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

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.

$$n_{HCl} = M_{HCl} V_{HCl} = M_{NaOH} V_{NaOH} = n_{NaOH}$$

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.

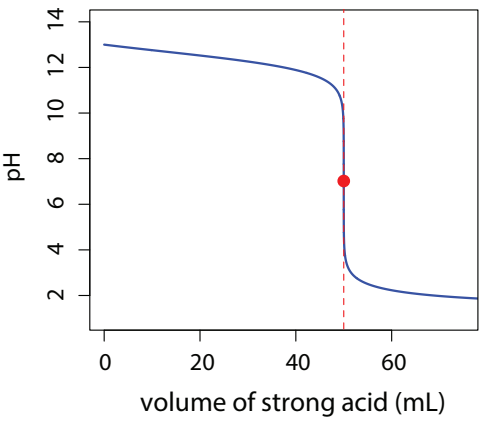

Figure SM9.1 The titration curve for 0.100 M NaOH using 0.100 M HCl as the titrant is shown in **blue**. The **red** dashed line marks the volume of titrant at the equivalence point and the **red** dot shows the equivalence point (see Problem 2a).

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

$$V_{eq.pt.} = V_{NaOH} = \frac{M_{HCOOH} V_{HCOOH}}{M_{NaOH}} = \frac{(0.0500\ M)(50.0\ mL)}{0.100\ M} = 25.0\ mL$$

The sample's initial pH of 2.54 is determined by the initial concentration of formic acid and its K_a value

$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{(x)(x)}{0.0500 - x} = 1.80 \times 10^{-4}$$

$$x = [H_3O^+] = 2.91 \times 10^{-3}\ M$$

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

$$[HCOOH] = \frac{M_{HCOOH} V_{HCOOH} - M_{NaOH} V_{NaOH}}{V_{HCOOH} + V_{NaOH}}$$

$$[HCOOH] = \frac{(0.0500\ M)(50.0\ mL) - (0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL}$$

$$[HCOOH] = 0.025\ M$$

$$[HCOO^-] = \frac{M_{NaOH} V_{NaOH}}{V_{HCOOH} + V_{NaOH}} = \frac{(0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL} = 0.0167\ M$$

$$pH = pK_a + \log\frac{[HCOO^-]}{[HCOOH]} = 3.745 + \log\frac{(0.0167)}{(0.0250)} = 3.57$$

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

$$[OH^-] = \frac{M_{NaOH} V_{NaOH} - M_{HCOOH} V_{HCOOH}}{V_{HCOOH} + V_{NaOH}}$$

$$[OH^-] = \frac{(0.100\ M)(35.0\ mL) - (0.0500\ M)(50.0\ mL)}{50.0\ mL + 35.0\ mL}$$

$$[OH^-] = 0.0118\ M$$

the pOH is 1.93, or a pH of 12.07. Figure SM9.2 shows the full titration curve.

See Chapter 6 for a review of how to solve equilibrium problems. In this chapter, we present the basic equation and the result of the calculation; the mathematical details are left to you.

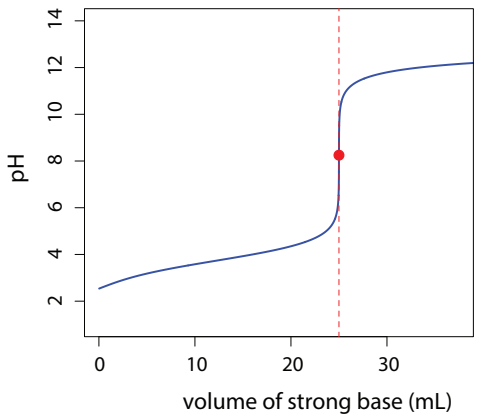

Figure SM9.2 The titration curve for 0.0500 M using 0.100 M NaOH as the titrant is shown in **blue**. The **red** dashed line marks the volume of titrant at the equivalence point and the **red** dot shows the equivalence point (see Problem 2b).

To sketch an approximate titration curve, use a ladder diagram for HCOOH 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.

(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

$$V_{eq.pt.} = V_{HCl} = \frac{M_{NH_3}V_{NH_3}}{M_{HCl}} = \frac{(0.100\text{ M})(50.0\text{ mL})}{0.100\text{ M}} = 50.0\text{ mL}$$

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

$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} = \frac{(x)(x)}{0.100 - x} = 1.75 \times 10^{-5}$$

$$x = [OH^-] = 1.31 \times 10^{-3}\text{ M}$$

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

$$[NH_3] = \frac{M_{NH_3}V_{NH_3} - M_{HCl}V_{HCl}}{V_{NH_3} + V_{HCl}}$$

$$[NH_3] = \frac{(0.100\text{ M})(50.0\text{ mL}) - (0.100\text{ M})(20.0\text{ mL})}{50.0\text{ mL} + 20.0\text{ mL}}$$

$$[NH_3] = 0.0429\text{ M}$$

$$[NH_4^+] = \frac{M_{HCl}V_{HCl}}{V_{NH_3} + V_{HCl}} = \frac{(0.100\text{ M})(20.0\text{ mL})}{50.0\text{ mL} + 20.0\text{ mL}} = 0.0286\text{ M}$$

$$\text{pH} = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = 9.244 + \log\frac{(0.0429)}{(0.0286)} = 9.42$$

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

$$[H_3O^+] = \frac{M_{HCl}V_{HCl} - M_{NH_3}V_{NH_3}}{V_{NH_3} + V_{HCl}}$$

$$[H_3O^+] = \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL} + 60.0\text{ mL}}$$

$$[H_3O^+] = 0.00909\text{ M}$$

the pH is 2.04. Figure SM9.3 shows the full titration curve.

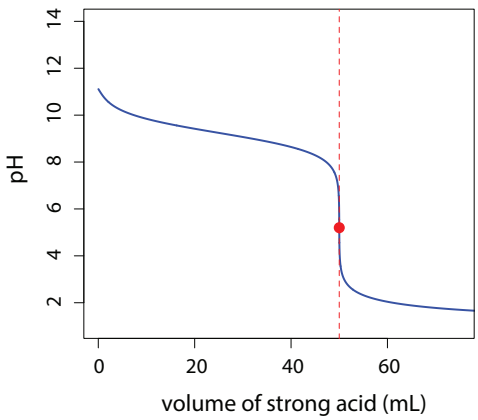

Figure SM9.3 The titration curve for 0.100 M NH_3 using a 0.100 M HCl as the titrant is shown in **blue**. The **red** dashed line marks the volume of titrant at the equivalence point and the **red** dot shows the equivalence point (see Problem 2c).

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

$$V_{eq.pt.1} = V_{HCl} = \frac{M_{en} V_{en}}{M_{HCl}} = \frac{(0.0500\ M)(50.0\ mL)}{0.100\ M} = 25.0\ mL$$

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

$$K_{b1} = \frac{[OH^-][Hen^+]}{[en]} = \frac{(x)(x)}{0.0500 - x} = 8.47 \times 10^{-5}$$

$$x = [OH^-] = 2.06 \times 10^{-3}\ M$$

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

$$[en] = \frac{M_{en} V_{en} - M_{HCl} V_{HCl}}{V_{en} + V_{HCl}}$$

$$[en] = \frac{(0.0500\ M)(50.0\ mL) - (0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL}$$

$$[en] = 0.0250\ M$$

$$[Hen^+] = \frac{M_{HCl} V_{HCl}}{V_{en} + V_{HCl}} = \frac{(0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL} = 0.0167\ M$$

$$pH = pK_{a2} + \log\frac{[en]}{[Hen^+]} = 9.928 + \log\frac{(0.0250)}{(0.0167)} = 10.10$$

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^+.

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

$$[Hen^+] = \frac{M_{en} V_{en} - M_{HCl}(V_{HCl} - V_{eq.pt.1})}{V_{en} + V_{HCl}}$$

$$[Hen^+] = \frac{(0.0500\ M)(50.0\ mL) - (0.100\ M)(35.0 - 25.0\ mL)}{50.0\ mL + 35.0\ mL}$$

$$[Hen^+] = 0.0176\ M$$

$$[H_2en^{2+}] = \frac{M_{HCl}(V_{HCl} - V_{eq.pt.1})}{V_{en} + V_{HCl}}$$

$$[H_2en^{2+}] = \frac{(0.100\ M)(35.0 - 25.0\ mL)}{50.0\ mL + 35.0\ mL}$$

$$[H_2en^{2+}] = 0.0118\ M$$

$$pH = pK_{a1} + \log\frac{[Hen^+]}{[H_2en^{2+}]} = 6.848 + \log\frac{(0.0176)}{(0.0118)} = 7.02$$

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

$$[H_3O^+] = \frac{M_{HCl}(V_{HCl} - V_{eq.pt2})}{V_{en} + V_{HCl}}$$

$$[H_3O^+] = \frac{(0.100\ M)(60.0 - 50.0\ mL)}{50.0\ mL + 60.0\ mL}$$

$$[H_3O^+] = 0.00909\ M$$

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

$$V_{eq.pt.1} = V_{NaOH} = \frac{M_{H_3A}M_{H_3A}}{M_{NaOH}} = \frac{(0.0400\ M)(50.0\ mL)}{0.120\ M} = 16.7\ mL$$

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

$$K_{a1} = \frac{[H_3O^+][H_2A^-]}{[H_3A]} = \frac{(x)(x)}{0.0400 - x} = 7.45 \times 10^{-4}$$

$$x = [H_3O^+] = 5.10 \times 10^{-3}\ M$$

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.

