amount of caffeine as 31.5 mg. Because the standards and the sample were prepared identically, these are the amounts of acetylsalicylic acid and of caffeine in the original tablet.

(b) Analgesic tablets contain some insoluble materials. If we do not remove these insoluble materials before we inject the sample, we will clog the column and degrade its performance.

(c) When we use an internal standard, the relative amount of solvent is not important as it does not affect the ratio of analyte-to-internal standard in any standard or sample. What does matter is that we know the mass of acetylsalicylic acid and the mass of caffeine in each standard, and that we know that each standard contains the same

mass of the internal standard, salicylic acid; we ensure this by adding exactly 10.00 mL of the same standard solution of salicylic acid to each standard and to each sample.

(d) If there is some decomposition of acetylsalicylic acid to salicylic acid, then the analysis is no longer possible as an unknown portion of salicylic acid's peak area will come from acetylsalicylic acid. One way to determine if this is a problem is to inject a sample without adding any salicylic acid and then look to see whether a peak appears at the retention time for salicylic acid; if a peak is present, then we cannot use this method to determine the concentration of acetylsalicylic acid or caffeine.

25. We begin by letting m_A represent the milligrams of vitamin A in a 10.067 g portion of cereal. Because we use a different amount of cereal in the standard addition, 10.093 g, the cereal's contribution of vitamin A to the standard addition is

$$m_A \times \frac{10.093 \text{ g}}{10.067 \text{ g}}$$

The following two equations relate the signal to the mass of vitamin A in the sample and in the standard addition

$$S_{\text{sample}} = km_A$$

$$S_{\text{std add}} = k \left\{ m_A \times \frac{10.093 \text{ g}}{10.067 \text{ g}} + 0.0200 \text{ mg} \right\}$$

Solving both equations for k and setting them equal to each other leaves us with

$$\frac{S_{\text{sample}}}{m_A} = \frac{S_{\text{int std}}}{m_A \times \dfrac{10.093 \text{ g}}{10.067 \text{ g}} + 0.0200 \text{ mg}}$$

Making appropriate substitutions and solving gives

$$\frac{6.77 \times 10^3}{m_A} = \frac{1.32 \times 10^4}{m_A \times \dfrac{10.093 \text{ g}}{10.067 \text{ g}} + 0.0200 \text{ mg}}$$

$$(6.7875 \times 10^3) \, m_A + 135.4 \text{ mg} = (1.32 \times 10^4) \, m_A$$

$$6412.5 m_A = 135.4 \text{ mg}$$

$$m_A = 0.0211 \text{ mg}$$

The vitamin A content of the cereal, therefore, is

$$\frac{0.0211 \text{ mg vitamin A}}{10.067 \text{ g sample}} \times 100 = 0.211 \text{ mg vitamin A/100 g cereal}$$

26. (a) The separation is based on an anion-exchange column, which will not bind with Ca^{2+} or Mg^{2+}. Adding EDTA, a ligand that forms stable complexes with Ca^{2+} and Mg^{2+}, converts them to the anions CaY^{2-} and MgY^{2-}.

(b) For a single standard we assume that $S = k_A C_A$, where S is the signal, k_A is the analyte's sensitivity, and C_A is the analyte's concentration. Given the data for the standard that contains all seven analytes, we obtain the following values of k_A

$$k_{HCO_3^-} = \frac{S}{C_{HCO_3^-}} = \frac{373.5}{1.0 \text{ mM}} = 373.5 \text{ mM}^{-1}$$

$$k_{Cl^-} = \frac{S}{C_{Cl^-}} = \frac{322.5}{0.20 \text{ mM}} = 1612 \text{ mM}^{-1}$$

$$k_{NO_2^-} = \frac{S}{C_{NO_2^-}} = \frac{264.8}{0.20 \text{ mM}} = 1324 \text{ mM}^{-1}$$

$$k_{NO_3^-} = \frac{S}{C_{NO_3^-}} = \frac{262.7}{0.20 \text{ mM}} = 1314 \text{ mM}^{-1}$$

$$k_{SO_4^-} = \frac{S}{C_{SO_4^-}} = \frac{341.3}{0.20 \text{ mM}} = 1706 \text{ mM}^{-1}$$

$$k_{Ca^{2+}} = \frac{S}{C_{Ca^{2+}}} = \frac{458.9}{0.20 \text{ mM}} = 2294 \text{ mM}^{-1}$$

$$k_{Mg^{2+}} = \frac{S}{C_{Mg^{2+}}} = \frac{352.0}{0.20 \text{ mM}} = 1760 \text{ mM}^{-1}$$

Now that we know each analyte's sensitivity, we can calculate each analyte's concentration in the sample; thus

$$C_{HCO_3^-} = \frac{S}{k_{HCO_3^-}} = \frac{310.0}{373.5 \text{ mM}^{-1}} = 0.83 \text{ mM}$$

$$C_{Cl^-} = \frac{S}{k_{Cl^-}} = \frac{403.1}{1612 \text{ mM}^{-1}} = 0.25 \text{ mM}$$

$$C_{NO_2^-} = \frac{S}{k_{NO_2^-}} = \frac{3.97}{1324 \text{ mM}^{-1}} = 0.0030 \text{ mM}$$

$$C_{NO_3^-} = \frac{S}{k_{NO_3^-}} = \frac{262.7}{1314 \text{ mM}^{-1}} = 0.12 \text{ mM}$$

$$C_{SO_4^-} = \frac{S}{k_{SO_4^-}} = \frac{324.3}{1706 \text{ mM}^{-1}} = 0.19 \text{ mM}$$

$$C_{Ca^{2+}} = \frac{S}{k_{Ca^{2+}}} = \frac{734.3}{2294 \text{ mM}^{-1}} = 0.32 \text{ mM}$$

$$C_{Mg^{2+}} = \frac{S}{k_{Mg^{2+}}} = \frac{193.6}{1760 \text{ mM}^{-1}} = 0.11 \text{ mM}$$

(c) A mass balance for HCO_3^- requires that

$$C_{NaHCO_3} = 0.83 \text{ mM} = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$

Given that the pH of 7.49 is closer to pK_{a1}, which is 6.352, than it is to pK_{a2}, which is 10.329, we will assume that we can simplify the mass balance equation to

$$C_{NaHCO_3} = 0.83 \text{ mM} = [H_2CO_3] + [HCO_3^-]$$

Using the K_a expression for H_2CO_3

$$K_a = 4.45 \times 10^{-7} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]}$$

and substituting in for $[H_3O^+]$ using the pH, and substituting in the mass balance equation for $[H_2CO_3]$, gives

$$4.45 \times 10^{-7} = \frac{(3.24 \times 10^{-8})[HCO_3^-]}{0.83 \text{ mM} - [HCO_3^-]}$$

which we solve to find that

$$3.69 \times 10^{-7} \text{mM} - (4.45 \times 10^{-7})[HCO_3^-] = (3.24 \times 10^{-8})[HCO_3^-]$$

$$(4.77 \times 10^{-7})[HCO_3^-] = 3.69 \times 10^{-7} \text{ mM}$$

$$[HCO_3^-] = 0.77 \text{ mM}$$

(d) The ion balance, IB, for this sample is

$$IB = \frac{[Na^+] + [NH_4^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}]}{[HCO_3^-] + [Cl^-] + [NO_2^-] + [NO_3^-] + 2[SO_4^{2-}]}$$

$$IB = \frac{0.60 + 0.014 + 0.046 + 2(0.32) + 2(0.11)}{0.77 + 0.25 + 0.0030 + 0.12 + 2(0.19)}$$

$$IB = \frac{1.520}{1.523} = 0.998 \approx 1$$

Note that each ion's concentration is multiplied by the absolute value of its charge as we are interested in the concentration of charge, not the concentrations of ions.

This is a reasonable result as the total concentration of positive charge equals the total concentration of negative charge, within experimental error, as expected for an electrically neutral solution.

27. For a single standard we assume that $S = k_A C_A$, where S is the signal, k_A is the analyte's sensitivity, and C_A is the analyte's concentration. Given the data for the standard that contains all three analytes, we obtain the following values of k_A

$$k_{Cl^-} = \frac{S}{C_{Cl^-}} = \frac{59.3}{10.0 \text{ ppm}} = 5.93 \text{ ppm}^{-1}$$

$$k_{NO_3^-} = \frac{S}{C_{NO_3^-}} = \frac{16.1}{2.00 \text{ ppm}} = 8.05 \text{ ppm}^{-1}$$

$$k_{SO_4^-} = \frac{S}{C_{SO_4^-}} = \frac{6.08}{5.00 \text{ ppm}} = 1.22 \text{ ppm}^{-1}$$

Now that we know each analyte's sensitivity, we can calculate each analyte's concentration in the sample; thus

Figure SM12.12 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 28. Note that this is an unusual calibration curve in that we place the dependent variable—what we measure, which in this case is retention volume for the standards—on the *x*-axis instead of the *y*-axis, and the independent variable—what we control, which in this case is the formula weight of our standards—on the *y*-axis instead of the *x*-axis. There is nothing wrong with this choice, although we cannot use equation 5.25 to estimate the uncertainty in our determination of a sample's formula weight.

$$C_{Cl^-} = \frac{S}{k_{Cl^-}} = \frac{44.2}{5.93 \text{ ppm}^{-1}} = 7.45 \text{ ppm}$$

$$C_{NO_3^-} = \frac{S}{k_{NO_3^-}} = \frac{2.73}{8.05 \text{ ppm}^{-1}} = 0.339 \text{ ppm}$$

$$C_{SO_4^-} = \frac{S}{k_{SO_4^-}} = \frac{5.04}{1.22 \text{ ppm}^{-1}} = 4.13 \text{ ppm}$$

These are the concentrations as analyzed; because the original sample was diluted by a factor of $10\times$, the actual concentrations in the wastewater are 74.5 ppm Cl^-, 3.39 ppm NO_3^-, and 41.3 ppm SO_4^{2-}.

28. In size-exclusion chromatography, the calibration curve is a plot of log(formula weight) as a function of retention volume. Figure SM12.12 shows the calibration data and the calibration curve for the standards, for which the calibration equation is

$$\log(\text{formula weight}) = 9.062 - (.5107 \text{ mL}^{-1})\,V$$

Substituting in the sample's retention volume of 8.45 mL, gives a result of 4.747 for log(formula weight), or a formula weight of 55,800 g/mol.

29. Given the pK_a values and a pH of 9.4, caffeine is present in its neutral form, and benzoic acid and aspartame are present as singly charged anions. Caffeine, therefore, is the first of the three analytes to elute because the general elution order for CZE is cations, neutrals, and anions. Benzoic acid is smaller than aspartame, which means its electrophoretic mobility, μ_{ep}, is more negative than that for aspartame, and that it total electrophoretic mobility, μ_{tot}, is less positive than that for aspartame; thus, aspartame elutes before benzoic acid.

30. Substituting in the area of 15 310 for the first sample into the calibration equation gives the concentration of Cl^- as 2.897 ppm in the sample as analyzed. The %w/w Cl^- in the original sample is

$$\frac{\left\{ \begin{array}{c} \dfrac{2.897 \text{ mg}}{L} \times \dfrac{50.00 \text{ mL}}{0.250 \text{ mL}} \\ \times\, 0.1000 \text{ L} \times \dfrac{1 \text{ g}}{1000 \text{ mg}} \end{array} \right\}}{0.1011 \text{ g sample}} \times 100 = 57.3\%\text{w/w } Cl^-$$

The remaining two samples give concentrations of 57.4%w/w Cl^- and %57.2%w/w Cl^-. The mean and the standard deviation for the three samples are 57.3%w/w Cl^- and 0.1%w/w Cl^-, respectively.

To evaluate the method's accuracy, we use a *t*-test of the following null and alternative hypotheses

$$H_0: \overline{X} = \mu \qquad H_A: \overline{X} \neq \mu$$

where μ is 57.22%w/w Cl^-. The test statistics is t_{exp}, for which

$$t_{exp} = \frac{|\mu - \overline{X}|\sqrt{n}}{s} = \frac{|57.22 - 57.3|\sqrt{3}}{0.10} = 1.39$$

The critical value for $t(0.05,2)$ is 4.303. Because t_{exp} is less than $t(0.05,2)$, we have no evidence at $\alpha = 0.05$ that there is a significant difference between our experimental mean of 57.33%w/w Cl^- and the accepted mean of 57.22%w/w Cl^-.

31. For the internal standard we have

$$\frac{S_{NO_3^-}}{S_{IO_4^-}} = \frac{95.0}{100.1} = K \times C_{NO_3^-} = K \times (15.0 \text{ ppm } NO_3^-)$$

for which K is 0.06327 ppm^{-1}. Using this value for K, for the sample we find that

$$\frac{S_{NO_3^-}}{S_{IO_4^-}} = \frac{29.2}{105.8} = 0.06327 \text{ ppm}^{-1} \times C_{NO_3^-}$$

the concentration of NO_3^- is 4.36 ppm in the sample as analyzed. Because the sample is diluted by a factor of $100\times$, the concentration of nitrate in the original sample is 436 ppm.

32. One approach to separating the compounds is to find a pH where one of the compounds is present as a cation, one of the compounds is present as a neutral species, and one of the compounds is present as an anion. Figure SM12.13, which you will recognize as an alternative form of a ladder diagram, shows the pH ranges where each of a compound's different forms is the predominate species, using blue to represent cations, green to represents neutrals, and red to represent anions. For pH levels between the two dashed lines—a range of pH values from 4.96 to 9.35—the three analytes have different charges and should elute as separate bands. The expected order of elution is benzylamine (as a cation), 4-methylphenol (as a neutral), and 2-aminobenzoic acid (as an anion).

