Chapter 14 Review Questions and Text Homework Solutions

Review Questions

1. A common ion is an ion that appears in an equilibrium reaction but came from a source other than that reaction. Addition of a common ion (H^+ or NO_2^-) to the reaction $HNO_2 \rightleftharpoons H^+ + NO_2^-$ will drive the equilibrium to the left as predicted by LeChâtelier's principle. When a weak acid solution has some of the conjugate base added from an outside source, this solution is called a buffer. Similarly, a weak base solution with its conjugate acid added from an outside source would also be classified as a buffer.

2. A buffer solution is one that resists a change in its pH when either hydroxide ions or protons (H^+) are added. Any solution that contains a weak acid and its conjugate base or a weak base and its conjugate acid is classified as a buffer. The pH of a buffer depends on the [base]/[acid] ratio. When H^+ is added to a buffer, the weak base component of the buffer reacts with the H^+ and forms the acid component of the buffer. Even though the concentrations of the acid and base component of the buffer change some, the ratio of [base]/[acid] does not change that much. This translates into a pH that doesn't change much. When OH^- is added to a buffer, the weak acid component is converted into the base component of the buffer. Again, the [base]/[acid] ratio does not change a lot (unless a large quantity of OH^- is added), so the pH does not change much.
   The concentrations of weak acid and weak base do not have to be equal in a buffer. As long as there are both a weak acid and a weak base present, the solution will be buffered. If the concentrations are the same, the buffer will have the same capacity towards added H^+ and added OH^-. Also, buffers with equal concentrations of weak acid and conjugate base have $pH = pK_a$.

   Because both the weak acid and conjugate base are major species present, both equilibriums that refer to these species must hold true. That is, the K_a equilibrium must hold because the weak acid is present, and the K_b equilibrium for the conjugate base must hold true because the conjugate base is a major species. Both the K_a and K_b equilibrium have the acid and conjugate base concentrations in their expressions. The same equilibrium concentrations of the acid and conjugate base must satisfy both equilibriums. In addition, the $[H^+]$ and $[OH^-]$ concentrations must be related through the K_w constant. This leads to the same pH answer whether the K_a or K_b equilibrium is used.
   The third method to solve a buffer problem is to use the Henderson-Hasselbalch equation. The equation is:

   $$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

   where the base is the conjugate base of the weak acid present or the acid is the conjugate acid of the weak base present. The equation takes into account the normal assumptions made for buffers. Specifically, it is assumed that the initial concentration of the acid and base component of the buffer equal the equilibrium concentrations. For any decent buffer, this will always hold true.

3. Whenever strong acid is added to a solution, always react the H^+ from the strong acid with the best base present in solution. The best base has the largest K_b value. For a buffer, this will be the conjugate base (A^-) of the acid component of the buffer. The H^+ reacts with the conjugate base, A^-, to produce the acid, HA. The assumption for this reaction is that because strong acids are great at what they do, they are assumed to donate the proton to the conjugate base 100% of the time. That is, the reaction is assumed to go to completion. Completion is when a reaction goes until one or both of the reactants runs out. This reaction is assumed to be a stoichiometry problem like those we solved in Chapter 5 of the text.

   Whenever a strong base is added to a buffer, the OH^- ions react with the best acid present. This reaction is also assumed to go to completion. In a buffer, the best acid present is the acid component of the buffer (HA). The OH^- rips a proton away from the acid to produce the conjugate base of the acid (A^-) and H_2O. Again, we know strong bases are great at accepting protons, so we assume this reaction goes to completion. It is assumed to be a stoichiometry problem like the ones we solved in Chapter 5. **Note**: For BH^+/B type buffers (buffers composed of a weak base B and its conjugate acid BH^+), added OH^- reacts to completion with BH^+ to produce B and H_2O, while added H^+ reacts to completion with B to produce BH^+. An example of a BH^+/B type buffer is NH_4^+/NH_3.