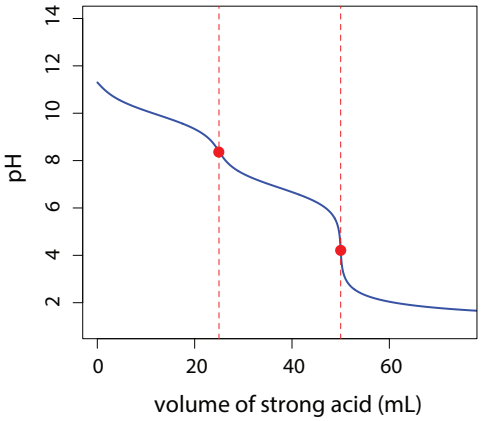

Figure SM9.4 The titration curve for 0.0500 M ethylenediamine using 0.100 M HCl as the titrant is shown in **blue**. The **red** dashed lines mark the volumes of titrant at the equivalence points and the **red** dots mark the equivalence points (see Problem 2d).

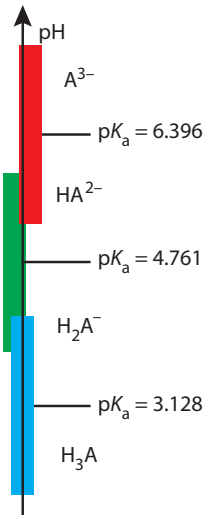

Figure SM9.5 Ladder diagram for citric acid with buffer regions for H_3A/H_2A^- (in **blue**), for H_2A^-/HA^{2-} (in **green**), and for HA^{2-}/A^{3-} (in **red**). The assumptions in the Henderson-Hasselbalch equation hold at pH levels where the buffers do not overlap.

$$[H_3A] = \frac{M_{H_3A} V_{H_3A} - M_{NaOH} V_{NaOH}}{V_{H_3A} + V_{NaOH}}$$

$$[H_3A] = \frac{(0.0400\ M)(50.0\ mL) - (0.120\ M)(5.00\ mL)}{50.0\ mL + 5.00\ mL}$$

$$[H_3A] = 0.0255\ M$$

$$[H_2A^-] = \frac{M_{NaOH} V_{NaOH}}{V_{H_3A} + V_{NaOH}} = \frac{(0.120\ M)(5.00\ mL)}{50.0\ mL + 5.00\ mL} = 0.0109\ M$$

$$pH = pK_{a1} + \log\frac{[H_2A^-]}{[H_3A]} = 3.128 + \log\frac{(0.0109)}{(0.0255)} = 2.76$$

After adding 30.00 mL of NaOH the pH is

$$[H_2A^-] = \frac{M_{H_3A} V_{H_3A} - M_{NaOH}(V_{NaOH} - V_{eq.pt.1)}}{V_{H_3A} + V_{NaOH}}$$

$$[H_2A^-] = \frac{(0.0400\ M)(50.0\ mL) - (0.120\ M)(30.0 - 16.7\ mL)}{50.0\ mL + 30.0\ mL}$$

$$[H_2A^-] = 5.05 \times 10^{-3}\ M$$

$$[HA^{2-}] = \frac{M_{NaOH}(V_{NaOH} - V_{eq.pt.1})}{V_{H_3A} + V_{NaOH}}$$

$$[HA^{2-}] = \frac{(0.120\ M)(30.0 - 16.7\ mL)}{50.0\ mL + 30.0\ mL}$$

$$[HA^{2-}] = 0.0200\ M$$

$$pH = pK_{a2} + \log\frac{[HA^{2-}]}{[H_2A^-]} = 4.761 + \log\frac{(0.0200)}{(0.00505)} = 5.36$$

and after adding 45.0 mL of NaOH the pH is

$$[HA^{2-}] = \frac{M_{H_3A} V_{H_3A} - M_{NaOH}(V_{NaOH} - V_{eq.pt.2})}{V_{H_3A} + V_{NaOH}}$$

$$[HA^{2-}] = \frac{(0.0400\ M)(50.0\ mL) - (0.120\ M)(45.0 - 33.3\ mL)}{50.0\ mL + 45.0\ mL}$$

$$[HA^{2-}] = 0.00627\ M$$

$$[A^{3-}] = \frac{M_{NaOH}(V_{NaOH} - V_{eq.pt.2})}{V_{H_3A} + V_{NaOH}}$$

$$[A^{3-}] = \frac{(0.120\ M)(45.0 - 33.3\ mL)}{50.0\ mL + 45.0\ mL}$$

$$[A^{3-}] = 0.0148\ M$$

$$pH = pK_{a3} + \log\frac{[A^{3-}]}{[HA^{2-}]} = 6.396 + \log\frac{(0.0148)}{(0.00627)} = 6.77$$

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.

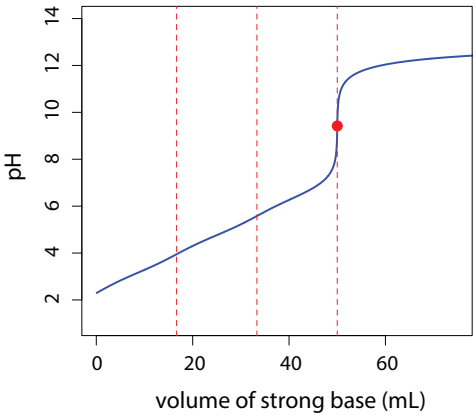

Figure SM9.6 The titration curve for 0.040 M citric acid using 0.120 M NaOH as the titrant is shown in **blue**. The **red** dashed lines mark the volumes of titrant at the equivalence points and the **red** dot marks the third equivalence point (see Problem 2e). Note that the pK_a values are sufficiently close in value that the first two equivalence points are not discernible.

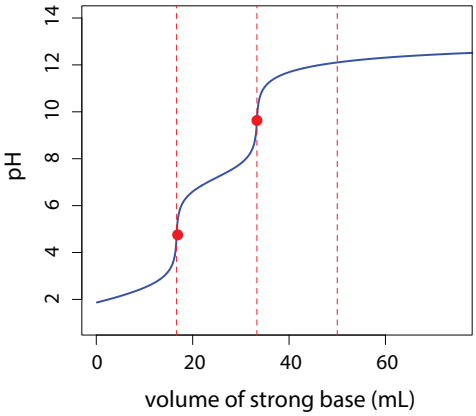

Figure SM9.7 The titration curve for 0.040 M H_3PO_4 using 0.120 M NaOH as the titrant is shown in **blue**. The **red** dashed lines mark volumes of titrant at the equivalence points and the **red** dots marks the first two equivalence points (see Problem 2f). Note that third equivalence point is not 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^+

To review the derivation of this equation, see section 6G.5 in Chapter 6.

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

$$[H_3O^+] = \sqrt{\frac{\left\{\begin{array}{r}(1.42 \times 10^{-7})(1.18 \times 10^{-10})(0.0333) \\ + (1.42 \times 10^{-7})(1.00 \times 10^{-14})\end{array}\right\}}{(0.0333) + (1.42 \times 10^{-7})}}$$

$$[H_3O^+] = 4.1 \times 10^{-9}$$

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

$$[H_3O^+] = \sqrt{\frac{K_{a1} K_{a2} C_{H_2PO_4^-} + K_{a1} K_w}{C_{H_2PO_4^-} + K_{a1}}}$$

$$[H_3O^+] = \sqrt{\frac{\left\{(7.11 \times 10^{-3})(6.32 \times 10^{-8})(0.0300) + (7.11 \times 10^{-3})(1.00 \times 10^{-14})\right\}}{(0.0300) + (7.11 \times 10^{-3})}}$$

$$[H_3O^+] = 1.91 \times 10^{-5}$$

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

$$[H_3O^+] = \sqrt{\frac{K_{a2}K_{a3}C_{HPO_4^{2-}} + K_{a2}K_w}{C_{HPO_4^{2-}} + K_{a2}}}$$

$$[H_3O^+] = \sqrt{\frac{\left\{\begin{array}{r}(6.32\times10^{-8})(4.5\times10^{-13})(0.0240)\\ +\,(6.32\times10^{-8})(1.00\times10^{-14})\end{array}\right\}}{(0.0240) + (6.32\times10^{-8})}}$$

$$[H_3O^+] = 2.34\times10^{-10}$$

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:

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.