33. (a) Using equation 12.42, we find that the electrophoretic mobility, μ_{ep}, is

$$t_m = \frac{lL}{(\mu_{ep} + \mu_{eof})V}$$

$$8.20 \text{ min} \times \frac{60 \text{ s}}{\text{min}} = \frac{(50 \text{ cm})(57 \text{ cm})}{(\mu_{ep} + 6.398 \times 10^{-5} \text{cm}^2\text{V}^{-1}\text{s}^{-1})(15 \times 10^3 \text{V})}$$

$$(7.38 \times 10^6 \text{Vs})\mu_{ep} + 472\text{cm}^2 = 2850\text{cm}^2$$

$$\mu_{ep} = 3.22 \times 10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

(b) From equation 12.43, the number of theoretical plates, N, is

$$N = \frac{(\mu_{ep} + \mu_{eof})El}{2DL}$$

Because the internal standard's concentration is the same in the standard and in the sample, we do not need to include it in this equation. If we did include it, then the equation is

$$\frac{S_{NO_3^-}}{S_{IO_4^-}} = K \times \frac{C_{NO_3^-}}{C_{IO_4^-}}$$

and the value for K is 0.6327.
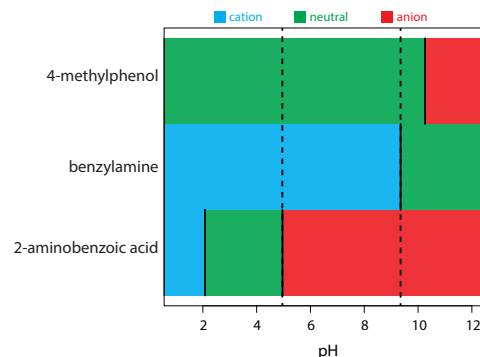
Figure SM12.13 Ladder diagram showing the predominate forms for 2-aminobenzoic acid, benzylamine, and 4-methylphenol as a function of pH. The color indicates the predominate form of each compound with **blue** representing cations, **green** representing neutrals, and **red** representing anions.

$$N = \frac{\left(\begin{array}{c}3.22 \times 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1} + \\ 6.398 \times 10^{-5}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}\end{array}\right)(15000\,\text{V})(50\,\text{cm})}{2(1.0 \times 10^{-5}\,\text{cm}^2\text{s}^{-2})(57\,\text{cm})}$$

$$N = 253934 \approx 254000$$

(c) Resolution is calculated using equation 12.43; first, however, we need to calculate the average electrophoretic mobility, μ_{avg}, for the two solutes

$$\mu_{avg} = \frac{3.366 \times 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1} + 3.397 \times 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}}{2}$$

which gives μ_{avg} as $3.3815 \times 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The resolution, therefore, is

$$R = \frac{0.177\,(\mu_{ep,2} - \mu_{ep,1})\sqrt{V}}{\sqrt{D(\mu_{avg} + \mu_{eof})}}$$

$$R = \frac{0.177\left(\begin{array}{c}3.397 \times 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1} - \\ 3.366 \times 10^{-5}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}\end{array}\right)\sqrt{15000\,\text{V}}}{\sqrt{(1.0 \times 10^{-5}\,\text{cm}^2\text{s}^{-2})\left(\begin{array}{c}3.3815 \times 10^{-4}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1} + \\ 6.398 \times 10^{-5}\,\text{cm}^2\text{V}^{-1}\text{s}^{-1}\end{array}\right)}}$$

$$R = 1.06 \approx 1.1$$

(d) From equation 12.35, we know that there is an inverse relationship between a solute's electrophoretic mobility, μ_{ep}, and its radius, r. For this set of compounds, the longer the alkyl chain attached to pyridine, the larger the compound; thus, electrophoretic mobility decreases from 2-methylpyridine to 2-hexylpyridine.

(e) These three isomeric ethylpyridines have the same effective radius, suggesting that they should have essentially identical electrophoretic mobilities. Equation 12.35, however, treats the solutes as if they are spheres. Of course, they are not spheres, and solutes that are of similar size but have a different shape may show a difference in their relative electrophoretic mobilities due to friction as they move through the buffer. At a pH of 2.5, all three solutes are present in their fully protonated, cationic form and are aligned with the applied field as shown in Figure SM12.14. Of the three solutes, 4-ethylpyridine is the most "stream-lined" and, therefore, has the largest electrophoretic mobility. Of the other two isomers, 2-ethylpyridine is the less "stream-lined" and, therefore, has the smallest electrophoretic mobility.

(f) At a pH of 7.5, the predominate form of pyridine is its neutral, weak base form. As it is neutral, its electrophoretic mobility is zero.

Figure SM12.14 Structures of the isomeric ethylpyridines in Problem 33e. In an applied field, the compounds are oriented so that their center of charge and their center of mass are aligned with the field's direction. For a more detailed discussion, see the reference in the text.

Chapter 13

1. To derive an appropriate equation we first note the following general relationship between the concentration of A at time t, $[A]_t$, the initial concentration of A, $[A]_0$, and the concentration of P at time t, $[P]_t$

$$[A]_t = [A]_0 - [P]_t$$

Substituting this relationship into equation 13.18 for times t_1 and t_2, gives the desired result

$$[A]_0 = \frac{[A]_{t1} - [A]_{t2}}{e^{-k't_1} - e^{-k't_2}}$$

$$[A]_0 = \frac{([A]_0 - [P]_{t1}) - ([A]_0 - [P]_{t2})}{e^{-k't_1} - e^{-k't_2}}$$

$$[A]_0 = \frac{[A]_0 - [P]_{t1} - [A]_0 + [P]_{t2}}{e^{-k't_1} - e^{-k't_2}}$$

$$[A]_0 = \frac{[P]_{t2} - [P]_{t1}}{e^{-k't_1} - e^{-k't_2}}$$

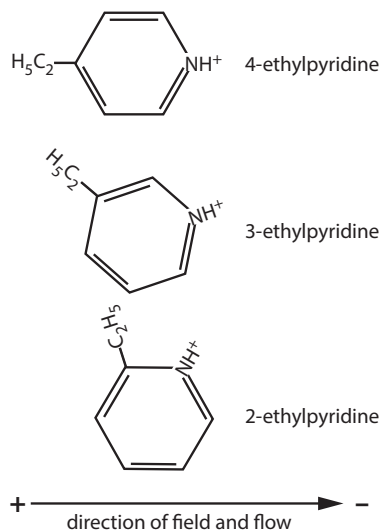2. For a one-point fixed time method, a pseudo-first order reaction obeys the equation

$$[A]_t = [A]_0 e^{-kt} = K[A]_0$$

where A is phenylacetate and K is equal to e^{-kt}. Using the standard, we find that K is

$$0.17 \text{ mM} = K(0.55 \text{ mM})$$

$$K = \frac{0.17 \text{ mM}}{0.55 \text{ mM}} = 0.309$$

Thus, for the sample, we have

$$[\text{phenylacetate}]_0 = \frac{0.23 \text{ mM}}{0.309} = 0.74 \text{ mM}$$

You can, of course, use the equation $[A]_t = [A]_0 e^{-kt}$ and the result for the standard to calculate the rate constant, k, and then use the same equation and the result for the sample to calculate the concentration of phenylacetate. The rate constant has a value of 0.0196 s^{-1}.

3. Because we are following the change in concentration for a product, the kinetics follow equation 13.15

$$[H_2O_2]_0 = \frac{[I_2]_t}{1 - e^{-k't}}$$

which we rearrange to solve for the product's concentration

$$[I_2]_t = [H_2O_2]_0 (1 - e^{-k't})$$

From Beer's law, we know that the absorbance, A, is
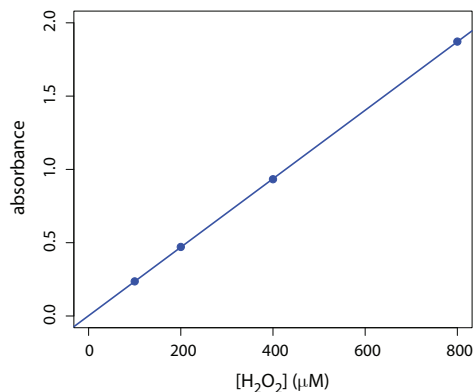
Figure SM13.1 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 3.

$$A_t = \varepsilon b [I_2]_t$$

Substituting this equation back into the previous equation gives

$$A_t = (\varepsilon b)^{-1}[H_2O_2]_0(1 - e^{-k't}) = K[H_2O_2]_0$$

where K is equal to $(\varepsilon b)^{-1}(1 - e^{-k't})$. Using the data for the external standards gives the calibration curve shown in Figure SM13.1, the equation for which is

$$A_t = 0.002 + 2.336 \times 10^{-3}\,\mu M^{-1}\,C_{H_2O_2}$$

Substituting in the sample's absorbance of 0.669 gives the concentration of H_2O_2 as 286 μM.

4. For a two-point fixed-time method, we use equation 13.18

$$[H_2CrO_4]_0 = \frac{[H_2CrO_4]_{t_1} - [H_2CrO_4]_{t_2}}{e^{-k't_1} - e^{-k't_2}}$$

From Beer's law, we know that

$$A_{t_1} = \varepsilon b[H_2CrO_4]_{t_1} \qquad A_{t_2} = \varepsilon b[H_2CrO_4]_{t_2}$$

Solving these two equations for the concentration of chromic acid at times t_1 and t_2, and substituting back gives

$$[H_2CrO_4]_0 = \frac{\dfrac{A_{t_1}}{\varepsilon b} - \dfrac{A_{t_2}}{\varepsilon b}}{e^{-k't_1} - e^{-k't_2}} = \frac{(\varepsilon b)^{-1}(A_{t_1} - A_{t_2})}{e^{-k't_1} - e^{-k't_2}} = K(A_{t_1} - A_{t_2})$$

Using the data for the external standard, we find that

$$K = \frac{[H_2CrO_4]_0}{(A_{t_1} - A_{t_2})} = \frac{5.1 \times 10^{-4}\,M}{0.855 - 0.709} = 3.49 \times 10^{-3}\,M$$

The concentration of chromic acid in the sample, therefore, is

$$[H_2CrO_4]_0 = K(A_{t_1} - A_{t_2}) =$$
$$3.49 \times 10^{-3}\,M\,(0.883 - 0.706) = 6.2 \times 10^{-4}\,M$$

5. For a variable time kinetic method, there is an inverse relationship between the elapsed time, Δt, and the concentration of glucose. Figure SM13.2 shows the resulting calibration data and calibration curve, for which the equation is

$$(\Delta t)^{-1} = -6.30 \times 10^{-4}\,s^{-1} + 1.50 \times 10^{-3}\,s^{-1}\,ppm^{-1}\,C_{glucose}$$

where Δt for each standard is the average of the three measurements. Substituting in the sample's Δt of 34.6 s, or a $(\Delta t)^{-1}$ of 0.02890 s^{-1}, gives the concentration of glucose as 19.7 ppm for the sample. The relative error in the analysis is

$$\frac{19.7\ ppm - 20.0\ ppm}{20.0\ ppm} \times 100 = -1.5\%\ error$$
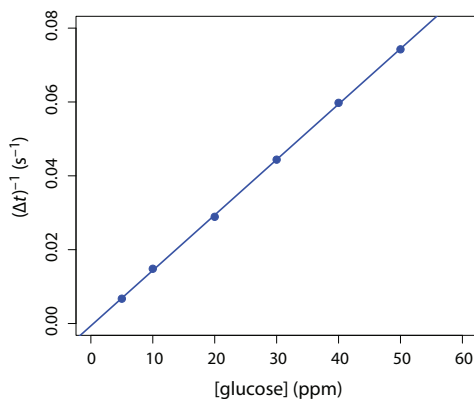
Figure SM13.2 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 5.

6. Substituting the sample's rate of 6.84×10^{-5} μmol mL^{-1}s^{-1} into the calibration equation gives the volume as

$$V = \frac{6.84 \times 10^{-5}\, \mu\text{mol}^{-1}\,\text{mL}^{-1}\,\text{s}^{-1} - 2.7 \times 10^{-7}\, \mu\text{mol}^{-1}\,\text{mL}^{-1}\,\text{s}^{-1}}{3.485 \times 10^{-5}\, \mu\text{mol}^{-1}\,\text{mL}^{-2}\,\text{s}^{-1}}$$

$$V = 1.95\ \text{mL}$$

This is the volume of the standard enzyme that has the same amount of enzyme as is in the 10.00 mL sample; thus, the concentration of enzyme in the sample is approximately 5× more dilute than the concentration of enzyme in the standard.

Figure SM13.3 Linearization of the data from Problem 6 for a reaction that is pseudo-first order in the analyte.

7. For a first-order reaction, a plot of $\ln[A]_t$ versus time gives a straight line with a slope equal to $-k$ and a y-intercept equal to $\ln[A]_0$. Figure SM13.3 shows the data and the regression line, for which the equation is

$$\ln[A]_t = 0.4069 - (0.04862\ \text{s}^{-1})\,t$$

From the slope, we know that the reaction's rate constant is $0.0486\ \text{s}^{-1}$. Using the y-intercept, we know that $\ln[A]_0$ is 0.4069, which makes the initial concentration of A equal to 1.50 mM.

8. Under these conditions—a concentration of acetylcholine that is significantly smaller than the constant, K_m—we can write the Michaelis-Menton equation as

$$R = \frac{k_2\,[E]_0\,[S]}{K_m}$$

where $[E]_0$ is the concentration of enzyme and $[S]$ is the concentration of the substrate acetylcholine; substituting in known values

$$12.33 \times 10^{-6}\ \text{Ms}^{-1} = \frac{(1.4 \times 10^{4}\,\text{s}^{-1})\,(6.61 \times 10^{-7}\,\text{M})\,[S]}{9 \times 10^{-5}\,\text{M}}$$

and solving gives the concentration of acetylcholine as 1.2×10^{-7} M.

9. Under these conditions—a concentration of fumarate that is significantly greater than the constant, K_m—we can write the Michaelis-Menton equation as

$$R = k_2\,[E]_0$$

where $[E]_0$ is the concentration of enzyme. Using the rate and concentration of enzyme for the standard, the value of k_2 is

$$k_2 = \frac{R}{[E]_0} = \frac{2.00\ \mu\text{M min}^{-1}}{0.150\ \mu\text{M}} = 13.33\ \text{min}^{-1}$$

Using this value for k_2 and the rate for the sample, we find that the enzyme's concentration in the sample is

$$[E]_0 = \frac{R}{k_2} = \frac{1.15\ \mu\text{M min}^{-1}}{13.33\ \text{min}^{-1}} = 0.0863\ \mu\text{M}$$

Figure SM13.4 Lineweaver-Burk plot of the data from Problem 10. The **blue** dots are the reciprocals of the concentration and rate data provided in the problem, and the **blue** line is the result of a regression analysis on the data.

10. Figure SM13.4 shows a Lineweaver-Burk plot of 1/rate as a function of 1/[urea], for which a regression analysis gives an equation of

$$\frac{1}{rate} = 2.464 \times 10^{-6}\,\mu M^{-1}s + \frac{(0.01600\ s)}{C_{urea}}$$

From the y-intercept we extract the value for the maximum rate; thus

$$V_{max} = \frac{1}{y-intercept} =$$

$$\frac{1}{2.464 \times 10^{-6}\,\mu M^{-1}s} = 4.058 \times 10^{5}\,\mu M\ s^{-1}$$

or 0.406 M/s. From the slope, we determine the value for K_m, finding that it is

$$K_m = (slope) \times V_{max} =$$

$$(0.01600\ s)(4.058 \times 10^{5}\,\mu M\ s^{-1}) = 6490\,\mu M$$

or 6.49×10^{-3} M. Finally, we know that $V_{max} = k_2\,[E]_0$, which we use to calculate the value for k_2

$$k_2 = \frac{4.058 \times 10^{5}\,\mu M\ s^{-1}}{5.0\,\mu M} = 8.1 \times 10^{4}\ s^{-1}$$

11. If V_{max} remains constant, then the y-intercept of a Lineweaver-Burk plot is independent of the inhibitor's concentration. If the value of K_m increases and the value of V_{max} remains constant for higher concentrations of the inhibitor, then the slope of a Lineweaver-Burk plot, which is equal to K_m/V_{max}, must increase for higher concentrations of the inhibitor. Figure 13.14 shows that both are consistent with competitive inhibition.