4. When $[HA] = [A^-]$ (or $[BH^+] = [B]$) for a buffer, the pH of the solution is equal to the pK_a value for the acid component of the buffer ($pH = pK_a$ because $[H^+] = K_a$). A best buffer has equal concentrations of the acid and base component so it can be equally efficient at absorbing added H^+ or OH^-. For a pH = 4.00 buffer, we would choose the acid component having a K_a close to $10^{-4.00} = 1.0 \times 10^{-4}$ ($pH = pK_a$ for a best buffer). For a pH = 10.00 buffer, we would want the acid component of the buffer to have a K_a close to $10^{-10.00} = 1.0 \times 10^{-10}$. Of course, we can have a buffer solution made from a weak base (B) and its conjugate acid (BH^+). For a pH = 10.00 buffer, our conjugate acid should have $K_a \approx 1.0 \times 10^{-10}$ which translates into a K_b value of the base close to 1.0×10^{-4} ($K_b = K_w/K_a$ for conjugate acid-base pairs).

   The capacity of a buffer is a measure of how much strong acid or strong base the buffer can neutralize. All the buffers listed have the same pH ($= pK_a = 4.74$) because they all have a 1:1 concentration ratio between the weak acid and the conjugate base. The 1.0 *M* buffer has the greatest capacity; the 0.01 *M* buffer the least capacity. In general, the larger the concentrations of weak acid and conjugate base, the greater the buffer capacity, i.e., the larger quantity of strong acid or strong base that can be neutralized with little pH change.

5. Let's review the strong acid-strong base titration using the example (case study) covered in section 14.4 of the text. The example used was the titration of 50.0 mL of 0.200 *M* HNO_3 titrated by 0.100 *M* NaOH. See Figure 14.1 for the titration curve. The important points are:

   a. Initially, before any strong base has been added. Major species: H^+, NO_3^-, and H_2O. To determine the pH, determine the $[H^+]$ in solution after the strong acid has completely dissociated as we always do for strong acid problems.

b. After some strong base has been added, up to the equivalence point. For our example, this is from just after 0.00 mL NaOH added up to just before 100.0 mL NaOH added. Major species before any reaction: H^+, NO_3^-, Na^+, OH^-, and H_2O. Na^+ and NO_3^- have no acidic or basic properties. In this region, the OH^- from the strong base reacts with some of the H^+ from the strong acid to produce water ($H^+ + OH^- \rightarrow H_2O$). As is always the case when something strong reacts, we assume the reaction goes to completion. Major species after reaction: H^+, NO_3^-, Na^+, and H_2O: To determine the pH of the solution, we first determine how much of the H^+ is neutralized by the OH^-. Then we determine the excess $[H^+]$ and take the –log of this quantity to determine pH. From 0.1 mL to 99.9 mL NaOH added, the excess H^+ from the strong acid determines the pH.

c. The equivalence point (100.0 mL NaOH added). Major species before reaction: H^+, NO_3^-, Na^+, OH^-, and H_2O. Here, we have added just enough OH^- to neutralize all of the H^+ from the strong acid (moles OH^- added = moles H^+ present). After the stoichiometry reaction ($H^+ + OH^- \rightarrow H_2O$), both H^+ and OH^- have run out (this is the definition of the equivalence point). Major species after reaction: Na^+, NO_3^-, and H_2O. All we have in solution are some ions with no acidic or basic properties (NO_3^- and Na^+ in H_2O). The pH = 7.00 at the equivalence point of a strong acid by a strong base.

d. Past the equivalence point (volume of NaOH added > 100.0 mL). Major species before reaction H^+, NO_3^-, Na^+, OH^-, and H_2O. After the stoichiometry reaction goes to completion ($H^+ + OH^- \rightarrow H_2O$), we have excess OH^- present. Major species after reaction: OH^-, Na^+, NO_3^-, and H_2O. We determine the excess $[OH^-]$ and convert this into the pH. After the equivalence point, the excess OH^- from the strong base determines the pH.

6. See Figure 14.2 of the text for a titration curve of a strong base by a strong acid. The stoichiometry problem is still the same, $H^+ + OH^- \rightarrow H_2O$, but what is in excess after this reaction goes to completion is reverse of the strong acid-strong base titration. The pH up to just before the equivalence point is determined by the excess OH^- present. At the equivalence point, pH = 7.00 because we have added just enough H^+ from the strong acid to react with all of the OH^- from the strong base (mole base present = mole acid added). Past the equivalence point, the pH is determined by the excess H^+ present. As can be seen from Figures 14.1 and 14.2, both strong by strong titrations have pH = 7.00 at the equivalence point, but the curves are the reverse of each other before and after the equivalence point.