(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.

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

$$0.045\ \text{L NaOH} \times \frac{0.10\ \text{mol NaOH}}{\text{L}} \times \frac{1\ \text{mol } H_2C_4H_4O_6}{2\ \text{mol NaOH}} \times \frac{150.1\ \text{g } H_2C_4H_4O_6}{\text{mol } H_2C_4H_4O_6} = 0.34\ \text{g } H_2C_4H_4O_6$$

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

$$\frac{\text{g } H_2C_4H_4O_6}{\text{g sample}} \times 100 = \%\text{w/w } H_2C_4H_4O_6$$

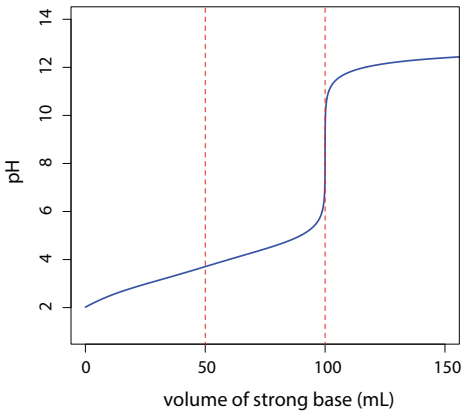

Figure SM9.8 The titration curve for 0.10 M tartaric acid using 0.10 M NaOH as the titrant is shown in **blue**. The **red** dashed lines mark the volumes of titrant at the equivalence points. Note that first equivalence point is not discernible.

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

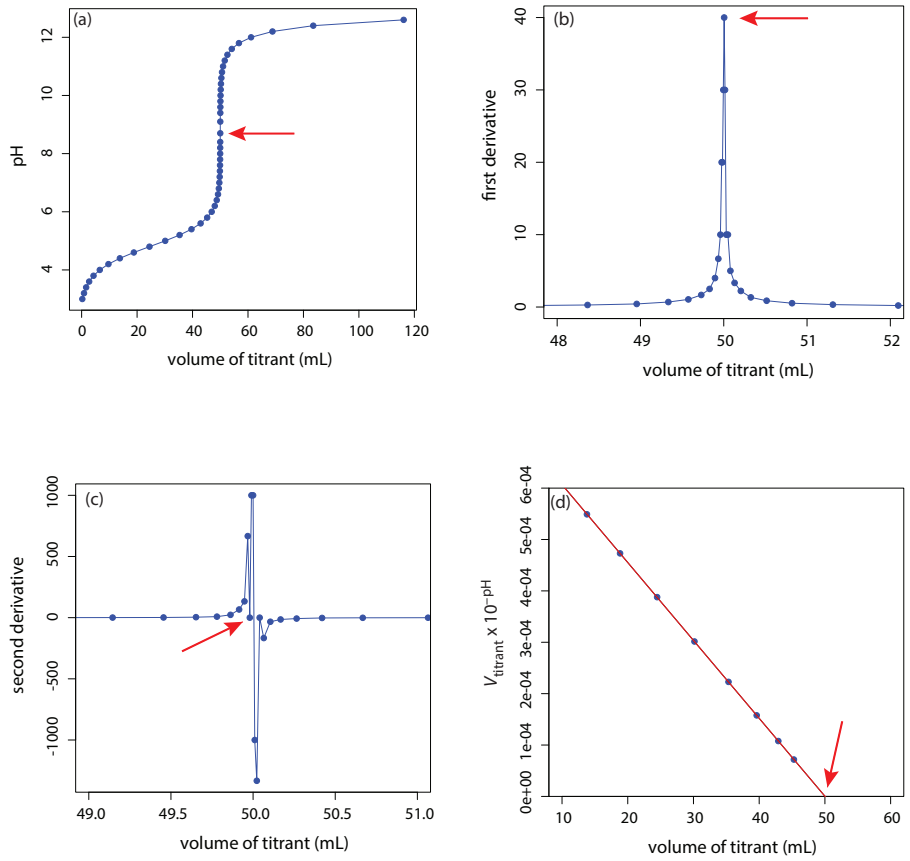

Figure SM9.9 Titration curves for a monoprotic weak acid using a strong base as the titrant: (a) normal titration curve; (b) first-derivative titration curve; (c) second-derivative titration curve; and (d) Gran's plot titration curve. For all four titration curves, the location of the equivalence point is shown by the **red** arrow. Note that titration curves in (b), (c), and (d) display the volume over a limited range of values.

$$\frac{\Delta^2 \text{pH}}{\Delta V^2} = \frac{0.260 - 0.328}{1.245 - 0.555} = -0.099$$

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 $V_{\text{NaOH}} \times 10^{-\text{pH}}$ 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

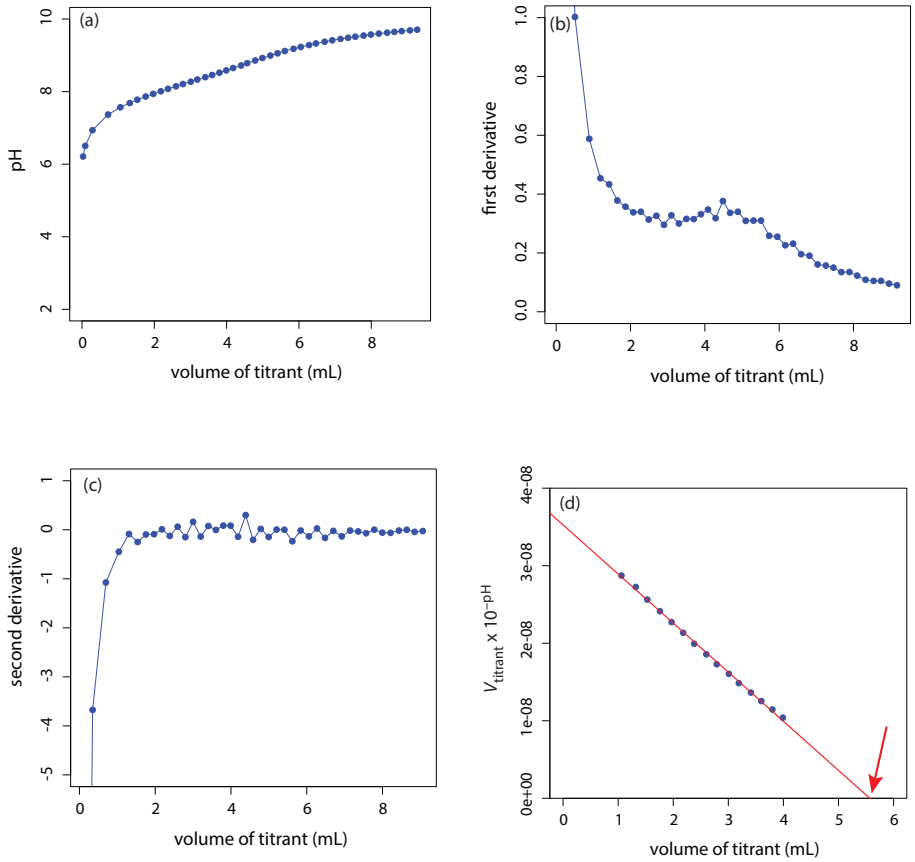

Figure SM9.10 Titration curves for the titration of a monoprotic weak acid with a strong base: (a) normal titration curve; (b) first-derivative titration curve; (c) second-derivative titration curve; and (d) Gran's plot titration curve. The experimental equivalence point for the Gran plot is shown by 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.

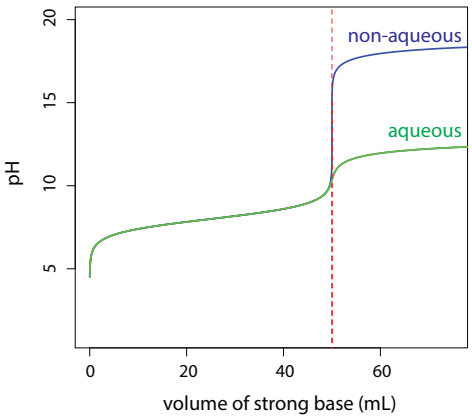

Figure SM9.11 Titration curves for Problem 9.8. The titration curve in **green** is in an aqueous solution with a pK_w of 14; the titration curve in **blue** is in a non-aqueous solvent with a pK_s of 20. The volume of titrant at the equivalence point is shown by the dashed **red** line.