12. For competitive inhibition, the initial concentration of enzyme is divided between free enzyme, E, enzyme complexed with the substrate, ES, and enzyme complexed with the inhibitor, EI; thus, a mass balance on the enzyme requires that

$$[E]_0 = [E] + [ES] + [EI]$$

If we assume that k_2 is much smaller than k_{-1}, then we can simplify the equation for K_m to

$$K_m = \frac{k_{-1} + k_2}{k_1} \approx \frac{k_{-1}}{k_1} = K_{ES} = \frac{[E]\,[S]}{[ES]}$$

where K_{ES} is the equilibrium dissociation constant for the enzyme-substrate complex. We also can write the equilibrium dissociation constant for the enzyme-inhibitor complex, which is

$$K_{EI} = \frac{[E]\,[I]}{[EI]}$$

Solving K_m and K_{EI} for the concentrations of E and of EI, respectively

$$[E] = \frac{K_m[ES]}{[S]} \qquad [EI] = \frac{[E][I]}{K_{EI}}$$

and substituting back into the mass balance equation gives

$$[E]_0 = \frac{K_m[ES]}{[S]} + [ES] + \frac{[E][I]}{K_{EI}}$$

$$[E]_0 = \frac{K_m[ES]}{[S]} + [ES] + \frac{K_m[ES][I]}{[S]K_{EI}}$$

Factoring out $[ES]$ from the right side of the equation

$$[E]_0 = [ES]\left\{ \frac{K_m}{[S]} + 1 + \frac{K_m[I]}{[S]K_{EI}} \right\}$$

and then solving for $[ES]$ gives

$$[ES] = \frac{[E]_0}{\left\{ \dfrac{K_m}{[S]} + 1 + \dfrac{K_m[I]}{[S]K_{EI}} \right\}}$$

Finally, the rate of the reaction, $d[P]/dt$, is equal to $k_2[ES]$, or

$$\frac{d[P]}{dt} = k_2[ES] = \frac{k_2[E]_0}{\left\{ \dfrac{K_m}{[S]} + 1 + \dfrac{K_m[I]}{[S]K_{EI}} \right\}}$$

$$\frac{d[P]}{dt} = \frac{k_2[E]_0[S]}{\left\{ K_m + [S] + \dfrac{K_m[I]}{K_{EI}} \right\}}$$

$$\frac{d[P]}{dt} = \frac{V_{max}[S]}{K_m\left(1 + \dfrac{[I]}{K_{EI}}\right) + [S]}$$

13. For first-order kinetics, we know that

$$\ln\frac{[A]_t}{[A]_0} = -k_A t \qquad \ln\frac{[B]_t}{[B]_0} = -k_B t$$

To obtain 0.001 for $[A]_t/[A]_0$ and 0.999 for $[B]_t/[B]_0$, the ratio of the rate constants must be

$$\frac{\ln\dfrac{[A]_t}{[A]_0}}{\ln\dfrac{[B]_t}{[B]_0}} = \frac{-k_A t}{-k_B t}$$

$$\frac{\ln(0.001)}{\ln(0.999)} = \frac{k_A}{k_B} = 6900$$

14. Figure SM13.5 shows a plot of the data, where we place $\ln[C]_t$ on the y-axis as the kinetics are first-order. Early in the reaction, the plot is curved because both A and B are reacting. Because A reacts faster than B, eventually the reaction mixture consists of B only, and the plot becomes linear. A linear regression analysis of the data from $t = 36$ min to $t = 71$ min gives a regression equation of
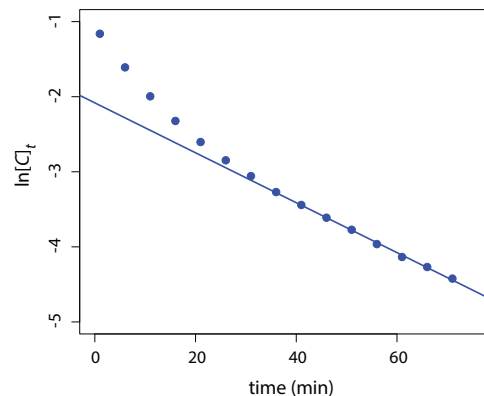
Figure SM13.5 Plot of the data for Problem 14. The **blue** dots are the original data and the **blue** line is a regression analysis restricted data from $t = 36$ min to $t = 71$ min when the reaction of A is complete.
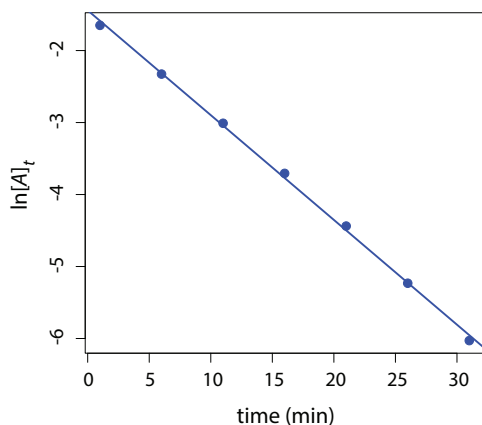
Figure SM13.6 Plot of the data for Problem 14 after we remove the contribution from B. The **blue** dots are the recalculated data and the **blue** line is a regression analysis restricted data from $t = 1$ min to $t = 31$ min when the reaction of A is complete.

$$\ln[C]_t \approx \ln[B]_t = -2.082 - (3.325 \times 10^{-2}\ \text{min}^{-1})\,t$$

The y-intercept of -2.082 is equivalent to $\ln[B]_0$; thus,

$$[B]_0 = e^{-2.082} = 0.125\ \text{mM}$$

The slope of the regression line in Figure SM13.5 gives the rate constant k_B, which is approximately $0.0332\ \text{min}^{-1}$. To find values for $[A]_0$ and for k_A, we must correct $[C]_t$ for the contribution of B. This is easy to do because we know that

$$[C]_t = [A]_t + [B]_t$$

and that

$$[B]_t = [B]_0 e^{-k_B t}$$

which means that

$$[A]_t = [C]_t - [B]_0 e^{-k_B t}$$

For example, at time $t = 1$, the concentration of B is 0.1209 mM and the concentration of A is 0.313 mM – 0.1209 mM = 0.1921 mM. Figure SM13.6 shows a plot of $\ln[A]_t$ versus time from $t = 1$ min to $t = 31$ min. A regression analysis of the data gives the following equation

$$\ln[A]_t = -1.442 - (0.1455\ \text{min}^{-1})\,t$$

from which the slope gives the value of k_A as $0.146\ \text{min}^{-1}$ and the y-intercept of -1.442 yields the initial concentration of A

$$[A]_0 = e^{-1.442} = 0.236\ \text{mM}$$

15. For radioactive decay, we know that $t_{1/2} = 0.693/\lambda$. Using the first entry in Table 13.1 as an example, we find that

$$\lambda_{^3\text{H}} = \frac{0.693}{12.5\ \text{yr}} = 5.54 \times 10^{-2}\,\text{yr}^{-2}$$

The decay constants for the isotopes in Table 13.1 are provided here

isotope	half-life	decay constant
^{3}H	12.5 yr	$5.54 \times 10^{-1}\ \text{yr}^{-2}$
^{14}C	5730 yr	$1.21 \times 10^{-4}\ \text{yr}^{-1}$
^{32}P	14.3 d	$4.85 \times 10^{-2}\ \text{d}^{-1}$
^{35}S	87.1 d	$7.96 \times 10^{-3}\ \text{d}^{-1}$
^{45}Ca	152 d	$4.56 \times 10^{-3}\ \text{d}^{-1}$
^{55}Fe	2.91 yr	$2.38 \times 10^{-1}\ \text{yr}^{-1}$
^{60}Co	5.3 yr	$1.31 \times 10^{-1}\ \text{yr}^{-1}$
^{131}I	8 d	$8.66 \times 10^{-2}\ \text{d}^{-1}$

16. Combining equation 13.33 and equation 13.37 allows us to calculate the number of atoms of ^{60}Co in a sample given the sample's activity, A, and the half-life for ^{60}Co

$$N = \frac{At_{1/2}}{0.693}$$

$$N = \frac{\dfrac{2.1 \times 10^7 \text{ atoms}}{s} \times \dfrac{3600 \text{ s}}{h} \times \dfrac{24 \text{ h}}{d} \times \dfrac{365 \text{ d}}{yr} \times 5.3 \text{ yr}}{0.693}$$

$$N = 5.06 \times 10^{15} \text{ atoms } ^{60}C$$

The concentration of ^{60}Co, therefore, is

$$\frac{5.06 \times 10^{15} \text{ atoms } ^{60}Co}{(6.022 \times 10^{23} \text{ atoms/mol})(0.00500 \text{ L})} = 1.7 \times 10^{-6} M$$

17. Using the data for the standard, we know that

$$k = \frac{(A_0)_s}{w_s} = \frac{3540 \text{ cpm}}{1.000 \text{ g} \times \dfrac{0.0593 \text{ g Ni}}{g}} = 5.97 \times 10^4 \text{ cpm/g Ni}$$

For the sample, therefore, we have

$$w_x = \frac{(A_0)_x}{k} = \frac{1020 \text{ cpm}}{5.97 \times 10^4 \text{ cpm/g Ni}} = 0.1709 \text{ g Ni}$$

Finally, the concentration of Ni in the sample is

$$\frac{0.1709 \text{ g Ni}}{0.500 \text{ g sample}} \times 100 = 34.2\% \text{w/w Ni}$$

18. Using equation 13.42, we find that mass of vitamin B_{12} in the sample as analyzed is

$$w = \frac{572 \text{ cpm}}{361 \text{ cpm}} \times 18.6 \text{ mg} - 0.500 \text{ mg} = 28.97 \text{ mg}$$

This represents half of the original sample; thus, there are 57.94 mg of vitamin B_{12} in the 10 tablets, or 5.79 mg/tablet.

19. For radioactive decay, we know that

$$\ln \frac{A_t}{A_0} = -\lambda t = -\frac{0.693}{t_{1/2}} \times t$$

Substituting in $t_{1/2}$ from Table 13.1 and letting $t = 30\,000$ yr, gives

$$\ln \frac{A_t}{A_0} = -\frac{0.693}{5730 \text{ yr}} \times 30000 \text{ yr} = -3.628$$

$$\frac{A_t}{A_0} = e^{-3.628} = 0.0266$$

The percentage of ^{14}C remaining, therefore, is 2.66%.

20. Because we assume that ^{40}Ar was not was present in the original sample, we know that the initial moles of ^{40}K is the sum of the moles of ^{40}Ar and of ^{40}K present when the sample is analyzed; thus

$$(n_{^{40}K})_0 = (4.63 \times 10^6 \text{ mol } ^{40}\text{K})_t +$$

$$(2.09 \times 10^6 \text{ mol } ^{40}\text{Ar})_t = 6.72 \times 10^6 \text{ mol}$$

Using the equation for first-order radioactive decay, we find that

$$\ln \frac{(n_{^{40}K})_t}{(n_{^{40}K})_0} = -kt = -\frac{0.693}{t_{1/2}} \times t$$

$$\ln \frac{4.63 \times 10^{-6} \text{ mol}}{6.72 \times 10^{-6} \text{ mol}} = -0.3725 = -\frac{0.693}{1.3 \times 10^9 \text{ yr}} \times t$$

$$t = \frac{(0.3725)(1.3 \times 10^9 \text{ yr})}{0.693} = 7.0 \times 10^8 \text{ yr}$$

21. The relationship between the percent relative standard deviation and the number of counts is

$$(\sigma_A)_{\text{rel}} = \frac{1}{\sqrt{M}} \times 100$$

where M is the number of counts. To obtain a percent relative standard deviation of 1%, therefore, requires

$$1.0 = \frac{1}{\sqrt{M}} \times 100$$

$$M = \left(\frac{100}{1.0}\right)^2 = 10000 \text{ counts}$$

To obtain 10 000 counts, we need a sample that contains

$$10000 \text{ counts} \times \frac{1.00 \text{ g C}}{12 \text{ cpm}} \times \frac{1}{60 \text{ min}} = 13.9 \text{ g C}$$

To obtain a 1% relative standard deviation when counting the radioactive decay from a 0.50 g sample of C, we must count for

$$10000 \text{ counts} \times \frac{1.00 \text{ g C}}{12 \text{ cpm}} \times \frac{1}{0.50 \text{ g C}} = 1333 \text{ min} \approx 1300 \text{ min}$$

22. Sensitivity in a flow-injection analysis is directly proportional to the height of an analyte's peak in the fiagram, which, in turn, is proportional to the analyte's concentration. As the analyte moves from the point of injection to the point of detection, it undergoes continuous dispersion, as shown in Figure 13.19. Because dispersion reduces the analyte's concentration at the center of its flow profile, anything that limits dispersion will increase peak height and improve sensitivity. Increasing the flow rate or decreasing the length and diameter of the manifold allows less time for dispersion, which improves sensitivity. Injecting a larger volume of sample means it will take more time for the analyte's concentration to decrease at the center of its flow profile,
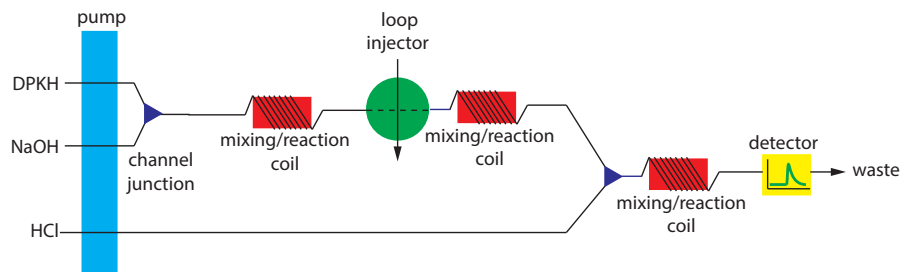
Figure SM13.7 One possible FIA manifold for the analysis described in Problem 24.

which also improves sensitivity. Finally, injecting the analyte into a channel results in its dilution and a loss of sensitivity. If we merge this channel with another channel, then we dilute further the analyte; whenever possible, we want to dilute the analyte just once, when we inject it into the manifold.