7. In Section 14.4 of the text, the case study for the weak acid-strong base titration is the titration of 50.0 mL of 0.10 *M* $HC_2H_3O_2$ by 0.10 *M* NaOH. See Figure 14.3 for the titration curve.

As soon as some NaOH has been added to the weak acid, OH^- reacts with the best acid present. This is the weak acid titrated ($HC_2H_3O_2$ in our problem). The reaction is: $OH^- + HC_2H_3O_2 \rightarrow H_2O + C_2H_3O_2^-$. Because something strong is reacting, we assume the reaction goes to completion. This is the stoichiometry part of a titration problem. To solve for the pH, we see what is in solution after the stoichiometry problem and decide how to proceed. The various parts to the titration are:

a. Initially, before any OH^- has been added. The major species present is the weak acid, $HC_2H_3O_2$, and water. We would use the K_a reaction for the weak acid and solve the equilibrium problem to determine the pH.

b. Just past the start of the titration up to just before the equivalence point (0.1 mL to 49.9 mL NaOH added). In this region, the major species present after the OH^- reacts to completion are $HC_2H_3O_2$, $C_2H_3O_2^-$, Na^+, and water. We have a buffer solution because both a weak acid and a conjugate base are present. We can solve the equilibrium buffer problem using the K_a reaction for $HC_2H_3O_2$, the K_b reaction for $C_2H_3O_2^-$, or the Henderson-Hasselbalch equation. A special point in the buffer region is the halfway point to equivalence. At this point (25.0 mL of NaOH added), exactly one-half of the weak acid has been converted into its conjugate base. At this point, we have [weak acid] = [conjugate base] so that $pH = pK_a$. For the $HC_2H_3O_2$ titration, the pH at 25.0 mL NaOH added is $-\log(1.8 \times 10^{-5}) = 4.74$; in this titration the pH is acidic at the halfway point to equivalence. However, other weak acid-strong base titrations could have basic pH values at the halfway point. This just indicates that the weak acid has $K_a < 1 \times 10^{-7}$, which is fine.

c. The equivalence point (50.0 mL NaOH added). Here we have added just enough OH^- to convert all of the weak acid into its conjugate base. In our example, the major species present are $C_2H_3O_2^-$, Na^+, and H_2O. Because the conjugate base of a weak acid is a weak base, we will have a basic pH ($pH > 7.0$) at the equivalence point. To calculate the pH, we write out the K_b reaction for the conjugate base and then set-up and solve the equilibrium problem. For our example, we would write out the K_b reaction for $C_2H_3O_2^-$.

d. Past the equivalence point ($V > 50.0$ mL). Here we added an excess of OH^-. After the stoichiometry part of the problem, the major species are OH^-, $C_2H_3O_2^-$, H_2O, and Na^+. We have two bases present, the excess OH^- and the weak conjugate base. The excess OH^- dominates the solution and thus determines the pH. We can ignore the OH^- contribution from the weak conjugate base.

See the titration curve before Figure 14.3 that compares and contrasts strong acid-strong base titrations to weak acid-strong base titration. The two curves have the same pH only after the equivalence point where the excess strong base added determines the pH. The strong acid titration is acidic at every point before the equivalence point, has a pH = 7.0 at the equivalence point, and is basic at every point after the equivalence point. The weak acid titration is much more complicated because we cannot ignore the basic properties of the conjugate base of the weak acid; we could ignore the conjugate base in the strong acid titration because it had no basic properties. In the weak acid titration, we start off acidic ($pH < 7.0$), but where it goes from here depends on the strength of the weak acid titrated. At the halfway point where $pH = pK_a$, the pH may be acidic or basic depending on the K_a value of the weak acid. At the equivalence, the pH must be basic. This is due to the presence of the weak conjugate base. Past the equivalence point, the strong acid and weak acid titrations both have their pH determined by the excess OH^- added.