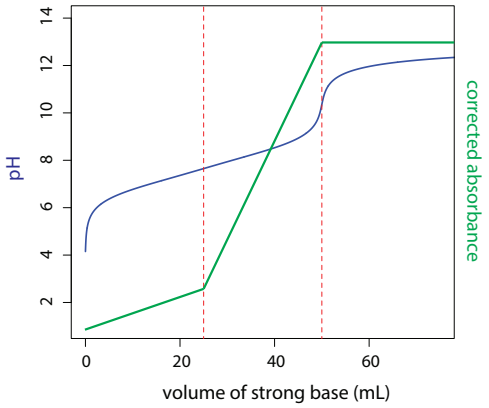

Figure SM9.12 Titration curves for Problem 9.9 with the volume of titrant at the equivalence points shown by the dashed **red** lines. The potentiometric titration curve is shown in **blue**. Of the two equivalence points, only the second—for *m*-nitrophenol—is discernible. The spectrophotometric titration curve, which is shown by the **green** line, has a distinct equivalence point for each analyte.

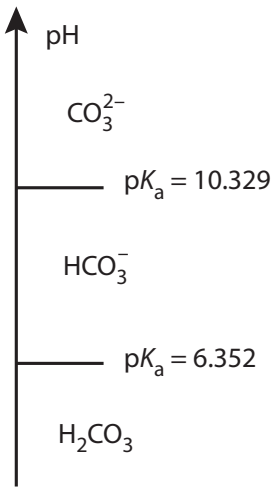

Figure SM9.13 Ladder diagram for H_2CO_3.

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.

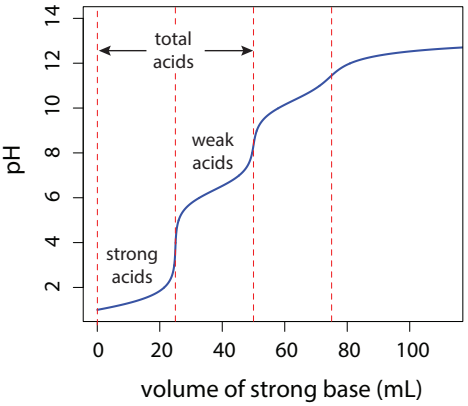

Figure SM9.14 Titration curve for a mixture of 0.10 M HCl and 0.10 M H_2CO_3 using 0.20 M NaOH as the titrant showing the contribution of strong acid acidity and weak acidity to the sample's total acidity.

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

$$V_b = V_{E1} - \frac{(V_a + V_b)\,d}{M_b}$$

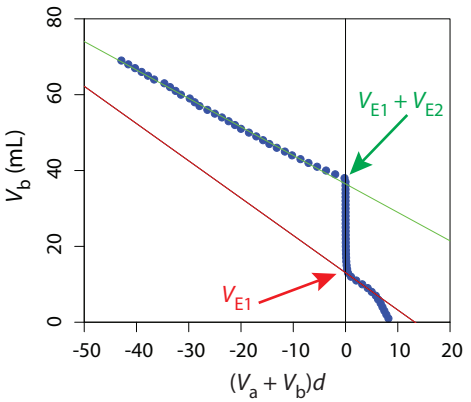

Figure SM9.15 Gran plot for the data in Problem 9.14. The linear regression lines are used to determine V_{E1} and $V_{E1} + V_{E2}$; see the solution for more details. The data, which I collected specifically for this problem, is a bit wonky as the two regression lines should have identical slopes of $1/M_b$. 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

$$0.02137\text{ L} \times \frac{(0.1198\text{ mol HCl})}{\text{L}} \times \frac{1\text{ mol OH}^-}{\text{mol HCl}} \times \frac{17.01\text{ g OH}^-}{\text{mol OH}^-} \times \frac{1000\text{ mg}}{\text{g}} = 43.5\text{ mg OH}^-$$

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

$$0.00567\ \text{L} \times \frac{(0.1198\ \text{mol HCl})}{\text{L}} \times \frac{1\ \text{mol } CO_3^{2-}}{\text{mol HCl}} \times \frac{60.01\ \text{g } CO_3^{2-}}{\text{mol } CO_3^{2-}} \times \frac{1000\ \text{mg}}{\text{g}} = 40.8\ \text{mg } CO_3^{2-}$$

$$\frac{40.8\ \text{mg } CO_3^{2-}}{0.02500\ \text{L}} = 1630\ \text{ppm } CO_3^{2-}$$

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

$$0.00979\ \text{L} \times \frac{(0.1198\ \text{mol HCl})}{\text{L}} \times \frac{1\ \text{mol } HCO_3^-}{\text{mol HCl}} \times \frac{61.02\ \text{g } HCO_3^-}{\text{mol } HCO_3^-} \times \frac{1000\ \text{mg}}{\text{g}} = 71.6\ \text{mg } HCO_3^-$$

$$\frac{71.6\ \text{mg } HCO_3^-}{0.02500\ \text{L}} = 2860\ \text{ppm } HCO_3^-$$

(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

$$0.01428\ \text{L} \times \frac{(0.1198\ \text{mol HCl})}{\text{L}} \times \frac{1\ \text{mol } HCO_3^-}{\text{mol HCl}} \times \frac{61.02\ \text{g } HCO_3^-}{\text{mol } HCO_3^-} \times \frac{1000\ \text{mg}}{\text{g}} = 104.4\ \text{mg } HCO_3^-$$

$$\frac{104.4\ \text{mg } HCO_3^-}{0.02500\ \text{L}} = 4180\ \text{ppm } HCO_3^-$$

(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

$$0.01712\ \text{L} \times \frac{(0.1198\ \text{mol HCl})}{\text{L}} \times \frac{1\ \text{mol } CO_3^{2-}}{\text{mol HCl}} \times \frac{60.01\ \text{g } CO_3^{2-}}{\text{mol } CO_3^{2-}} \times \frac{1000\ \text{mg}}{\text{g}} = 123.1\ \text{mg } CO_3^{2-}$$

$$\frac{123.1\ \text{mg } CO_3^{2-}}{0.02500\ \text{L}} = 4920\ \text{ppm } CO_3^{2-}$$

We can use the volume to reach the bromocresol green end point as well, substituting

$$\frac{1\ \text{mol } CO_3^{2-}}{2\ \text{mol HCl}}$$

for

$$\frac{1\ \text{mol } CO_3^{2-}}{1\ \text{mol HCl}}$$

(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

$$0.00433\text{ L} \times \frac{(0.1198\text{ mol HCl})}{\text{L}} \times \frac{1\text{ mol } CO_3^{2-}}{\text{mol HCl}} \times \frac{60.01\text{ g } CO_3^{2-}}{\text{mol } CO_3^{2-}} \times \frac{1000\text{ mg}}{\text{g}} = 31.1\text{ mg } CO_3^{2-}$$

$$\frac{31.1\text{ mg } CO_3^{2-}}{0.02500\text{ L}} = 1240\text{ ppm } CO_3^{2-}$$

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

$$0.01703\text{ L} \times \frac{(0.1198\text{ mol HCl})}{\text{L}} \times \frac{1\text{ mol } OH^-}{\text{mol HCl}} \times \frac{17.01\text{ g } OH^-}{\text{mol } OH^-} \times \frac{1000\text{ mg}}{\text{g}} = 34.7\text{ mg } OH^-$$

$$\frac{34.7\text{ mg } OH^-}{0.02500\text{ L}} = 1390\text{ ppm } OH^-$$

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

$$M_{PO_4^{3-}} = \frac{M_{HCl}\,V_{HCl}}{V_{sample}} = \frac{(0.1198\text{ M})\,(11.54\text{ mL})}{25.00\text{ mL}} = 0.0553\text{ M}$$

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

$$M_{HPO_4^{3-}} = \frac{M_{HCl}\,V_{HCl}}{V_{sample}} = \frac{(0.1198\text{ M})\,(12.21\text{ mL})}{25.00\text{ mL}} = 0.0585\text{ M}$$

(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

$$M_{H_3PO_4} = \frac{M_{NaOH}\,V_{NaOH}}{V_{sample}} = \frac{(0.1198\text{ M})\,(9.89\text{ mL})}{25.00\text{ mL}} = 0.0474\text{ M}$$