23. Depending on your measurements, your answers may vary slightly from those given here: the travel time, t_a, is 14.1 s; the residence time, T, is 15.8 s; the baseline-to-baseline time, Δt, is 15.2 s; the return time, T', is 13.5 s; and the difference between the residence time and the travel time, t', is 1.7 s. The peak height is 0.762 absorbance units; thus, the sensitivity is

$$k = \frac{A}{C} = \frac{0.762}{100.0 \text{ ppm}} = 7.62 \times 10^{-3} \text{ ppm}^{-1}$$

We can make injections at a rate of one per unit return time, which for this system is 1 every 13.5 s; thus, in one hour we can analyze

$$1 \text{ hr} \times \frac{3600 \text{ s}}{\text{hr}} \times \frac{1 \text{ sample}}{13.5 \text{ s}} = 267 \approx 260 \text{ to } 270 \text{ samples/hr}$$

24. Figure SM13.7 shows one possible manifold. Separate reagent channels of DPKH and NaOH are merged together and mixed, and the sample injected into their combined channel. After allowing sufficient time for the reaction to occur, the carrier stream is merged with a reagent channel that contains HCl, the concentration of which is sufficient to neutralize the NaOH and to make the carrier stream acidic.

25. Figure SM13.8 shows the calibration data and the calibration curve, the equation for which is

$$A = 2.28 \times 10^{-3} + (1.146 \times 10^{-2} \text{ ppm}^{-1}) \, C_{ppm}$$

Substituting in the sample's absorbance of 0.317 gives the concentration of Cl^- as 27.46 ppm in the sample as analyzed, which means the concentration of Cl^- in the original sample of seawater is

$$24.76 \text{ ppm } Cl^- \times \frac{500.0 \text{ mL}}{1.00 \text{ mL}} = 13700 \text{ ppm } Cl^-$$
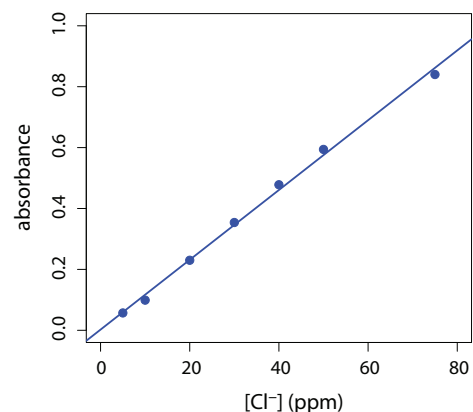
Figure SM13.8 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 25.
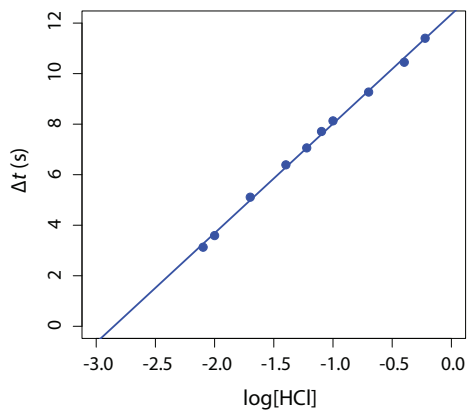
Figure SM13.9 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 26.
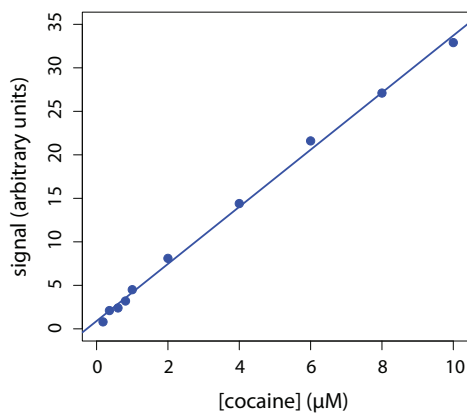
Figure SM13.10 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 28.
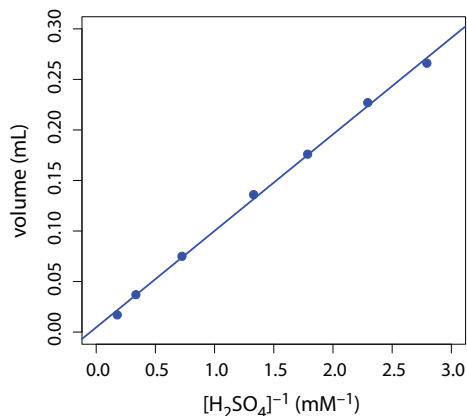
Figure SM13.11 Calibration data (**blue** dots) and calibration curve (**blue** line) for the data in Problem 29.

26. Figure SM13.9 shows the calibration data and the calibration curve, which for an FIA titration is a plot of Δt as a function of $\log[\text{HCl}]$. The equation for this calibration curve is

$$\Delta t = 12.349 \text{ s} + (4.331 \text{ s}) \times \log[\text{HCl}]$$

The average Δt for the five trials is 7.364 s. Substituting this back into the calibration equation gives

$$\log[\text{HCl}] = \frac{7.364 \text{ s} - 12.349 \text{ s}}{4.331 \text{ s}} = -1.151$$

$$[\text{HCl}] = 10^{-1.151} = 0.0706 \text{ M}$$

27. Using the data for the single external standard, we know that

$$k = \frac{S}{C_{\text{glucose}}} = \frac{7.13 \text{ nA}}{6.93 \text{ mM}} = 1.029 \text{ nA mM}^{-1}$$

Using this value for k, the concentration of glucose in the sample is

$$C_{\text{glucose}} = \frac{11.50 \text{ nM}}{1.029 \text{ nA mM}^{-1}} = 11.2 \text{ mM}$$

28. (a) The mean and the standard deviation for the 12 replicate samples are 23.97 and 0.605, respectively. The relative standard deviation, therefore, is

$$\frac{0.605}{23.97} \times 100 = 2.52\%$$

(b) Figure SM13.10 shows the calibration data and the calibration curve, for which the equation is

$$S = 0.8979 + 3.281 C_{\text{cocaine}}$$

Substituting the sample's signal of 21.4 into the calibration equation gives the concentration of cocaine as 6.249 µM as analyzed. The concentration of cocaine in the original sample, therefore, is

$$\frac{\left\{ \begin{array}{c} \dfrac{6.249 \times 10^{-6} \text{ mol}}{\text{L}} \times \dfrac{25.00 \text{ mL}}{0.125 \text{ mL}} \times \\[2mm] 0.02500 \text{ L} \times \dfrac{303.36 \text{ g}}{\text{mol}} \times \dfrac{1000 \text{ mg}}{\text{g}} \end{array} \right\}}{10.0 \text{ mg}} \times 100 = 94.8\% \text{w/w}$$

29. Figure SM13.11 shows the calibration data and the calibration curve, for which the equation is

$$V = 4.632 \times 10^{-3} \text{ mL} + \frac{9.550 \times 10^{-2} \text{ mM mL}}{C_{\text{H}_2\text{SO}_4}}$$

Substituting in a volume of 0.157 mL for the sample, gives the concentration of H_2SO_4 as 0.627 mM.

Chapter 14

1. (a) The response when $A = 0$ and $B = 0$ is 1.68, which we represent
    as (A, B, *response*) or, in this case, (0, 0, 1.68). For the first cycle, we
    increase A in steps of one until the response begins to decrease or until
    we reach a boundary, obtaining the following additional results:

    (1, 0, 1.88), (2, 0, 2.00), (3, 0, 2.04), (4, 0, 2.00)

    For the second cycle, we return to (3, 0, 2.04) and increase B in steps
    of one, obtaining these results:

    (3, 1, 2.56), (3, 2, 3.00), (3, 3, 3.36), (3, 4, 3.64),

    (3, 5, 3.84), (3, 6, 3.96), (3, 7, 4.00), (3, 8, 3.96)

    For the third cycle, we return to (3, 7, 4.00) and increase A in steps of
    one, obtaining a result of (4, 7, 3.96). Because this response is smaller
    than our current best response of 4.00, we try decreasing A by a step
    of one, which gives (2, 7, 3.96). Having explored the response in all
    directions around (3, 7, 4.00), we know that the optimum response
    is 4.00 at $A = 3$ and $B = 7$.

    Figure SM14.1a shows the progress of the optimization as a three-di-
    mensional scatterplot with the figure's floor showing a contour plot
    of the response surface. Figure SM14.1b shows a three-dimensional
    surface plot of the response surface.

    (b) The response when $A = 0$ and $B = 0$ is 4.00, which we represent as
    (0, 0, 4.00). For the first cycle, we increase A in steps of one until the
    response begins to decrease or until we reach a boundary, obtaining a
    results of (1, 0, 3.60); as this response is smaller than the initial step,
    this ends the first cycle.

Figure SM14.1 The progress of a one-factor-at-a-time optimization for the equa-
tion in Problem 1a is shown in (a) as a scatterplot in three dimensions with a
contour plot of the response surface on the figure's floor. The full response surface
is shown in (b). The legend shows the colors used for the individual contour lines;
the response surface provides for a greater resolution in the response by using
gradations between these colors.
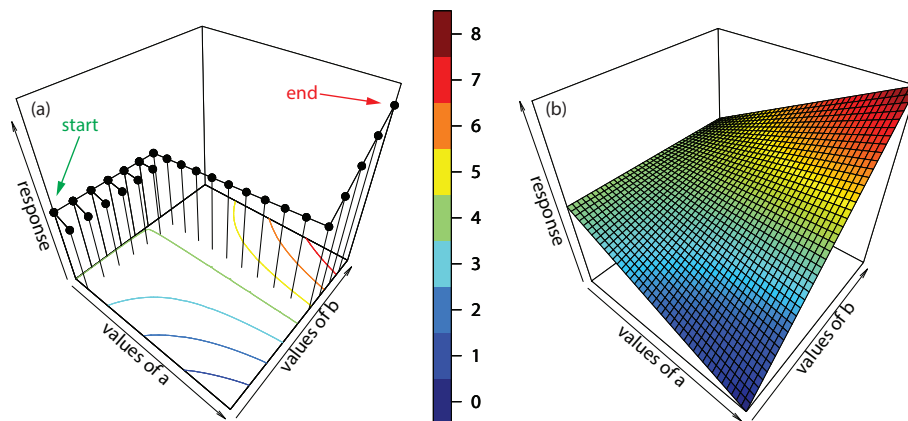
Figure SM14.2 The progress of a one-factor-at-a-time optimization for the equation in Problem 1b is shown in (a) as a scatterplot in three dimensions with a contour plot of the response surface on the figure's floor. The full response surface is shown in (b). The legend shows the colors used for the individual contour lines; the response surface provides for a greater resolution in the response by using gradations between these colors.

We begin the second cycle by returning to (0, 0, 4.00) and increase the value of B by one, obtaining a result of (0, 1, 4.00). Because the response did not increase, we end the second cycle and, for the third cycle, we increase the value of A, obtaining a result of (1, 1, 3.68). Continuing in this fashion, the remainder of the steps are

(0, 1, 4.00), (0, 2, 4.00), (1, 2, 3.76), (0, 2, 4.00), (0, 3, 4.00)

(1, 3, 3.84), (0, 3, 4.00), (0, 4, 4.00), (1, 4, 3.92), (0, 4, 4.00)

(0, 5, 4.00), (1, 5, 4.00), (0, 5, 4.00), (0, 6, 4.00), (1, 6, 4.08)

(2, 6, 4.16), (3, 6, 4.24), (4, 6, 4.32), (5, 6, 4.40), (6, 6, 4.48)

(7, 6, 4.56), (8, 6, 4.64), (9, 6, 4.72), (10, 6, 4.80), (10, 7, 5.60)

(10, 8, 6.40), (10, 9, 7.20), (10, 10, 8.00)

The optimum response is 8.00 at $A = 10$ and $B = 10$.

Figure SM14.2a shows the progress of the optimization as a three-dimensional scatterplot with the figure's floor showing a contour plot for the response surface. Figure SM14.2b shows a three-dimensional surface plot of the response surface.

(c) The response when $A = 0$ and $B = 0$ is 3.267, which we represent as (0, 0, 3.267). For the first cycle, we increase A in steps of one until the response begins to decrease or until we reach a boundary, obtaining the following additional results:

(1, 0, 4.651), (2, 0, 5.736), (3, 0, 6.521),

(4, 0, 7.004), (5, 0, 7.187), (6, 0, 7.068)

For the second cycle, we return to (5, 0, 7.187) and increase B in steps of one, obtaining these results:

Note that until we reach $A = 0$ and $B = 6$, we keep probing toward larger values of A without increasing the response, and then probing toward larger values of B, also without increasing the response. Once we reach $A = 0$ and $B = 6$, however, we find that an increase in A finally increases the response. Once we reach the boundary for A, we continue to increase B until we reach the optimum response at $A = 10$ and $B = 10$.

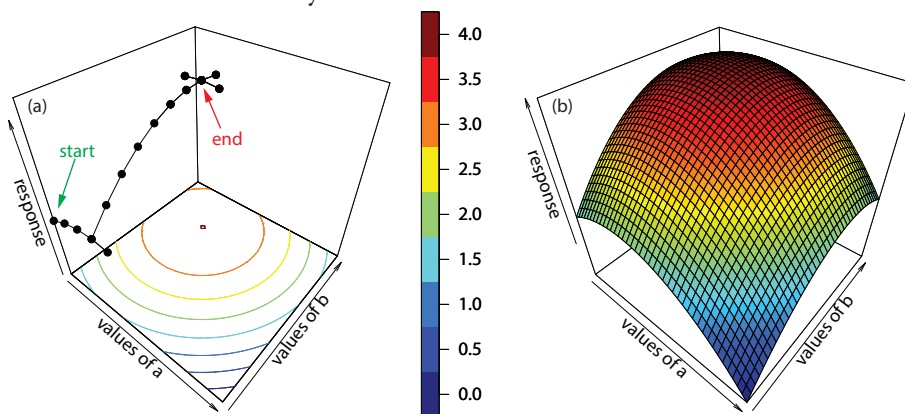At this point, our best response is 7.187 at $A = 5$ and at $B = 0$.
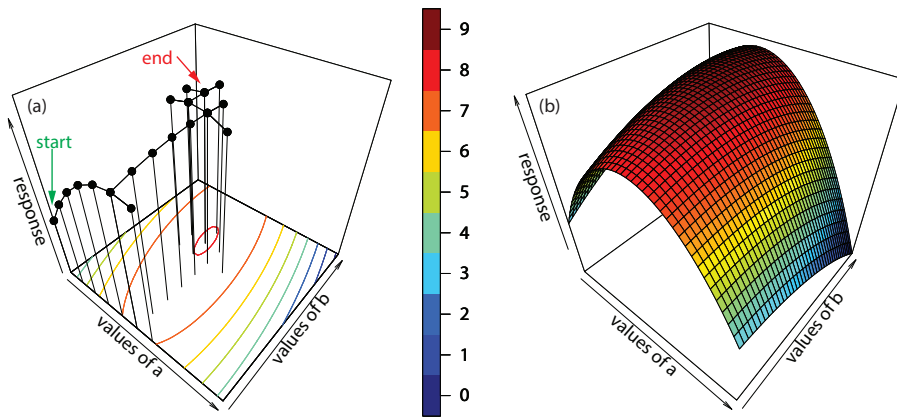
Figure SM14.3 The progress of a one-factor-at-a-time optimization for the equation in Problem 1c is shown in (a) as a scatterplot in three dimensions with a contour plot of the response surface on the figure's floor. The full response surface is shown in (b). The legend shows the colors used for the individual contour lines; the response surface provides for a greater resolution in the response by using gradations between these colors.

$$(5, 1, 7.436), (5, 2, 7.631), (5, 3, 7.772),$$
$$(5, 4, 7.858), (5, 5, 7.889), (5, 6, 7.865)$$

At this point, our best response is 7.889 at $A = 5$ and at $B = 5$.