8. The case study of a weak base-strong acid titration in Section 14.4 of the text is the titration of 100.0 mL of 0.050 *M* NH_3 by 0.10 M HCl. The titration curve is in Figure 14.5.
   As HCl is added, the H^+ from the strong acid reacts with the best base present, NH_3. Because something strong is reacted, we assume the reaction goes to completion. The reaction used for the stoichiometry part of the problem is: $H^+ + NH_3 \rightarrow NH_4^+$. Note that the effect of this reaction is to convert the weak base into its conjugate acid. The various parts to a weak base-strong acid titration are:

   a. Initially before any strong acid is added. We have a weak base in water. Write out the K_b reaction for the weak base, set-up the ICE table, and then solve.

   b. From 0.1 mL HCl added to just before the equivalence point (49.9 mL HCl added). The major species present in this region are NH_3, NH_4^+, Cl^-, and water. We have a weak base and its conjugate acid present at the same time; we have a buffer. Solve the buffer problem using the K_a reaction for NH_4^+, the K_b reaction for NH_3, or the Henderson-Hasselbalch equation. The special point in the buffer region of the titration is the halfway point to equivalence. Here, $[NH_3] = [NH_4^+]$, so $pH = pK_a = -\log(5.6 \times 10^{-10}) = 9.25$. For this titration, the pH is basic at the halfway point. However, if the K_a for the weak acid component of the buffer has a $K_a > 1 \times 10^{-7}$ (K_b for the base $< 1 \times 10^{-7}$), then the pH will be acidic at the halfway point. This is fine. In this review question, it is asked what is the K_b value for the weak base where the halfway point to equivalence has $pH = 6.0$ (which is acidic). Because $pH = pK_a$ at this point, $pK_a = 6.0$, so $pK_b = 14.00 - 6.0 = 8.0$; $K_b = 10^{-8.0} = 1.0 \times 10^{-8}$.

   c. The equivalence point (50.0 mL HCl added). Here, just enough H^+ has been added to convert all of the NH_3 into NH_4^+. The major species present are NH_4^+, Cl^- and H_2O. The only important species present is NH_4^+, a weak acid. This is always the case in a weak base-strong acid titration. Because a weak acid is always present at the equivalence point, the pH is always acidic ($pH < 7.0$). To solve for the pH, write down the K_a reaction for the conjugate acid and then determine K_a ($= K_w/K_b$). Fill in the ICE table for the problem, and then solve to determine pH.

   d. Past the equivalence point ($V > 50.0$ mL HCl added). The excess strong acid added determines the pH. The major species present for our example would be H^+ (excess),

NH_4^+, Cl^-, and H_2O. We have two acids present, but NH_4^+ is a weak acid. Its H^+ contribution will be negligible compared to the excess H^+ added from the strong acid. The pH is determined by the molarity of the excess H^+.

Examine Figures 14.2 and 14.5 to compare and contrast a strong base-strong acid titration with a weak base-strong acid titration. The points in common are only after the equivalence point has been reached where excess strong acid determines the pH. Leading up to and including the equivalence point, the two titrations are very different. This is because the conjugate acid of a weak base is a weak acid, whereas, when a strong base dissolves in water, only OH^- is important; the cation in the strong base is garbage (has no acidic/basic properties). There is no conjugate acid to worry about when a strong base is titrated. This is not the case when a weak base is titrated.

For a strong base-strong acid titration, the excess OH^- from the strong base determines the pH from the initial point all the way up to the equivalence point. At the equivalence point, the added H^+ has reacted with all the OH^- and pH = 7.0. For a weak base-strong acid, we initially have a weak base problem to solve in order to calculate the pH. After H^+ has been added, some of the weak base is converted into its conjugate acid and we have buffer solutions to solve in order to calculate the pH. At the equivalence point, we have a weak acid problem to solve. Here, all of the weak base has been converted into its conjugate acid by the added H^+.

Text Homework

10. $\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$; when [acid] > [base], then $\frac{[\text{base}]}{[\text{acid}]} < 1$ and $\log\left(\frac{[\text{base}]}{[\text{acid}]}\right) < 0$.