(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

$$\frac{7.78 \text{ mg } SO_2 \times \dfrac{1 \text{ mL}}{2.86 \text{ mg } SO_2} \times \dfrac{1000 \text{ µL}}{\text{mL}}}{75.0 \text{ L}} = 36.7 \text{ µL/L } SO_2$$

20. We begin the analysis with

$$\frac{0.0200 \text{ mol } Ba(OH)_2}{\text{L}} \times 0.05000 \text{ L} = 1.00 \times 10^{-3} \text{ mol } Ba(OH)_2$$

The titration of $Ba(OH)_2$ by HCl consumes two moles of HCl for every mole of $Ba(OH)_2$; thus,

$$0.03858 \text{ mL} \times \frac{0.0316 \text{ M HCl}}{\text{L}} \times \frac{1 \text{ mol } Ba(OH)_2}{2 \text{ mol HCl}} = 6.10 \times 10^{-4} \text{ mol } Ba(OH)_2$$

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

$$3.90 \times 10^{-4} \text{ mol } CO_2 \times \frac{44.01 \text{ g } CO_2}{\text{mol } CO_2} = 0.01716 \text{ g } CO_2$$

$$\frac{0.01716 \text{ g } CO_2 \times \dfrac{1 \text{ L } CO_2}{1.98 \text{ g } CO_2} \times \dfrac{10^6 \text{ µL}}{\text{L}}}{3.5 \text{ L}} = 2480 \text{ µL/L } CO_2$$

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

$$0.03268 \text{ mL} \times \frac{0.9989 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol } C_4H_8O}{\text{mol NaOH}} \times \frac{72.11 \text{ g } C_4H_8O}{\text{mol } C_4H_8O} = 2.354 \text{ g } C_4H_8O$$

$$\frac{2.354 \text{ g } C_4H_8O \times \dfrac{1 \text{ mL}}{0.805 \text{ g}}}{3.00 \text{ mL sample}} \times 100 = 97.47\%$$

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

$$0.02500 \text{ L} \times \frac{0.5131 \text{ mol KOH}}{\text{L}} = 0.01283 \text{ mol KOH}$$

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.

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.

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.

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.

The change in volume of NaOH in the buret is equivalent to the volume of the air bubble.

(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.

(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

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.

$$n_{Mg} = M_{Mg} V_{Mg} = M_{EDTA} V_{EDTA} = n_{EDTA}$$

where n is the moles of Mg^{2+} or of EDTA; thus

$$V_{eq.pt.} = V_{EDTA} = \frac{M_{Mg} V_{Mg}}{M_{EDTA}} = \frac{(0.100\ M)(50.0\ mL)}{(0.100\ M)} = 50.0\ mL$$

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

$$[Mg^{2+}] = \frac{M_{Mg} V_{Mg} - M_{EDTA} V_{EDTA}}{V_{Mg} + V_{EDTA}}$$

$$[Mg^{2+}] = \frac{(0.100\ M)(50.0\ mL) - (0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL}$$

$$[Mg^{2+}] = 0.0667\ M$$

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

$$[MgY^{2-}] = \frac{M_{Mg} V_{Mg}}{V_{EDTA} + V_{Mg}} = \frac{(0.100\ M)(50.0\ mL)}{60.0\ mL + 50.0\ mL}$$

$$[MgY^{2-}] = 4.55 \times 10^{-2}\ M$$

$$C_{EDTA} = \frac{M_{EDTA} V_{EDTA} - M_{Mg} V_{Mg}}{V_{EDTA} + V_{Mg}}$$

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.

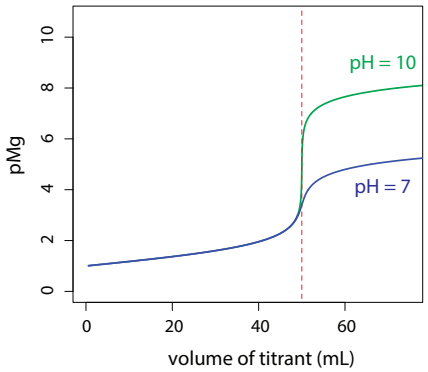

Figure SM9.16 Complexometric titration curves for 50.0 mL of 0.100 M Mg^{2+} using 0.100 M EDTA as the titrant at a pH of 7 (**blue**) and at a pH of 10 (**green**). The volume of titrant at the equivalence point for both titrations is shown by the dashed **red** line.

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

$$[Cu^{2+}] = C_{Cu} \times \alpha_{Cu^{2+}} = (0.0500\ M)(0.00415) = 2.08 \times 10^{-4}\text{ M}$$

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

$$C_{Cu} = \frac{M_{Cu} V_{Cu} - M_{EDTA} V_{EDTA}}{V_{Cu} + V_{EDTA}}$$

$$C_{Cu} = \frac{(0.0500\text{ M})(25.0\text{ mL}) - (0.0250\text{ M})(10.0\text{ mL})}{25.0\text{ mL} + 10.0\text{ mL}}$$

$$C_{Cu} = 2.86 \times 10^{-2}\text{ M}$$

$$[Cu^{2+}] = C_{Cu} \times \alpha_{Cu^{2+}} = (0.0286\ M)(0.00415) = 1.19 \times 10^{-4}\text{ M}$$

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

$$[CuY^{2-}] = \frac{M_{Cu} V_{Cu}}{V_{EDTA} + V_{Cu}} = \frac{(0.0500\ M)(25.0\ mL)}{60.0\ mL + 25.0\ mL}$$

$$[CuY^{2-}] = 1.47 \times 10^{-2}\ M$$

$$C_{EDTA} = \frac{M_{EDTA} V_{EDTA} - M_{Cu} V_{Cu}}{V_{EDTA} + V_{Cu}}$$

$$C_{EDTA} = \frac{(0.0250\ M)(60.0\ mL) - (0.0500\ M)(25.0\ mL)}{60.0\ mL + 25.0\ mL}$$

$$C_{EDTA} = 2.94 \times 10^{-3}\ M$$

For a pH of 10, substituting these concentrations into the conditional formation constant for CuY^{2-} and solving for $[Cu^{2+}]$

$$\frac{[CuY^{2-}]}{C_{Cu} C_{EDTA}} = K_f \alpha_{Cu^{2+}} \alpha_{Y^{4-}} =$$

$$(6.3 \times 10^{18})(0.00415)(0.367) = 9.6 \times 10^{15}$$

$$\frac{1.47 \times 10^{-2}}{C_{Cu}(2.94 \times 10^{-3})} = 9.6 \times 10^{15}$$

$$C_{Cu} = 5.0 \times 10^{-16}\ M$$

$$[Cu^{2+}] = C_{Cu} \times \alpha_{Cu^{2+}} =$$

$$(5.00 \times 10^{-16}\ M)(0.00415) = 2.1 \times 10^{-18}\ M$$

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.

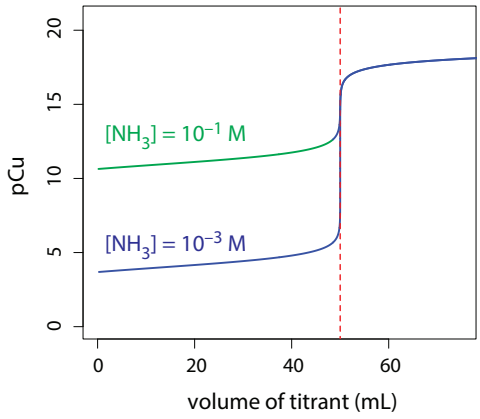

Figure SM9.17 Complexometric titration curves for 25.0 mL of 0.0500 M Cu^{2+} in the presence of 10^{-3} M NH_3 (**blue**) and 10^{-1} M NH_3 (**green**) using 0.0250 M EDTA as the titrant. The pH is 10 for both titration curves. The volume of titrant at the equivalence point for both titrations is shown by the dashed **red** line.

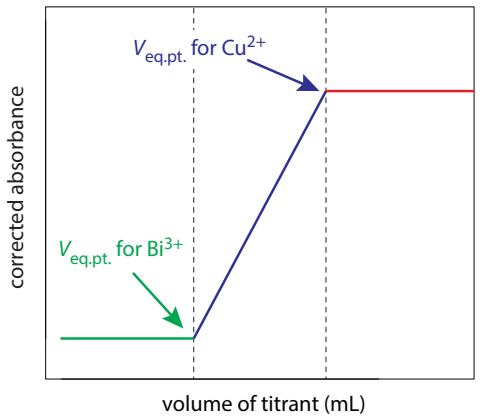

Figure SM9.18 Spectrophotometric titration curve for Problem 9.33. The **green** branch of the titration curve is the reaction between Bi^{3+} and EDTA and the **blue** branch of the titration curve is the reaction between Cu^{2+} and EDTA. Once the titration of Cu^{2+} is complete, the absorbance remains constant, as shown by the titration curve's **red** branch.