For the next cycle, we return to $(5, 5, 7.889)$ and increase A in steps of one, obtaining a response for $(6, 5, 7.481)$ that is smaller; probing in the other direction gives $(4, 5, 7.996)$ and then $(3, 5, 7.801)$. Returning to $(4, 5, 7.966)$, we find our optimum response at $(4, 6, 8.003)$, with movement in all other directions giving a smaller response. Note that using a fixed step size of one prevents us from reaching the true optimum at $A = 3.91$ and $B = 6.22$.

Figure SM14.3a shows the progress of the optimization as a three-dimensional scatterplot with the figure's floor showing a contour plot for the response surface. Figure SM14.3b shows a three-dimensional surface plot of the response surface.

2. Given a step size of 1.0 in both directions and $A = 0$ and $B = 0$ as the starting point for the first simplex, the other two vertices for the first simplex are at $A = 1$ and at $B = 0$, and at $A = 1.5$ and at $B = 0.87$. The responses for the first three vertices are $(0, 0, 3.264)$, $(1.0, 0, 4.651)$, and $(0.5, 0.87, 4.442)$, respectively. The vertex with the worst response is $(0, 0, 3.264)$; thus, we reject this vertex and replace it with coordinates of

$$A = 2\left(\frac{1 + 0.5}{2}\right) - 0 = 1.5$$

$$B = 2\left(\frac{0.87 + 0}{2}\right) - 0 = 0.87$$

The following table summarizes all the steps in the simplex optimization. The column labeled "vertex" shows the 25 unique experiments along with their values for A, for B, and for the response. The column
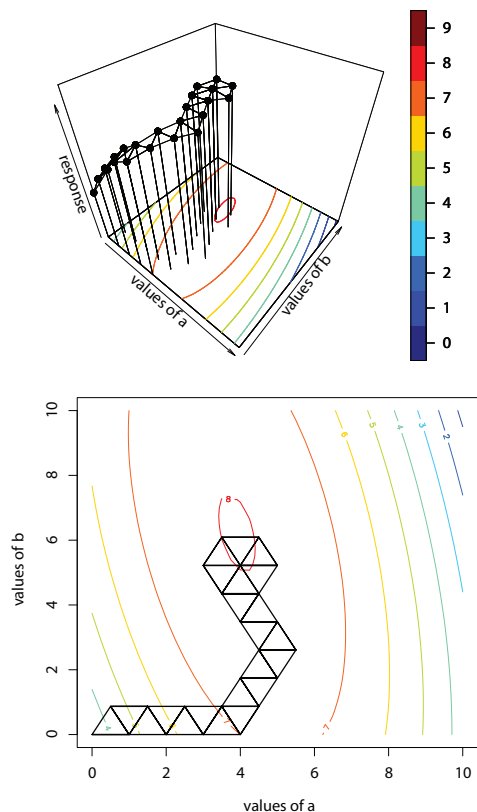
Figure SM14.4 Two views showing the progress of a simplex optimization of the equation in Problem 1c in (a) three dimensions and in (b) two dimensions. The legend shows the colors used for the individual contour lines. Figure SM14.3b shows the full response surface for this problem.
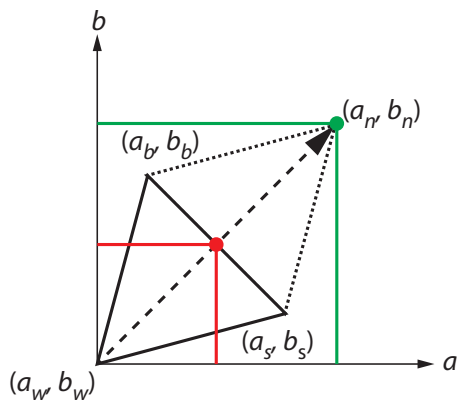
Figure SM14.5 Diagram showing vertices of original simplex and the reflection of the worst vertex across the midpoint (**red** circle) of the best and the next-best vertices to give the new vertex (**green** circle). See text for additional details.

labeled "simplex" shows the three vertices that make up each simplex. For each simplex, the vertex that we reject is shown in **bold** font; note that on two occasions, the rejected vertex, shown in **bold-italic** font, has the second-worst response (either because of a boundary condition or because the new vertex has the worst response)

vertex	A	B	response	simplex
1	0	0	3.264	—
2	1.0	0	4.651	—
3	0.5	0.87	4.442	**1**, 2, 3
4	1.5	0.87	5.627	2, **3**, 4
5	2.0	0	5.736	**2**, 4, 5
6	2.5	0.87	6.512	**4**, 5, 6
7	3.0	0	6.521	**5**, 6, 7
8	3.5	0.87	7.096	**6**, 7, 8
9	4.0	0	7.004	**7**, 8, 9
10	4.5	0.87	7.378	8, **9**, 10
11	4.0	1.74	7.504	**8**, 10, 11
12	5.0	1.74	7.586	**10**, 11, 12
13	4.5	2.61	7.745	**11**, 12, 13
14	5.5	2.61	7.626	**12**, 13, 14
15	5.0	3.48	7.820	13, **14**, 15
16	4.0	3.48	7.839	**13**, 15, 16
17	4.5	4.35	7.947	**15**, 16, 17
18	3.5	4.35	7.866	**16**, 17, 18
19	4.0	5.22	8.008	17, **18**, 19
20	5.0	5.22	7.888	**17**, 19, 20
21	4.5	6.09	7.983	19, **20**, 21
22	3.5	6.09	8.002	19, **21**, 22
23	3.0	5.22	7.826	19, **22**, 23
24	3.5	4.35	7.866	19, **23**, 24
25	4.5	4.35	7.947	19, 24, 25

Figure SM14.4 shows the progress of the simplex optimization in three dimensions and in two dimensions.

3. To help us in the derivation, we will use the diagram shown in Figure SM14.5 where a and b are the coordinates of a vertex, and w, b, s, and n identify the vertex with, respectively, the worst response, the best response, the second-best response, and the new vertex. The **red** circle marks the midpoint between the best vertex and the second-best vertex; its coordinates are

$$a_{mp} = \frac{a_b + a_s}{2}$$

$$b_{mp} = \frac{b_b + b_s}{2}$$

The distance along the a-axis between the worst vertex's coordinate of a_w and the midpoint's coordinate of a_{mp} is

$$\frac{a_b + a_s}{2} - a_w$$

The distance along the a-axis between the worst vertex's coordinate and the new vertex's coordinate is twice that to the midpoint, which means the a coordinate for the new vertex is

$$a_n = 2\left(\frac{a_b + a_s}{2} - a_w\right) + a_w$$

The value for the coordinate a_n is the value for the coordinate a_w plus the distance along the a-axis between the new vertex and the worst vertex.

which simplifies to equation 14.3

$$a_n = 2\left(\frac{a_b + a_s}{2}\right) - a_w$$

Using the same approach for coordinates relative to the b-axis yields equation 14.4

$$b_n = 2\left(\frac{b_b + b_s}{2}\right) - b_w$$

4.   In coded form, the values for b_0, b_a, b_b, and b_{ab} are

$$b_0 = \frac{1}{4}(5.92 + 2.08 + 4.48 + 3.52) = 4.00$$

$$b_a = \frac{1}{4}(5.92 + 2.08 - 4.48 - 3.52) = 0$$

$$b_b = \frac{1}{4}(5.92 - 2.08 + 4.48 - 3.52) = 1.20$$

$$b_{ab} = \frac{1}{4}(5.92 - 2.08 - 4.48 + 3.52) = 0.72$$

which gives us the following equation for the response surface in coded form

$$R = 4.00 + 1.20B^* + 0.72A^*B^*$$

To convert this equation into its uncoded form, we first note the following relationships between coded and uncoded values for A and for B

$$A = 5 + 3A^* \qquad B = 5 + 3B^*$$

$$A^* = \frac{A}{3} - \frac{5}{3} \qquad B^* = \frac{B}{3} - \frac{5}{3}$$

Substituting these two equations back into the response surface's coded equation gives
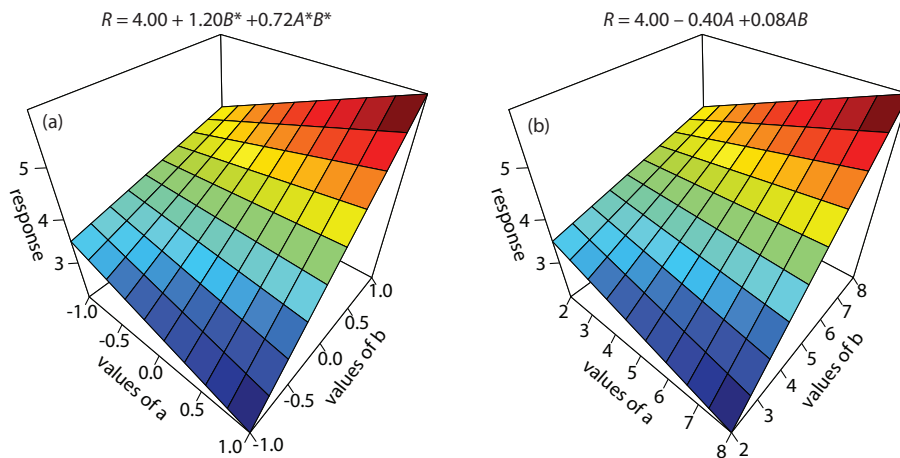
Figure SM14.6 Response surfaces based on the (a) coded and the (b) uncoded equations derived from the data in Problem 4. Note that the two response surfaces are identical even though their equations are very different.

$$R = 4.00 + 1.20\left(\frac{B}{3} - \frac{5}{3}\right) + 0.72\left(\frac{A}{3} - \frac{5}{3}\right)\left(\frac{B}{3} - \frac{5}{3}\right)$$

$$R = 4.00 + 0.40B - 2.00 + 0.08AB - 0.40A - 0.40B + 2.00$$

$$R = 4.00 - 0.40A + 0.08AB$$

When we examine carefully both equations, we see they convey the same information: that the system's response depends on the relative values of A and B (or A* and B*) and that the affect of A (or A*) depends on the value of B (or B*), with larger values of A (or more positive values of A*) decreasing the response for smaller values of B (or more negative values of B*).

Although the mathematical form of the equation is important, it is more important that we interpret what it tells us about how each factor affects the response.

At first glance, the coded and the uncoded equations seem quite different, with the coded equation showing a first-order effect in B* and an interaction between A* and B*, and the uncoded equation showing a first-order effect in A and an interaction between A and B. As we see in Figure SM14.6, however, their respective response surfaces are identical.

5. (a) Letting a represent Ca and letting b represent Al, the values for b_0, b_a, b_b, and b_{ab} in coded form are

$$b_0 = \frac{1}{4}(54.29 + 98.44 + 19.18 + 38.53) = 52.61$$

$$b_a = \frac{1}{4}(54.29 + 98.44 - 19.18 - 38.53) = 23.755$$

$$b_b = \frac{1}{4}(54.29 - 98.44 + 19.18 - 38.53) = -15.875$$

$$b_{ab} = \frac{1}{4}(54.29 - 98.44 - 19.18 + 38.53) = -6.20$$

which gives us the following equation for the response surface in coded form

$$R = 52.610 + 23.755Ca^* - 15.875Al^* - 6.20Ca^*Al^*$$

(b) The original data shows that a larger concentration of Al suppresses the signal for Ca; thus, we want to find the maximum concentration of Al that results in a decrease in the response of less than

5%. First, we determine the response for a solution that is 6.00 ppm in Ca and that has no Al. The following equations relate the actual concentrations of each species to its coded form

$$Ca = 7 + 3Ca^* \qquad Al = 80 + 80Al^*$$

Substituting in 6.00 ppm for Ca and 0.00 ppm for Al gives $-1/3$ for Ca^* and -1 for Al^*. Substituting these values back into the response surface's coded equation

$$R = 52.610 + 23.755\left(\frac{-1}{3}\right) - 15.875\,(-1) - 6.20\left(\frac{-1}{3}\right)(-1)$$

gives the response as 58.50. Decreasing this response by 5% leaves us with a response of 55.58. Substituting this response into the response surface's coded equation, along with the coded value of $-1/3$ for Ca^*, and solving for Al^* gives

$$55.58 = 52.610 + 23.755\left(\frac{-1}{3}\right) - 15.875Al^* - 6.20\left(\frac{-1}{3}\right)Al^*$$

$$10.88 = -13.81Al^*$$

$$Al^* = -0.789$$

The maximum allowed concentration of aluminum, therefore, is

$$Al = 80 + 80\,(-0.789) = 16.9 \text{ ppm Al}$$

6. (a) The values for b_0, b_x, b_y, b_z, b_{xy}, b_{xz}, b_{yz}, and b_{xyz} in coded form are

$$b_0 = \frac{1}{8}\binom{28 + 17 + 41 + 34 +}{56 + 51 + 42 + 36} = 38.125 \approx 38.1$$

$$b_x = \frac{1}{8}\binom{-28 + 17 - 41 + 34 -}{56 + 51 - 42 + 36} = -3.625 \approx -3.6$$

$$b_y = \frac{1}{8}\binom{-28 - 17 + 41 + 34 -}{56 - 51 + 42 + 36} = 0.125 \approx 0.1$$

$$b_z = \frac{1}{8}\binom{-28 - 17 - 41 - 34 +}{56 + 51 + 42 + 36} = 8.125 \approx 8.1$$

$$b_{xy} = \frac{1}{8}\binom{28 - 17 - 41 + 34 +}{56 - 51 - 42 + 36} = 0.375 \approx 0.4$$

$$b_{xz} = \frac{1}{8}\binom{28 - 17 + 41 - 34 -}{56 + 51 - 42 + 36} = 0.875 \approx 0.9$$

$$b_{yz} = \frac{1}{8}\binom{28 + 17 - 41 - 34 -}{56 - 51 + 42 + 36} = -7.375 \approx -7.4$$

$$b_{xyz} = \frac{1}{8}\binom{-28 + 17 + 41 - 34 +}{56 - 51 - 42 + 36} = -0.625 \approx -0.6$$

The coded equation for the response surface, therefore, is

$$R = 38.1 - 3.6X^* + 0.1Y^* + 8.1Z^* +$$
$$0.4X^*Y^* + 0.9X^*Z^* - 7.4Y^*Z^* - 0.6X^*Y^*Z^*$$

(b) The important effects are the temperature (X^*) and the reactant's concentration (Z^*), and an interaction between the reactant's concentration and the type of catalyst (Y^*Z^*), which leave us with

$$R = 38.1 - 3.6X^* + 8.1Z^* - 7.4Y^*Z^*$$

(c) Because the catalyst is a categorical variable, not a numerical variable, we cannot transform its coded value (Y^*) into a number.