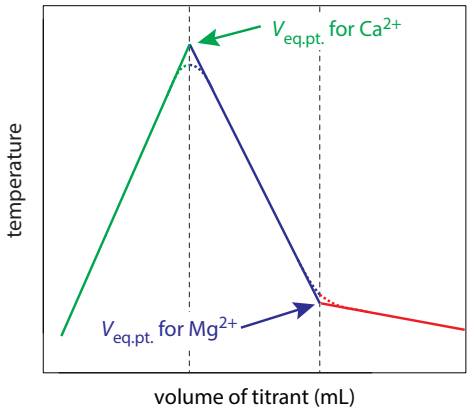

Figure SM9.19 Thermometric titration curve for Problem 9.34. The **green** branch of the titration curve is the titration of Ca^{2+} using EDTA and the **blue** branch of the titration curve is the titration of Mg^{2+} with EDTA. Once the titration of Mg^{2+} is complete, the temperature continues to 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

$$2.68 \times 10^{-4}\ \text{L} \times \frac{0.0119\ \text{mol EDTA}}{\text{L}} \times \frac{1\ \text{mol Ca}}{\text{mol EDTA}} \times \frac{40.08\ \text{g Ca}}{\text{mol Ca}} \times \frac{1000\ \text{mg}}{\text{g}} = 0.128\ \text{mg Ca}$$

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

$$0.04411\ \text{L} \times \frac{0.04988\ \text{mol EDTA}}{\text{L}} \times \frac{1\ \text{mol Ca}}{\text{mol EDTA}} \times \frac{100.09\ \text{g CaCO}_3}{\text{mol Ca}} = 0.2202\ \text{g CaCO}_3$$

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

$$\frac{0.2002\ \text{g CaCO}_3 \times \frac{250.0\ \text{mL}}{10.00\ \text{mL}}}{5.613\ \text{g sample}} \times 100 = 98.08\%\text{w/w CaCO}_3$$

38. The mass of NaCN in the sample as analyzed is

$$0.02736\ \text{L} \times \frac{0.1012\ \text{mol AgNO}_3}{\text{L}} \times \frac{2\ \text{mol NaCN}}{1\ \text{mol AgNO}_3} \times \frac{49.01\ \text{g NaCN}}{\text{mol NaCN}} \times \frac{1000\ \text{mg}}{\text{g}} = 271.4\ \text{mg NaCN}$$

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

$$\frac{271.4\ \text{mg NaCN}}{5.00 \times 10^{-3}\ \text{L sample}} = 5.43 \times 10^{4}\ \text{ppm NaCN}$$

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

$$\frac{1.768 \times 10^{-3}\ \text{mol EDTA} \times \dfrac{1\ \text{mol Al}^{3+}}{\text{mol EDTA}}}{0.05000\ \text{L}} = 0.03536\ \text{M Al}^{3+}$$

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, therefore, 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 concentration 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 $\alpha_{Y^{4-}}$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{\left\{\begin{array}{l}\dfrac{[Y^{4-}][H_3O^+]^6}{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[Y^{4-}][H_3O^+]^5}{K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \\ \qquad \dfrac{[Y^{4-}][H_3O^+]^4}{K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[Y^{4-}][H_3O^+]^3}{K_{a4}K_{a5}K_{a6}} + \\ \qquad \dfrac{[Y^{4-}][H_3O^+]^2}{K_{a5}K_{a6}} + \dfrac{[Y^{4-}][H_3O^+]}{K_{a6}} + [Y^{4-}]\end{array}\right\}}$$

This equation looks imposing, but we can simplify it by factoring $[Y^{4-}]$ out of the denominator and simplifying

$$\alpha_{Y^{4-}} = \frac{1}{\left\{\begin{array}{l}\dfrac{[H_3O^+]^6}{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[H_3O^+]^5}{K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}} + \\ \qquad \dfrac{[H_3O^+]^4}{K_{a3}K_{a4}K_{a5}K_{a6}} + \dfrac{[H_3O^+]^3}{K_{a4}K_{a5}K_{a6}} + \\ \qquad \dfrac{[H_3O^+]^2}{K_{a5}K_{a6}} + \dfrac{[H_3O^+]}{K_{a6}} + 1\end{array}\right\}}$$

and then multiplying through by $K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}$ to arrive at our final equation

$$\alpha_{Y^{4-}} = \frac{K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}}{\left\{\begin{array}{l}[H_3O^+]^6 + K_{a1}[H_3O^+]^5 + K_{a1}K_{a2}[H_3O^+]^4 + \\ \quad K_{a1}K_{a2}K_{a3}[H_3O^+]^3 + K_{a1}K_{a2}K_{a3}K_{a4}[H_3O^+]^2 + \\ \quad\quad K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}[H_3O^+] + K_{a1}K_{a2}K_{a3}K_{a4}K_{a5}K_{a6}\end{array}\right\}}$$

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.

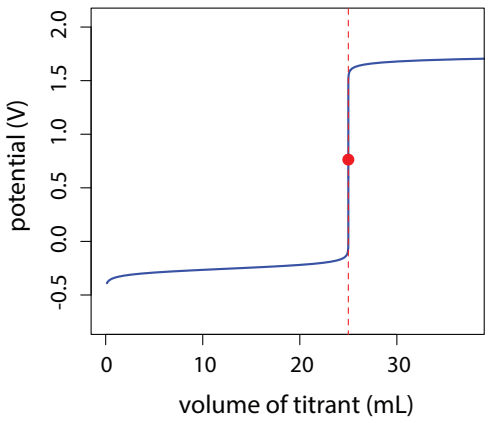

Figure SM9.20 The titration curve for 0.0100 M V^{2+} using 0.0100 M Ce^{3+} as the titrant is shown in **blue**. The **red** dashed lines mark the volume of titrant at the equivalence point and the **red** dot marks the equivalence point (see Problem 44a).

(b) The titration of Sn^{2+} with Ce^{4+} is an example of a redox titration. The titration's equivalence point is reached when

$$n_{Sn} = 2 \times M_{Sn} V_{Sn} = M_{Ce} V_{Ce} = n_{Ce}$$

where n is the moles of Sn^{2+} or of Ce^{4+}; thus

$$V_{eq.pt.} = V_{Ce} = \frac{2 \times M_{Sn} V_{Sn}}{M_{Ce}} = \frac{(2)(0.0100\ M)(25.0\ mL)}{(0.0100\ M)} = 50.0\ mL$$

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

$$[Sn^{2+}] = \frac{M_{Sn} V_{Sn} - 0.5 \times M_{Ce} V_{Ce}}{V_{Sn} + V_{Ce}}$$

$$[Sn^{2+}] = \frac{(0.0100\ M)(25.0\ mL) - (0.5)(0.0100\ M)(10.0\ mL)}{25.0\ mL + 10.0\ mL}$$

$$[Sn^{2+}] = 5.71 \times 10^{-3}\ M$$

$$[Sn^{4+}] = \frac{0.5 \times M_{Ce} V_{Ce}}{V_{Sn} + V_{Ce}} = \frac{(0.5)(0.0100\ M)(10.0\ mL)}{25.0\ mL + 10.0\ mL} = 1.43 \times 10^{-3}\ M$$

which gives us a potential of

$$E = 0.154 - \frac{0.05916}{2} \log \frac{5.71 \times 10^{-3}}{1.43 \times 10^{-3}} = 0.136\ V$$

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

$$[Ce^{4+}] = \frac{M_{Ce} V_{Ce} - 2 \times M_{Sn} V_{Sn}}{V_{Ce} + V_{Sn}}$$

$$[Ce^{4+}] = \frac{(0.0100\ M)(60.0\ mL) - (2)(0.0100\ M)(25.0\ mL)}{60.0\ mL + 25.0\ mL}$$

$$[Ce^{4+}] = 1.18 \times 10^{-3}\ M$$

$$[Ce^{3+}] = \frac{2 \times M_{Sn} V_{Sn}}{V_{Sn} + V_{Ce}} = \frac{(2)(0.0100\ M)(25.0\ mL)}{25.0\ mL + 60.0\ mL} = 5.88 \times 10^{-3}\ M$$

which gives us a potential of

$$E = +1.72 - 0.05916 \log \frac{5.88 \times 10^{-3}}{1.18 \times 10^{-3}} = +1.68\ V$$

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

$$V_{eq.pt.} = V_{Mn} = \frac{M_{Fe} V_{Fe}}{5 \times M_{Mn}} = \frac{(0.0100\ M)(25.0\ mL)}{(5)(0.0100\ M)} = 5.00\ mL$$

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

$$[Fe^{2+}] = \frac{M_{Fe} V_{Fe} - 5 \times M_{Mn} V_{Mn}}{V_{Fe} + V_{Mn}}$$

$$[Fe^{2+}] = \frac{(0.0100\ M)(25.0\ mL) - (5)(0.0100\ M)(3.00\ mL)}{25.0\ mL + 3.00\ mL}$$

$$[Fe^{2+}] = 3.57 \times 10^{-3}\ M$$

$$[Fe^{3+}] = \frac{5 \times M_{Mn} V_{Mn}}{V_{Fe} + V_{Mn}} = \frac{(5)(0.0100\ M)(3.00\ mL)}{25.0\ mL + 3.00\ mL} = 5.36 \times 10^{-3}\ M$$

which gives us a potential of

$$E = 0.771 - 0.05916 \log \frac{3.57 \times 10^{-3}}{5.36 \times 10^{-3}} = 0.781\ V$$

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.

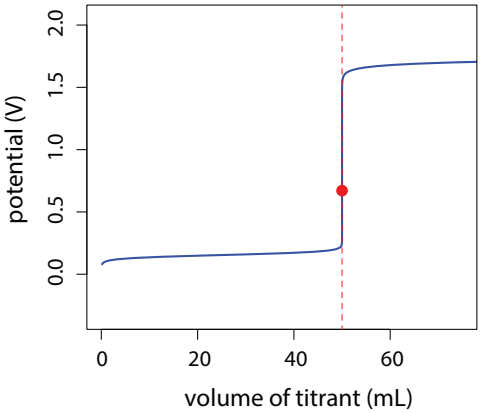

Figure SM9.21 The titration curve for 0.0100 M Sn^{2+} using 0.0100 M Ce^{3+} as the titrant is shown in **blue**. The **red** dashed lines mark the volume of titrant at the equivalence point and the **red** dot marks the equivalence point (see Problem 44b).

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.

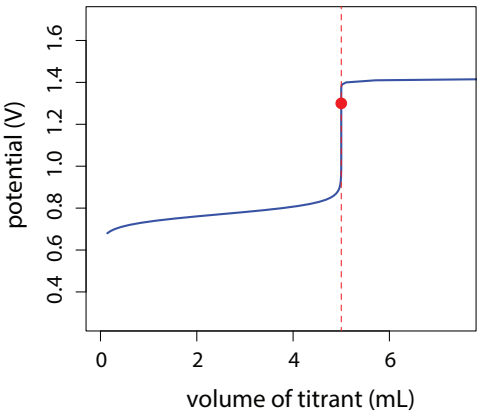

Figure SM9.22 The titration curve for 0.0100 M Fe^{2+} using 0.0100 M MnO_4^- as the titrant is shown in **blue**. The **red** dashed lines mark the volume of titrant at the equivalence point and the **red** dot marks the equivalence point (see Problem 44c).

$$E = E^\circ_{MnO_4^-/Mn^{2+}} - \frac{0.05916}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$E = +1.51 - \frac{0.05916}{5}\log\frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

For example, after adding 7.00 mL of titrant, the concentrations of MnO_4^- and of Mn^{2+} are

$$[MnO_4^-] = \frac{5 \times M_{Mn} V_{Mn} - M_{Fe} V_{Fe}}{V_{Mn} + V_{Fe}}$$

$$[MnO_4^-] = \frac{(5)(0.0100\text{ M})(7.00\text{ mL}) - (0.0100\text{ M})(25.0\text{ mL})}{7.00\text{ mL} + 25.0\text{ mL}}$$

$$[MnO_4^-] = 3.12 \times 10^{-3}\text{ M}$$

$$[Mn^{2+}] = \frac{0.2 \times M_{Fe} V_{Fe}}{V_{Fe} + V_{Mn}} = \frac{(0.2)(0.0100\text{ M})(25.0\text{ mL})}{25.0\text{ mL} + 7.00\text{ mL}} = 1.56 \times 10^{-3}\text{ M}$$

which gives us a potential of

$$E = +1.51 - \frac{0.05916}{5}\log\frac{1.56 \times 10^{-3}}{(3.12 \times 10^{-3})(0.1)^8} = +1.42\text{ V}$$

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

$$E_{eq.pt.} = \frac{E^\circ_{V^{3+}/V^{2+}} + E^\circ_{Ce^{4+}/Ce^{3+}}}{2} = \frac{-0.255\text{ V} + 1.72\text{V}}{2} = 0.73\text{ V}$$

(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

$$E_{eq.pt.} = \frac{2E^\circ_{Sn^{4+}/Sn^{2+}} + E^\circ_{Ce^{4+}/Ce^{3+}}}{3} = \frac{(2)(0.154\text{ V}) + 1.72\text{V}}{3} = 0.68\text{ V}$$

(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

$$E_{eq.pt.} = \frac{E^\circ_{Fe^{3+}/Fe^{2+}} + 5E^\circ_{MnO_4^-/Mn^{2+}}}{6} - 0.07888\text{pH} = \frac{0.771\text{ V} + (5)(1.51\text{V})}{6} = 1.31\text{ V}$$

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

$$0.04127\ \text{L} \times \frac{0.02500\ \text{mol}\ MnO_4^-}{\text{L}} \times \frac{5\ \text{mol}\ Fe^{2+}}{\text{mol}\ MnO_4^-} = 5.159 \times 10^{-3}\ \text{mol}\ Fe^{2+}$$

in the sample as analyzed. The concentration of Fe_2O_3 in the original sample is

$$5.159 \times 10^{-3}\ \text{mol}\ Fe^{2+} \times \frac{1\ \text{mol}\ Fe_2O_3}{2\ \text{mol}\ Fe^{2+}} \times \frac{159.69\ \text{g}\ Fe_2O_3}{\text{mol}\ Fe_2O_3} = 0.4119\ \text{g}\ Fe_2O_3$$

$$\frac{0.4119\ \text{g}\ Fe_2O_3}{0.4185\ \text{g sample}} \times 100 = 98.42\%\text{w/w}\ Fe_2O_3$$

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

$$0.03488\ \text{L} \times \frac{0.03358\ \text{mol}\ MnO_4^-}{\text{L}} \times \frac{3\ \text{mol}\ Mn^{2+}}{2\ \text{mol}\ MnO_4^-} \times \frac{54.938\ \text{g}\ Mn^{2+}}{\text{mol}\ Mn^{2+}} = 0.09652\ \text{g}\ Mn^{2+}$$

in the sample as analyzed. The concentration of Mn^{2+} in the original sample is

$$\frac{0.09652\ \text{g}\ Mn^{2+}}{0.5165\ \text{g sample}} \times 100 = 18.69\%\text{w/w}\ Mn^{2+}$$

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

$$0.01052\ \text{L} \times \frac{0.00987\ \text{mol}\ K_2Cr_2O_7}{\text{L}} \times \frac{6\ \text{mol}\ Fe^{2+}}{\text{mol}\ K_2Cr_2O_7} = 6.23 \times 10^{-4}\ \text{mol}\ Fe^{2+}$$

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

$$\frac{3.12 \times 10^{-4}\ \text{mol}\ U^{4+} \times \frac{238.08\ \text{g}\ U^{4+}}{\text{mol}\ U^{4+}}}{0.315\ \text{g sample}} \times 100 = 23.6\%\text{w/w}\ U^{4+}$$

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

$$0.500\ \text{g}\ Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O \times \frac{1\ \text{mol}\ Fe^{2+}}{392.12\ \text{g}\ Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O} = 1.28 \times 10^{-3}\ \text{mol}\ Fe^{2+}$$

Of this iron, the moles that react with the titrant, $K_2Cr_2O_7$ are

$$0.01829\ \text{L} \times \frac{0.00389\ \text{mol}\ K_2Cr_2O_7}{\text{L}} \times \frac{6\ \text{mol}\ Fe^{2+}}{\text{mol}\ K_2Cr_2O_7} = 4.27 \times 10^{-4}\ \text{mol}\ Fe^{2+}$$

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

$$8.53 \times 10^{-4}\ \text{mol}\ Fe^{2+} \times \frac{1\ \text{mol}\ Cr_2O_7^{2-}}{6\ \text{mol}\ Fe^{2+}} \times \frac{2\ \text{mol Cr}}{\text{mol}\ Cr_2O_7^{2-}} \times \frac{51.996\ \text{g Cr}}{\text{mol Cr}} = 0.0149\ \text{g Cr}$$

and the thickness of chromium is

$$\text{thickness} = \frac{\text{volume}}{\text{area}} = \frac{0.0149\ \text{g} \times \frac{1\ \text{mL}}{7.20\ \text{g}} \times \frac{1\ \text{cm}^3}{\text{mL}}}{30.0\ \text{cm}^2} = 6.90 \times 10^{-5}\ \text{cm}$$