(d) The response surface's simple coded equation shows us that the effect of the catalyst depends on the reactant's concentration as it appears only in the interaction term Y^*Z^*. For smaller concentrations of reactant—when Z^* is less than 0 or the reactant's concentration is less than 0.375 M—catalyst B is the best choice because the term $-7.4Y^*Z^*$ is positive; the opposite is true for larger concentrations of reactant—when Z^* is greater than 0 or the reactant's concentration is greater than 0.375 M—where catalyst A is the best choice.

(e) For the temperature and the concentration of reactant, the following equations relate a coded value to its actual value

$$X = 130 + 10X^* \qquad Z = 0.375 + 0.125Z^*$$

Substituting in the desired temperature and concentration, and solving for X^* and for Z^* gives

$$125 = 130 + 10X^* \qquad 0.45 = 0.375 + 0.125Z^*$$

$$-5 = 10X^* \qquad 0.075 + 0.125Z^*$$

$$X^* = -0.5 \qquad Z^* = 0.6$$

Because Z^* is greater than zero, we know that the best catalyst is type A, for which Y^* is –1. Substituting these values into the response surface's coded equation gives the percent yield as

$$R = 38.1 - 3.6(-0.5) + 8.1(0.6) - 7.4(-1)(0.6) = 49.2\%$$

7. (a) The values for b_0, b_x, b_y, b_z, b_{xy}, b_{xz}, b_{yz}, and b_{xyz} in coded form are

$$b_0 = \frac{1}{8}\begin{pmatrix} 1.55 + 5.40 + 3.50 + 6.75 + \\ 2.45 + 3.60 + 3.05 + 7.10 \end{pmatrix} = 4.175 \approx 4.18$$

$$b_x = \frac{1}{8}\begin{pmatrix} -1.55 + 5.40 - 3.50 + 6.75 - \\ 2.45 + 3.60 - 3.05 + 7.10 \end{pmatrix} = 1.538 \approx 1.54$$

$$b_y = \frac{1}{8}\begin{pmatrix} -1.55 - 5.40 + 3.50 + 6.75 - \\ 2.45 - 3.60 + 3.05 + 7.10 \end{pmatrix} = 0.925 \approx 0.92$$

$$b_z = \frac{1}{8}\left(\begin{array}{c} -1.55 - 5.40 - 3.50 - 6.75 + \\ 2.45 + 3.60 + 3.05 + 7.10 \end{array}\right) = -0.125 \approx -0.12$$

$$b_{xy} = \frac{1}{8}\left(\begin{array}{c} 1.55 - 5.40 - 3.50 + 6.75 + \\ 2.45 - 3.60 - 3.05 + 7.10 \end{array}\right) = 0.288 \approx 0.29$$

$$b_{xz} = \frac{1}{8}\left(\begin{array}{c} 1.55 - 5.40 + 3.50 - 6.75 - \\ 2.45 + 3.60 - 3.05 + 7.10 \end{array}\right) = -0.238 \approx -0.24$$

$$b_{yz} = \frac{1}{8}\left(\begin{array}{c} 1.55 + 5.40 - 3.50 - 6.75 - \\ 2.45 - 3.60 + 3.05 + 7.10 \end{array}\right) = 0.100 \approx 0.10$$

$$b_{xyz} = \frac{1}{8}\left(\begin{array}{c} -1.55 + 5.40 + 3.50 - 6.75 + \\ 2.45 - 3.60 - 3.05 + 7.10 \end{array}\right) = 0.438 \approx 0.44$$

The coded equation for the response surface, therefore, is

$$R = 4.18 + 1.54X^* + 0.92Y^* - 0.12Z^* +$$
$$0.29X^*Y^* - 0.24X^*Z^* + 0.1Y^*Z^* + 0.44X^*Y^*Z^*$$

(b) The important effects are the presence or absence of benzocaine (X^*) and the temperature (Y^*), which leave us with

$$R = 4.18 + 1.54X^* + 0.92Y^*$$

8. (a) The values for b_0, b_x, b_y, b_z, b_{xy}, b_{xz}, b_{yz}, and b_{xyz} in coded form are

$$b_0 = \frac{1}{8}(2 + 6 + 4 + 8 + 10 + 18 + 8 + 12) = 8.5$$

$$b_x = \frac{1}{8}(-2 + 6 - 4 + 8 - 10 + 18 - 8 + 12) = 2.5$$

$$b_y = \frac{1}{8}(-2 - 6 + 4 + 8 - 10 - 18 + 8 + 12) = -0.5$$

$$b_z = \frac{1}{8}(-2 - 6 - 4 - 8 + 10 + 18 + 8 + 12) = 3.5$$

$$b_{xy} = \frac{1}{8}(2 - 6 - 4 + 8 + 10 - 18 - 8 + 12) = -0.5$$

$$b_{xz} = \frac{1}{8}(2 - 6 + 4 - 8 - 10 + 18 - 8 + 12) = 0.5$$

$$b_{yz} = \frac{1}{8}(2 + 6 - 4 - 8 - 10 - 18 + 8 + 12) = -1.5$$

$$b_{xyz} = \frac{1}{8}(-2 + 6 + 4 - 8 + 10 - 18 - 8 + 12) = -0.5$$

The coded equation for the response surface, therefore, is

$$R = 8.5 + 2.5X^* - 0.5Y^* + 3.5Z^* -$$
$$0.5X^*Y^* + 0.5X^*Z^* - 1.5Y^*Z^* - 0.5X^*Y^*Z^*$$

(b) The important effects are the temperature (X^*), the pressure (Y^*), and the interaction between the pressure and the residence time (Y^*Z^*), which leave us with

$$R = 8.5 + 2.5X^* + 3.5Z^* - 1.5Y^*Z^*$$

(c) The mean response is an 8.6% yield for the three trials at the center of the experimental design, with a standard deviation of 0.529%. A 95% confidence interval for the mean response is

$$\mu = \overline{X} \pm \frac{ts}{\sqrt{n}} = 8.60\% \pm \frac{(4.303)(0.529\%)}{\sqrt{3}} = 8.60\% \pm 1.31\%$$

The average response for the eight trials in the experimental design is given by b_0 and is equal to 8.5; as this falls within the confidence interval, there is no evidence, at $\alpha = 0.05$, of curvature in the data and a first-order model is a reasonable choice.

9. (a) When considering the response in terms of ΔE, the values for b_0, b_x, b_y, b_z, b_{xy}, b_{xz}, b_{yz}, and b_{xyz} in coded form are

$$b_0 = \frac{1}{8}\left(\begin{array}{l} 37.45 + 31.70 + 32.10 + 27.20 + \\ 39.85 + 32.85 + 35.00 + 32.15 \end{array}\right) = 33.54$$

$$b_x = \frac{1}{8}\left(\begin{array}{l} -37.45 + 31.70 - 32.10 + 27.20 - \\ 39.85 + 32.85 - 35.00 + 32.15 \end{array}\right) = -2.56$$

$$b_y = \frac{1}{8}\left(\begin{array}{l} -37.45 - 31.70 + 32.10 + 27.20 - \\ 39.85 - 32.85 + 35.00 + 32.15 \end{array}\right) = -1.92$$

$$b_z = \frac{1}{8}\left(\begin{array}{l} -37.45 - 31.70 - 32.10 - 27.20 + \\ 39.85 + 32.85 + 35.00 + 32.15 \end{array}\right) = 1.42$$

$$b_{xy} = \frac{1}{8}\left(\begin{array}{l} 37.45 - 31.70 - 32.10 + 27.20 + \\ 39.85 - 32.85 - 35.00 + 32.15 \end{array}\right) = 0.62$$

$$b_{xz} = \frac{1}{8}\left(\begin{array}{l} 37.45 - 31.70 + 32.10 - 27.20 - \\ 39.85 + 32.85 - 35.00 + 32.15 \end{array}\right) = 0.10$$

$$b_{yz} = \frac{1}{8}\left(\begin{array}{l} 37.45 + 31.70 - 32.10 - 27.20 - \\ 39.85 - 32.85 + 35.00 + 32.15 \end{array}\right) = 0.54$$

$$b_{xyz} = \frac{1}{8}\left(\begin{array}{l} -37.45 + 31.70 + 32.10 - 27.20 + \\ 39.85 - 32.85 - 35.00 + 32.15 \end{array}\right) = 0.41$$

The coded equation for the response surface, therefore, is

$$R = 33.54 - 2.56X^* - 1.92Y^* + 1.42Z^* + $$
$$0.62X^*Y^* + 0.10X^*Z^* + 0.54Y^*Z^* + 0.41X^*Y^*Z^*$$

(b) When considering the response in terms of samples per hour, the values for b_0, b_x, b_y, b_z, b_{xy}, b_{xz}, b_{yz}, and b_{xyz} in coded form are

$$b_0 = \frac{1}{8}\left(\begin{array}{l} 21.5 + 26.0 + 30.0 + 33.0 + \\ 21.0 + 19.5 + 30.0 + 34.0 \end{array}\right) = 26.9$$

$$b_x = \frac{1}{8}\left(\begin{array}{l} -21.5 + 26.0 - 30.0 + 33.0 - \\ 21.0 + 19.5 - 30.0 + 34.0 \end{array}\right) = 1.2$$

$$b_y = \frac{1}{8}\left(\begin{array}{l}-21.5 - 26.0 + 30.0 + 33.0 - \\ 21.0 - 19.5 + 30.0 + 34.0\end{array}\right) = 4.9$$

$$b_z = \frac{1}{8}\left(\begin{array}{l}-21.5 - 26.0 - 30.0 - 33.0 + \\ 21.0 + 19.5 + 30.0 + 34.0\end{array}\right) = -0.8$$

$$b_{xy} = \frac{1}{8}\left(\begin{array}{l}21.5 - 26.0 - 30.0 + 33.0 + \\ 21.0 - 19.5 - 30.0 + 34.0\end{array}\right) = 0.5$$

$$b_{xz} = \frac{1}{8}\left(\begin{array}{l}21.5 - 26.0 + 30.0 - 33.0 - \\ 21.0 + 19.5 - 30.0 + 34.0\end{array}\right) = -0.6$$

$$b_{yz} = \frac{1}{8}\left(\begin{array}{l}21.5 + 26.0 - 30.0 - 33.0 - \\ 21.0 - 19.5 + 30.0 + 34.0\end{array}\right) = 1.0$$

$$b_{xyz} = \frac{1}{8}\left(\begin{array}{l}-21.5 + 26.0 + 30.0 - 33.0 + \\ 21.0 - 19.5 - 30.0 + 34.0\end{array}\right) = 0.9$$

The coded equation for the response surface, therefore, is

$$R = 26.9 + 1.2X^* + 4.9Y^* - 0.8Z^* +$$
$$0.5X^*Y^* - 0.6X^*Z^* + Y^*Z^* + 0.9X^*Y^*Z^*$$

(c) To help us compare the response surfaces, let's gather the values for each term into a table; thus

parameter	ΔE	sample/h
b_0	33.54	26.9
b_x	−2.56	1.2
b_y	−1.92	4.9
b_z	1.42	−0.8
b_{xy}	0.62	0.5
b_{xz}	0.10	−0.6
b_{yz}	0.54	1.0
b_{xyz}	0.41	0.9

Looking at the main effects (b_x, b_y, and b_z), we see from the signs that the parameters that favor a high sampling rate (a smaller volume of sample, a shorter reactor length, and a faster carrier flow rate) result in smaller values for ΔE; thus, the conditions that favor sensitivity do not favor the sampling rate.

(d) One way to answer this question is to look at the original data and see if for any individual experiment, the sensitivity and the sampling rate both exceed their mean values as given by their respective values for b_0: 33.54 for ΔE and 26.9 sample/h for the sampling rate. Of the original experiments, this is the case only for run 7; thus, a reactor length of 1.5 cm ($X^* = -1$), a carrier flow rate of 2.2 mL/min
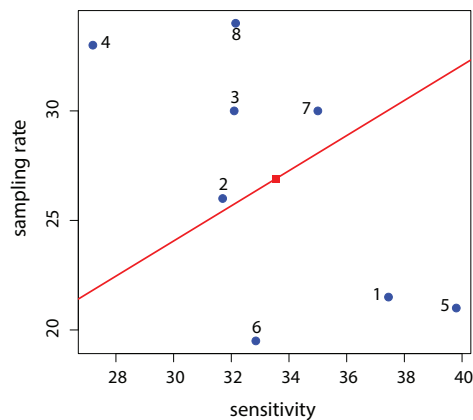
Figure SM14.7 Plot of sampling rate vs. sensitivity for the data in Problem 9. The **blue** dots are the results for the experimental runs used to model the response surface, the **red** square shows the mean sensitivity and mean sampling rate for the experimental data, and the **red** line shows equal percentage changes in sensitivity and sampling rate relative to their respective mean values. See text for further details.

$(Y^* = +1)$, and a sample volume of 150 µL provides the best compromise between sensitivity and sampling rate.

Another approach is to plot the sampling rate versus the sensitivity for each experimental run, as shown in Figure SM14.7 where the **blue** dots are the results for the eight experiments, the **red** square is the average sensitivity and the average rate, and the **red** line shows conditions that result in an equal percentage change in the sensitivity and the sampling rate relative to their mean values. The best experimental run is the one that lies closest to the **red** line and furthest to the upper-right corner. Again, the seventh experiment provides the best compromise between sampling rate and sensitivity.