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

$$0.00717 \text{ L } S_2O_3^- \times \frac{0.00329 \text{ mol } S_2O_3^{2-}}{\text{L}} = 2.36 \times 10^{-5} \text{ mol } S_2O_3^{2-}$$

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

$$4.79 \text{ L} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1.23 \times 10^{-3} \text{ g}}{\text{mL}} = 5.89 \text{ g}$$

which makes the concentration of CO in the air

$$\frac{1.65 \times 10^{-3} \text{ g CO} \times \dfrac{10^6 \text{ µg}}{\text{g}}}{5.89 \text{ g air}} = 2.80 \times 10^2 \text{ ppm CO}$$

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

$$0.00890 \text{ L } S_2O_3^- \times \frac{0.00870 \text{ mol } S_2O_3^{2-}}{\text{L}} = 7.74 \times 10^{-5} \text{ mol } S_2O_3^{2-}$$

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

$$\frac{6.21 \times 10^{-4}\ \text{g } O_2 \times \dfrac{10^6\ \mu\text{g}}{\text{g}}}{100.0\ \text{mL}} = 6.21\ \text{ppm } O_2$$

55. The titration of KI with $AgNO_3$ is an example of a precipitation titration. The titration's equivalence point is reached when

For the titration curves in this problem and in the next problem, we will calculate pAnalyte or pTitrant for one volume before each equivalence point and for one volume after the final equivalence point.

$$n_I = M_I V_I = M_{Ag} V_{Ag} = n_{Ag}$$

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

$$[Ag^+] = \frac{M_{Ag} V_{Ag} - M_I V_I}{V_{Ag} + V_I}$$

$$[Ag^+] = \frac{(0.0500\ \text{M})(35.0\ \text{mL}) - (0.0250\ \text{M})(50.0\ \text{ml})}{35.0\ \text{mL} + 50.0\ \text{mL}}$$

$$[Ag^+] = 5.88 \times 10^{-3}\ \text{M}$$

$$[I^-] = \frac{K_{sp,AgI}}{[Ag^+]} = \frac{8.32 \times 10^{-17}}{5.88 \times 10^{-3}} = 1.41 \times 10^{-14}\ \text{M}$$

To sketch an approximate titration curve, calculate any two points before the equivalence point and any two points after equivalence point. Use the lines passing through each pair of points and the vertical line at the equivalence point volume to sketch the titration curve.

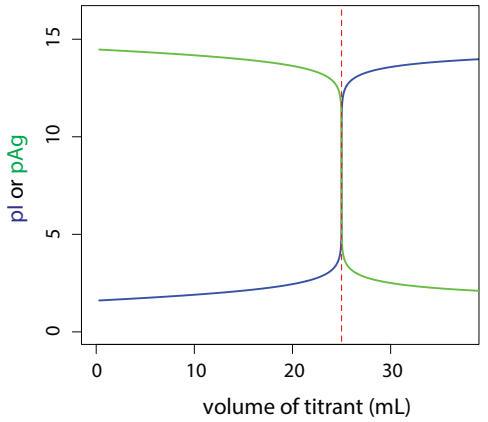

Figure SM9.23 The titration curve for 0.0250 M KI using 0.0500 M $AgNO_3$ as the titrant. The titration curve shown in **blue** is recorded by following the concentration of I^- and the titration curve shown in green is recorded by following the concentration of Ag^+. The **red** dashed line marks the 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

$$V_{eq.pt.1} = V_{Ag} = \frac{M_I V_I}{M_{Ag}} = \frac{(0.0500\ M)(25.0\ mL)}{(0.0500\ M)} = 25.0\ mL$$

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

$$[I^-] = \frac{M_I V_I - M_{Ag} V_{Ag}}{V_I + V_{Ag}}$$

$$[I^-] = \frac{(0.0500\ M)(25.0\ mL) - (0.0500\ M)(10.0\ ml)}{25.0\ mL + 10.0\ mL}$$

$$[I^-] = 0.0214\ M$$

$$[Ag^+] = \frac{K_{sp,AgI}}{[I^-]} = \frac{8.32 \times 10^{-17}}{0.0214} = 3.89 \times 10^{-15}\ M$$

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

$$V_{eq.pt.2} = V_{Ag} = \frac{M_I V_I + M_{SCN} V_{SCN}}{M_{Ag}} =$$

$$\frac{(0.0500\ M)(25.0\ mL) + (0.0500\ M)(25.0\ mL)}{(0.0500\ M)} = 50.0\ mL$$

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

$$[SCN^-] = \frac{M_{SCN} V_{SCN} - M_{Ag}(V_{Ag} - 25.0\ ml)}{V_{SCN} + V_{Ag}}$$

$$[SCN^-] = \frac{(0.0500\ M)(25.0\ mL) - (0.0500\ M)(35.0 - 25.0\ ml)}{25.0\ mL + 35.0\ mL}$$

$$[SCN^-] = 0.0125\ M$$

$$[Ag^+] = \frac{K_{sp,AgSCN}}{[I^-]} = \frac{1.1 \times 10^{-12}}{0.0125} = 8.8 \times 10^{-11}\ M$$

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

$$[Ag^+] = \frac{M_{Ag}V_{Ag} - M_I V_I - M_{SCN}V_{SCN}}{V_{Ag} + V_I}$$

$$[Ag^+] = \frac{\left\{\begin{array}{c}(0.0500\text{ M})(60.0\text{ mL}) - (0.0500\text{ M})(25.0\text{ ml}) \\ -(0.0500\text{ M})(25.0\text{ ml})\end{array}\right\}}{60.0\text{ mL} + 25.0\text{ mL}}$$

$$[Ag^+] = 5.88 \times 10^{-3}\text{ M}$$

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.

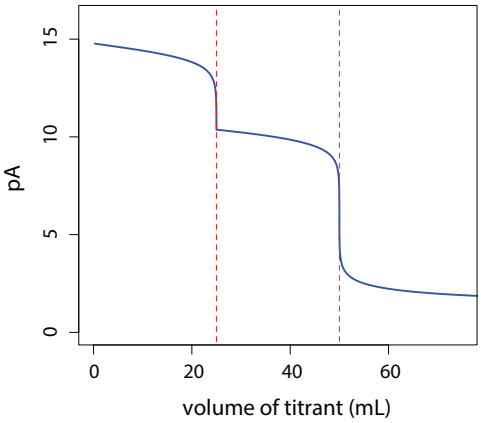

Figure SM9.24 The titration curve for the titration of a mixture of 0.0500 M KI and 0.0500 M KSCN using 0.0500 M $AgNO_3$ as the titrant. The titration curve shown in **blue** is recorded by following the concentration of Ag^+. The **red** dashed lines mark the volume of titrant at the equivalence points.

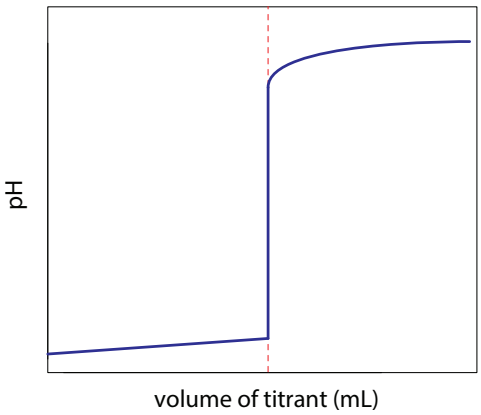

Figure SM9.25 The titration curve for Pb^{2+} using $KCrO_4$ as the titrant. The titration curve shown in **blue** is recorded by following the solution's pH. The **red** dashed line marks the volume of titrant at the equivalence point.

$$0.02448\ \text{L} \times \frac{0.04614\ \text{mol AgNO}_3}{\text{L}} \times \frac{1\ \text{mol KBr}}{\text{mol AgNO}_3} \times \frac{119.00\ \text{g KBr}}{\text{mol KBr}} = 0.1344\ \text{g KBr}$$

$$\frac{0.1344\ \text{g KBr}}{0.5131\ \text{g sample}} \times 100 = 26.19\%\text{w/w KBr}$$

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 $3.456\times10^{-3} - 1.582\times10^{-3} = 1.874\times10^{-3}$ 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

$$\frac{0.03095\ \text{g BaCl}_2}{0.1036\ \text{g sample}} \times 100 = 29.97\%\text{w/w BaCl}_2$$