10. (a) There are a total of 32 terms to calculate: one average (b_0), five main effects (b_a, b_b, b_c, b_d, and b_e), 10 binary interactions (b_{ab}, b_{ac}, b_{ad}, b_{ae}, b_{bc}, b_{bd}, b_{be}, b_{cd}, b_{ce}, and b_{de}), 10 ternary interactions (b_{abc}, b_{abd}, b_{abe}, b_{acd}, b_{ace}, b_{ade}, b_{bcd}, b_{bce}, b_{bde}, and b_{cde}), five quaternary interactions (b_{abcd}, b_{abce}, b_{abde}, b_{acde}, and b_{bdce}), and one quinary interaction (b_{abcde}). We will not show here the equations for all 32 terms; instead, we provide the equation for one term in each set and summarize the results in a table.

$$b_0 = \frac{1}{32}\sum_{i=1}^{32} R_i \qquad b_a = \frac{1}{32}\sum_{i=1}^{32} A_i^* R_i$$

$$b_{ab} = \frac{1}{32}\sum_{i=1}^{32} A_i^* B_i^* R_i \qquad b_{abc} = \frac{1}{32}\sum_{i=1}^{32} A_i^* B_i^* C_i^* R_i$$

$$b_{abcd} = \frac{1}{32}\sum_{i=1}^{32} A_i^* B_i^* C_i^* D_i^* R_i \qquad b_{abcde} = \frac{1}{32}\sum_{i=1}^{32} A_i^* B_i^* C_i^* D_i^* E_i^* R_i$$

term	value	term	value	term	value
b_0	0.49	b_{bd}	−0.008	b_{bcd}	0.001
b_a	0.050	b_{be}	0.008	b_{bce}	0
b_b	−0.071	b_{cd}	−0.021	b_{bde}	0.006
b_c	0.039	b_{ce}	−0.12	b_{cde}	0.025
b_d	0.074	b_{de}	−0.007	b_{abcd}	0.006
b_e	−0.15	b_{abc}	0.003	b_{abce}	0.007
b_{ab}	0.001	b_{abd}	0.005	b_{abde}	0.004
b_{ac}	−0.007	b_{abe}	−0.004	b_{acde}	0.009
b_{ad}	0.013	b_{acd}	0.003	b_{bdce}	0.005
b_{ae}	0.009	b_{ace}	0.049	b_{abcde}	−0.14
b_{bc}	0.014	b_{ade}	0.019		

If we ignore any term with an absolute value less than 0.03, then the coded equation for the response surface is

$$R = 0.49 + 0.50A^* - 0.071B^* + 0.039C^*$$
$$+ 0.074D^* - 0.15E^* - 0.12C^*E^* + 0.049A^*C^*E^*$$

(b) The coded equation suggests that the most desirable values for A^* and for D^* are positive as they appear only in terms with positive coefficients, and that the most desirable values for B^* are negative as it appears only in a term with a negative coefficient. Because E^* is held at its high, or $+1$ level, the most desirable value for C^* is negative as this will make $-0.12C^*E^*$ more positive than the term $0.049A^*C^*E^*$ is negative. This is consistent with the results from the simplex optimization as the flow rate (A) of 2278 mL/min is greater than its average factor level of 1421 mL/min (A^*), the amount of SiH_4 used (B) of 9.90 ppm is less than its average factor level of 16.1 ppm (B^*), the $O_2 + N_2$ flow rate (C) of 260.6 mL/min is greater its average factor level C^*) of 232.5 mL/min, and the O_2/N_2 ratio (D) of 1.71 is greater than its average factor level (D^*) of 1.275.

11. Substituting in values of $X_1 = 10$ and $X_2 = 0$ gives a response of 519.7, or an absorbance of 0.520. Repeating using values of $X_1 = 0$ and $X_2 = 10$ gives a response of 637.5, or an absorbance of 0.638. Finally, letting $X_1 = 0$ and $X_2 = 0$ gives a response of 835.9, or an absorbance of 0.836.

These values are not reasonable as both H_2O_2 and H_2SO_4 are required reagents if the reaction is to develop color. Although the empirical model works well within the limit $8 \leq X_1 \leq 22$ and the limit $8 \leq X_2 \leq 22$, we cannot extend the model outside this range without introducing error.

This is, of course, the inherent danger of extrapolation.

12. The mean and the standard deviation for the 10 trials are 1.355 ppm and 0.1183 ppm, respectively. The relative standard deviation of

$$s_{rel} = \frac{0.1183 \text{ ppm}}{1.355 \text{ ppm}} \times 100 = 8.73\%$$

and the bias of

$$\frac{1.355 \text{ ppm} - 1.30 \text{ ppm}}{1.30 \text{ ppm}} \times 100 = 4.23\%$$

are within the prescribed limits; thus, the single operator characteristics are acceptable.

13. The following calculations show the effect of a change in each factor's level

$$E_A = \frac{98.9 + 98.5 + 97.7 + 97.0}{4}$$
$$- \frac{98.8 + 98.5 + 97.7 + 97.3}{4} = -0.05$$

$$E_B = \frac{98.9 + 98.5 + 98.8 + 98.5}{4}$$
$$- \frac{97.7 + 97.0 + 97.7 + 97.3}{4} = 1.25$$

$$E_C = \frac{98.9 + 97.7 + 98.8 + 97.7}{4}$$
$$- \frac{98.5 + 97.0 + 98.5 + 97.3}{4} = 0.45$$

$$E_D = \frac{98.9 + 98.5 + 97.7 + 97.3}{4}$$
$$- \frac{97.7 + 97.0 + 98.8 + 98.5}{4} = 0.10$$

$$E_E = \frac{98.9 + 97.7 + 98.5 + 97.3}{4}$$
$$- \frac{98.5 + 97.0 + 98.8 + 97.7}{4} = 0.10$$

$$E_F = \frac{98.9 + 97.0 + 98.8 + 97.3}{4}$$
$$- \frac{98.5 + 97.7 + 98.5 + 97.7}{4} = -0.10$$

$$E_G = \frac{98.9 + 97.0 + 98.5 + 97.7}{4}$$
$$- \frac{98.5 + 97.7 + 98.8 + 97.3}{4} = -0.05$$

The only significant factors are pH (factor B) and the digestion time (factor C). Both have a positive factor effect, which indicates that each factor's high level produces a more favorable recovery. The method's estimated standard deviation is

$$s = \sqrt{\frac{2}{7}\left\{ \begin{array}{l} (-0.05)^2 + (1.25)^2 + (0.45)^2 + \\ (0.10)^2 + (0.10)^2 + (-0.10)^2 + (-0.05)^2 \end{array} \right\}} = 0.72$$

14. (a) The most accurate analyst is the one whose results are closest to the true mean values, which is indicated by the **red** star; thus, analyst 2 has the most accurate results.

(b) The most precise analyst is the one whose results are closest to the diagonal line that represents no indeterminate error; thus, analyst 8 has the most precise results.

Note that the results for analyst 8 remind us that accuracy and precision are not related, and that it is possible for work to be very precise and yet wholly inaccurate (or very accurate and very imprecise).

(c) The least accurate analyst is the one whose results are furthest from the true mean values, which is indicated by the **red** star; thus, analyst 8 has the most accurate results.

(d) The least precise analyst is the one whose results are furthest from the diagonal line that represents no indeterminate error; thus, analysts 1 and 10 have the least precise results.

15. Figure SM14.8 shows the two sample plot where the mean for the first sample is 1.38 and the mean for the second sample is 1.50. A casual examination of the plot shows that six of the eight points are in the $(+,+)$ or the $(-,-)$ quadrants and that the distribution of the points is more elliptical than spherical; both suggest that systematic errors are present.

To estimate values for σ_{rand} and for σ_{sys}, we first calculate the differences, D_i, and the totals, T_i, for each analyst; thus

analyst	D_i	T_i
1	−0.22	2.92
2	0.02	2.68
3	−0.13	2.81
4	−0.10	3.10
5	−0.10	3.14
6	−0.13	2.91
7	−0.06	2.66
8	−0.21	2.85

To calculate the experimental standard deviations for the differences and the totals, we use equation 14.18 and equation 14.20, respectively, and are easy to calculate if first we find the regular standard deviation and then we divide it by $\sqrt{2}$; thus

$$s_D = 0.1232 \qquad s_T = 0.0549$$

To determine if the systematic errors are significant, we us the following null hypothesis and one-tailed alternative hypothesis

$$H_0: s_T = s_D \qquad H_A: s_T > s_D$$

Because the value of F_{exp}

$$F_{exp} = \frac{(s_T)^2}{(s_D)^2} = \frac{(0.1232)^2}{(0.0549)^2} = 5.04$$

exceeds the critical value of $F(0.05,7,7)$ of 3.787; thus, we reject the null hypothesis and accept the alternative hypothesis, finding evidence at $\alpha = 0.5$ that systematic errors are present in the data. The estimated precision for a single analyst is

$$\sigma_{rand} = s_D = 0.055$$

and the estimated standard deviation due to systematic differences between the analysts is

$$\sigma_{sys} = \sqrt{\frac{\sigma_T^2 - \sigma_D^2}{2}} = \sqrt{\frac{(0.1232)^2 - (0.0549)^2}{2}} = 0.078$$
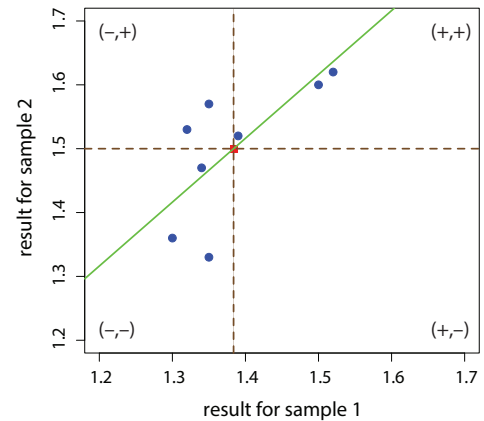
Figure SM14.8 Two-sample plot for the data in Problem 15. The **blue** dots are the results for each analyst, the **red** square is the average results for the two samples, the dashed **brown** lines divide the plot into four quadrants where the results for both samples exceeds the mean $(+,+)$, where both samples are below the mean $(-,-)$, and where one sample is above the mean and one below the mean, $(+,-)$ and $(-,+)$. The solid **green** line shows results with identical systematic errors.

Here we use a one-tailed alternative hypothesis because we are interested only in whether s_T is significantly greater than s_D.

16. (a) For an analysis of variance, we begin by calculating the global mean and the global variance for all 35 measurements using equation 14.22 and equation 14.23, respectively, obtaining values of $\overline{\overline{X}} = 3.542$ and $\overline{\overline{s^2}} = 1.989$. Next, we calculate the mean value for each of the seven labs, obtaining results of

$$\overline{X}_A = 2.40 \quad \overline{X}_B = 3.60 \quad \overline{X}_C = 2.00$$

$$\overline{X}_D = 2.60 \quad \overline{X}_E = 4.80 \quad \overline{X}_F = 5.00 \quad \overline{X}_G = 4.40$$

To calculate the variance within the labs and the variance between the labs, we use the equations from Table 14.7; thus, the total sum-of-squares is

$$SS_t = \overline{\overline{s^2}}(N-1) = (1.989)(35-1) = 67.626$$

and the between lab sum-of-squares is

$$SS_b = \sum_{i=1}^{b} n_i(\overline{X}_i - \overline{\overline{X}})^2 = (5)(2.40 - 3.542)^2$$
$$+ (5)(3.60 - 3.542)^2 + (5)(2.00 - 3.542)^2$$
$$+ (5)(2.60 - 3.542)^2 + (5)(4.80 - 3.542)^2$$
$$+ (5)(5.00 - 3.542)^2 + (5)(4.40 - 3.542)^2 = 45.086$$

and the within lab sum-of-squares is

$$SS_w = SS_t - SS_b = 67.626 - 45.086 = 22.540$$

The between lab variance, s_b^2, and the within lab variance, s_w^2, are

$$s_b^2 = \frac{SS_b}{b-1} = \frac{45.086}{7-1} = 7.514$$

$$s_w^2 = \frac{SS_w}{N-b} = \frac{22.540}{35-7} = 0.805$$

To determine if there is evidence that the differences between the labs is significant, we use an F-test of the following hull hypothesis and one-tailed alternative hypothesis

$$H_0: s_b^2 = s_w^2 \quad H_A: s_b^2 > s_w^2$$

Because the value of F_{exp}

$$F_{exp} = \frac{s_b^2}{s_w^2} = \frac{(7.514)^2}{(0.805)^2} = 87.13$$

exceeds the critical value for $F(0.05,6,28)$, which is between 2.099 and 2.599, we reject the null hypothesis and accept the alternative hypothesis, finding evidence at $\alpha = 0.5$ that there are systematic differences between the results of the seven labs.

To evaluate the source(s) of this systematic difference, we use equation 14.27 to calculate t_{exp} for the difference between mean values, comparing t_{exp} to a critical value of 1.705 for a one-tailed t-test with

28 degrees of freedom. For example, when comparing lab A to lab C, the two labs with the smallest mean values, we find

$$t_{exp} = \frac{|\overline{X}_A - \overline{X}_C|}{\sqrt{s_w^2}} \times \sqrt{\frac{n_A n_C}{n_A + n_C}} =$$

$$\frac{|2.40 - 2.00|}{\sqrt{0.805}} \times \sqrt{\frac{5 \times 5}{5 + 5}} = 0.705$$

no evidence for a systematic difference at $\alpha = 0.05$ between lab A and lab C. The table below summarizes results for all seven labs

lab	C	A	D	B	G	E	F
$\overline{X}$	2.00	2.40	2.60	3.60	4.40	4.80	5.00
t_{exp}		0.705		1.762		0.705	
			0.352		1.410		0.352

where there is no evidence of a significant difference between the results for labs C, A, and D (as shown by the **green** bar), where there is no evidence of a significant difference between the results for labs G, E, and F (as shown by the **blue** bar), and where there is no significant difference between the results for labs B and G (as shown by the **red** bar).

(b) The estimated values for σ_{rand}^2 and for σ_{sys}^2 are

$$\sigma_{rand}^2 \approx s_w^2 = 0.805$$

$$\sigma_{sys}^2 = \frac{s_b^2 - \sigma_{rand}^2}{n} = \frac{7.514 - 0.805}{5} = 1.34$$

17. First, let's write out the three sum-of-squares terms that appear in equation 14.23 (SS_t), equation 14.24 (SS_w), and equation 14.25 (SS_b)

$$SS_t = \sum_{i=1}^{h} \sum_{j=1}^{n_i} (X_{ij} - \overline{\overline{X}})^2$$

$$SS_w = \sum_{i=1}^{h} \sum_{j=1}^{n_i} (X_{ij} - \overline{X}_i)^2$$

$$SS_b = \sum_{i=1}^{h} n_i (\overline{X}_i - \overline{\overline{X}})^2$$

so that we have them in front of us. Looking at the equation for SS_t, let's pull out the term within the parentheses,

$$X_{ij} - \overline{\overline{X}}$$

and then subtract and add the term $\overline{X}_i$ to it, grouping together parts of the equation using parentheses

$$\left(X_{ij} - \overline{\overline{X}}\right) = (X_{ij} - \overline{X}_i) + (\overline{X}_i - \overline{\overline{X}})$$

Next, let's square both sides of the equation

$$\left(X_{ij} - \overline{\overline{X}}\right)^2 = \left\{\left(X_{ij} - \overline{X}_i\right) + \left(\overline{X}_i - \overline{\overline{X}}\right)\right\}^2$$

$$\left(X_{ij} - \overline{\overline{X}}\right)^2 = \left(X_{ij} - \overline{X}_i\right)^2 + \left(\overline{X}_i - \overline{\overline{X}}\right)^2 + 2\left(X_{ij} - \overline{X}_i\right)\left(\overline{X}_i - \overline{\overline{X}}\right)$$

and then substitute the right side of this equation back into the summation term for SS_t

$$SS_t = \sum_{i=1}^{h}\sum_{j=1}^{n_i}\left\{\left(X_{ij} - \overline{X}_i\right)^2 + \left(\overline{X}_i - \overline{\overline{X}}\right)^2 + 2\left(X_{ij} - \overline{X}_i\right)\left(\overline{X}_i - \overline{\overline{X}}\right)\right\}$$

and expand the summation across the terms in the curly parentheses

$$SS_t = \sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(X_{ij} - \overline{X}_i\right)^2$$
$$+ \sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(\overline{X}_i - \overline{\overline{X}}\right)^2$$
$$+ 2\sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(X_{ij} - \overline{X}_i\right)\left(\overline{X}_i - \overline{\overline{X}}\right)$$

Note that this is not the case for the first two terms in this expanded equation for SS_t because these terms sum up the squares of the differences, which always are positive, not the differences themselves, which are both positive and negative.

The last of these terms is equal to zero because this always is the result when you sum up the difference between a mean and the values that give the mean; thus, we now have this simpler equation

$$SS_t = \sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(X_{ij} - \overline{X}_i\right)^2 + \sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(\overline{X}_i - \overline{\overline{X}}\right)^2$$

Finally, we note that

$$\sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(\overline{X}_i - \overline{\overline{X}}\right)^2 = \sum_{i=1}^{h}n_i\left(\overline{X}_i - \overline{\overline{X}}\right)^2$$

because, for each of the h samples, the inner summation term simply adds together the term $\left(\overline{X}_i - \overline{\overline{X}}\right)^2$ a total of n_i times. Substituting this back into our equation for SS_t gives

$$SS_t = \sum_{i=1}^{h}\sum_{j=1}^{n_i}\left(X_{ij} - \overline{X}_i\right)^2 + \sum_{i=1}^{h}n_i\left(\overline{X}_i - \overline{\overline{X}}\right)^2$$

which is equivalent to $SS_t = SS_w + SS_b$.

18. (a) Using equation 14.28, our estimate for the relative standard deviation is

$$R = 2^{(1-0.5\log C)} = 2^{(1-0.5\log(0.0026))} = 4.9\%$$

(b) The mean and the standard deviation for the data set are 0.257%w/w and 0.0164%w/w respectively. The experimental percent relative standard deviation, therefore, is

$$s_r = \frac{0.0164\%\text{w/w}}{0.257\%\text{w/w}} \times 100 = 6.4\%$$

Because this value is within the range of $0.5\times$ to $2.0\times$ of R, the variability in the individual results is reasonable.

Chapter 15

1. Answers will vary depending on the labs you have done and the guidelines provided by your instructor. Of the examples cited in the text, those that likely are most relevant to your experience are properly recording data and maintaining records, specifying and purifying chemical reagents, cleaning and calibrating glassware and other equipment, and maintaining the laboratory facilities and general laboratory equipment.

2. Although your answers may include additional details, here are some specific issues you should include.

    (a) If necessary, clean and rinse the buret with water. When clean, rinse the buret with several portions of your reagent and then fill the buret with reagent so that it is below the buret's 0.00 mL mark. Be sure that the buret's tip is filled and that an air bubble is not present. Read the buret's initial volume. Dispense the reagent, being sure that each drop falls into your sample's flask. If splashing occurs, rinse the walls of the sample's flask to ensure that the reagent makes it into the flask. If a drop of reagent remains suspended on the buret's tip when you are done adding reagent, rinse it into the sample's flask. Record the final volume of reagent in the buret.

    (b) Calibrate the pH meter using two buffers, one near a pH of 7 and one that is more acidic or more basic, depending on the samples you will analyze. When transferring the pH electrode to a new solution, rinse it with distilled water and carefully dry it with a tissue to remove the rinse water. Place the pH electrode in the solution you are analyzing and allow the electrode to equilibrate before recording the pH.

    (c) Turn on the instrument and allow sufficient time for the light source to warm up. Adjust the wavelength to the appropriate value. Adjust the instrument's 0%T (infinite absorbance) without a sample in the cell and with the light source blocked from reaching the detector. Fill a suitable cuvette with an appropriate blank solution, clean the cuvette's exterior surface with a tissue, place the cuvette in the sample holder, and adjust the instrument's 100%T (zero absorbance). Rinse the cuvette with several small portions of your sample and then fill the cuvette with sample. Place the cuvette in the sample holder and record the sample's %T or absorbance.

3. Substituting each sample's signal into the equation for the calibration curve gives the concentration of lead in the samples as 1.59 ppm and 1.48 ppm. The absolute difference, d, and the relative difference, $(d)_r$, are

$$d = 1.59 \text{ ppm} - 1.48 \text{ ppm} = 0.11 \text{ ppm}$$

$$(d)_r = \frac{0.11 \text{ ppm}}{0.5\,(1.59 \text{ ppm} + 1.48 \text{ ppm})} \times 100 = 7.2\%$$

For a trace metal whose concentration is more than $20\times$ the method's detection limit of 10.0 ppb, the relative difference should not exceed 10%; with a $(d)_r$ of 7.2%, the duplicate analysis is acceptable.

4. In order, the differences are 0.12, −0.08, 0.12, −0.05, −0.10, and 0.07 ppm. The standard deviation for the duplicates is

$$s = \sqrt{\frac{\sum_{i=1}^{n}(d_i)^2}{2n}} = \sqrt{\frac{\begin{bmatrix}(0.12)^2 + (-0.08)^2 + \\ (0.12)^2 + (-0.05)^2 + \\ (-0.10)^2 + (0.07)^2\end{bmatrix}}{2 \times 6}} = 0.066 \text{ ppm}$$

The mean concentration of NO_3^- for all 12 samples is 5.005 ppm, which makes the relative standard deviation

$$s_r = \frac{0.066 \text{ ppm}}{5.005 \text{ ppm}} \times 100 = 1.3\%$$

a value that is less than the maximum limit of 1.5%.

5. For the first spike recovery, the result is

$$R = \frac{0.342 \text{ mg/g} - 0.20 \text{ mg/g}}{0.135 \text{ mg/g}} \times 100 = 105.2\%$$

The recoveries for the remaining four trials are 103.7%, 103.7%, 91.9%, and 90.4%. The mean recovery for all five trials is 99.0%.

6. (a) Using the equation for the calibration curve, the concentration of analyte in the spiked field blank is 2.10 ppm. The recovery on the spike, therefore, is

$$R = \frac{2.10 \text{ ppm} - 0 \text{ ppm}}{2.00 \text{ ppm}} \times 100 = 105\%$$

Because this recovery is within the limit of ±10%, the field blank's recovery is acceptable.

(b) Using the equation for the calibration curve, the concentration of analyte in the spiked method blank is 1.70 ppm. The recovery on the spike, therefore, is

$$R = \frac{1.70 \text{ ppm} - 0 \text{ ppm}}{2.00 \text{ ppm}} \times 100 = 85\%$$

Because this recovery exceeds the limit of ±10%, the method blank's recovery is not acceptable and there is a systematic error in the laboratory.

(c) Using the equation for the calibration curve, the concentration of analyte in the sample before the spike is 1.67 ppm and its concentration after the spike is 3.77 ppm. The recovery on the spike is

$$R = \frac{3.77 \text{ ppm} - 1.67 \text{ ppm}}{2.00 \text{ ppm}} \times 100 = 105\%$$

Because this recovery is within the limit of $\pm 10\%$, the laboratory spike's recovery is acceptable, suggesting a time-dependent change in the analyte's concentration.

7. The mean and the standard deviation for the 25 samples are 34.01 ppm and 1.828 ppm, respectively, which gives us the following warning limits and control limits

$$UCL = 34.01 + (3)(1.828) = 39.5$$

$$UWL = 34.01 + (2)(1.828) = 37.7$$

$$LWL = 34.01 - (2)(1.828) = 30.4$$

$$LCL = 34.01 - (3)(1.828) = 28.5$$

Figure SM15.1 shows the property control chart. Note that the highlighted region contains 14 consecutive cycles (15 samples) in which the results oscillate up and down, indicating that the system is not in a state of statistical control.

8. The mean and the standard deviation for the 25 samples are 99.84% and 14.08%, respectively, which gives us the following warning limits and control limits

$$UCL = 99.84 + (3)(14.08) = 142.1$$

$$UWL = 99.84 + (2)(14.08) = 128.0$$

$$LWL = 99.84 - (2)(14.08) = 71.7$$

$$LCL = 99.84 - (3)(14.08) = 57.6$$

Figure SM15.2 shows the property control chart, which has no features to suggest that the system is not in a state of statistical control.

9. The 25 range values are 4, 1, 3, 3, 2, 0, 2, 4, 3, 1, 4, 1, 2, 0, 2, 4, 3, 4, 1, 1, 2, 1, 2, 3, 3, with a mean of 2.24. The control and warning limits, therefore, are

$$UCL = (3.267)(2.24) = 7.3$$

$$UWL = (2.512)(2.24) = 5.6$$

Figure SM15.2 shows the precision control chart, which has no features to suggest that the system is not in a state of statistical control.
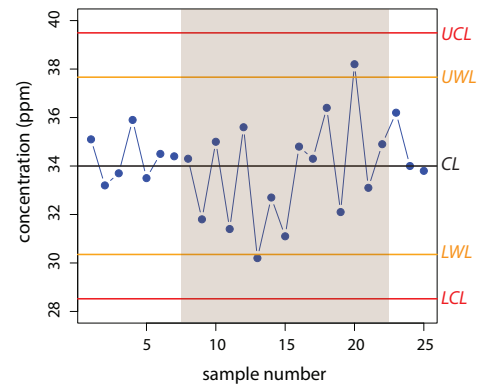

Figure SM15.1 Property control chart for the data in Problem 7. The highlighted region shows 14 consecutive cycles in which the results oscillate up and down, a sign that system is not in a state of statistical control.
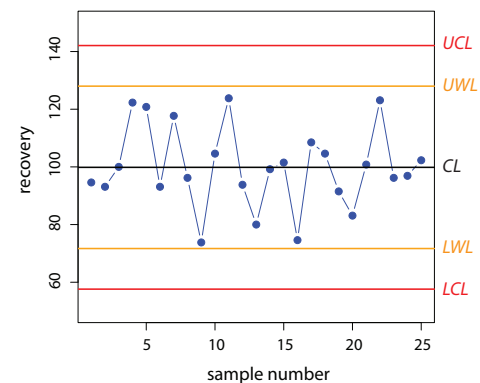

Figure SM15.2 Property control chart for the data in Problem 8.
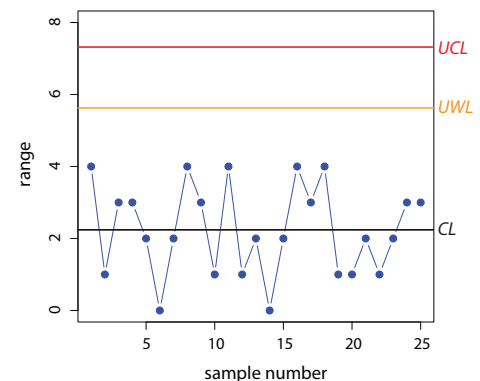

Figure SM15.3 Precision control chart for the data in Problem 9.

Appendix

The solutions here are for the problems in Appendix 9.

1. (a) Without accounting for buoyancy, the volume of water is

$$\frac{9.9814\ \text{g}}{0.99707\ \text{g/cm}^3} = 10.011\ \text{cm}^3 = 10.011\ \text{mL}$$

When we correct for buoyancy, however, the volume is

$$W_v = 9.9814\ \text{g} \times \left[1 + \left\{ \frac{\frac{1}{0.99707\ \text{g/cm}^3}}{-\frac{1}{8.40\ \text{g/cm}^3}} \right\} \times 0.0012\text{g/cm}^3 \right]$$

$$W_v = 9.9920\ \text{g}$$

(b) The absolute and relative errors in the mass are

$$10.011\ \text{mL} - 10.021\ \text{mL} = -0.010\ \text{mL}$$

$$\frac{-0.010\ \text{mL}}{10.021\ \text{mL}} \times 100 = -0.10\%$$

Table 4.9 shows us that the standard deviation for the calibration of a 10-mL pipet is on the order of ± 0.006 mL. Failing to correct for the effect of buoyancy gives a determinate error of -0.010 mL that is slightly larger than ± 0.006 mL, suggesting that it introduces a small, but significant determinate error.

2. The sample's true weight is

$$W_v = 0.2500\ \text{g} \times \left[1 + \left\{ \frac{\frac{1}{2.50\ \text{g/cm}^3}}{-\frac{1}{8.40\ \text{g/cm}^3}} \right\} \times 0.0012\text{g/cm}^3 \right]$$

$$W_v = 0.2501\ \text{g}$$

In this case the absolute and relative errors in mass are -0.0001 g and -0.040%.

3. The true weight is the product of the weight measured in air and the buoyancy correction factor, which makes this a proportional error. The percentage error introduced when we ignore the buoyancy correction is independent of mass and a function only of the difference between the density of the object being weighed and the density of the calibration weights.

4. To determine the minimum density, we note that the buoyancy correction factor equals 1.00 if the density of the calibration weights and the density of the sample are the same. The correction factor is greater than 1.00 if D_o is smaller than D_w; thus, the following inequality applies

$$\left(\frac{1}{D_o} - \frac{1}{8.40}\right) \times 0.0012 \leq (1.00)(0.0001)$$

Solving for D_o shows that the sample's density must be greater than 4.94 g/cm^3 to ensure an error of less than 0.01%.