From the Henderson-Hasselbalch equation, if the log term is negative, then pH < $\text{p}K_a$. When one has more acid than base in a buffer, the pH will be on the acidic side of the $\text{p}K_a$ value; that is, the pH is at a value lower than the $\text{p}K_a$ value. When one has more base than acid in a buffer ([conjugate base] > [weak acid]), then the log term in the Henderson-Hasselbalch equation is positive, resulting in pH > $\text{p}K_a$. When one has more base than acid in a buffer, the pH is on the basic side of the $\text{p}K_a$ value; that is, the pH is at a value greater than the $\text{p}K_a$ value. The other scenario you can run across in a buffer is when [acid] = [base]. Here, the log term is equal to zero, and pH = $\text{p}K_a$.

11. The more weak acid and conjugate base present, the more H^+ and/or OH^- that can be absorbed by the buffer without significant pH change. When the concentrations of weak acid and conjugate base are equal (so that pH = $\text{p}K_a$), the buffer system is equally efficient at absorbing either H^+ or OH^-. If the buffer is overloaded with weak acid or with conjugate base, then the buffer is not equally efficient at absorbing either H^+ or OH^-.

12. a. The red plot is the pH curve for the strong acid and the blue plot is the pH curve for the weak acid. The pH at the equivalence point is 7.00 for the strong acid-strong base titration, while the pH is greater than 7.00 if a weak acid is titrated. Another point one could look at is the initial point. Because both acids have the same concentration, the strong acid curve will be at the lowest initial pH. Actually, any point at any volume up to the equivalence point for the strong acid plot will have a lower pH than the weak acid plot (assuming equal concentrations

and volumes). Another difference would be the pH at the halfway point to equivalence. For the weak acid titration, the pH of solution equals the pK_a value for the weak acid at the halfway point to equivalence; this is not the case when a strong acid is titrated.

b. A buffer is a solution that resists pH change. From this definition, both titrations have regions where the pH doesn't change much on addition of strong base, so both could be labeled to have buffer regions. However, we don't normally include strong acids as a component of buffer solutions. Strong acids certainly can absorb added OH^- by reacting with it to form water. But when more strong acid is added, the H^+ concentration increases steadily; there is nothing present in a strong acid solution to react with added H^+.

This is not the case in the weak acid-strong base titration. After some OH^- has been added, some weak acid is converted into its conjugate base. We now have a typical buffer solution because there are significant amounts of weak acid and conjugate base present at the same time. The buffer region extends from a little past the initial point in the titration up to just a little before the equivalence point. This entire region is a buffer region because both the weak acid and conjugate base are present in significant quantities in this region.

c. True; $HA + OH^- \rightarrow A^- + H_2O$; both reactions have the same neutralization reaction. In both cases, the equivalence point is reached when enough OH^- has been added to exactly react with the acid present initially. Because all acid concentrations and volumes are the same, we have equal moles of each acid which requires the same moles of OH^- to reach the equivalence point. Therefore, each acid requires the same volume of 0.10 *M* NaOH to reach the equivalence point.

d. False; the pH for the strong acid-strong base titration will be 7.00 at the equivalence point. The pH for the weak acid-strong base titration will be greater than 7.00 at the equivalence point. In both titrations, the major species present at the equivalence points are Na^+, H_2O, and the conjugate base of the acid titrated. Because the conjugate base of a strong acid has no basic characteristics, pH = 7.00 at the equivalence point. However, the conjugate base of a weak acid is a weak base. A weak base is present at the equivalence point of a weak acid-strong base titration, so the pH is basic (pH > 7.0).

13. a. Let's call the acid HA, which is a weak acid. When HA is present in the beakers, it exists in the undissociated form, making it a weak acid. A strong acid would exist as separate H^+ and A^- ions.

b. Beaker a contains 4 HA molecules and 2 A^- ions, beaker b contains 6 A^- ions, beaker c contains 6 HA molecules, beaker d contains 6 A^- and 6 OH^- ions, and beaker e contains 3 HA molecules and 3 A^- ions. $HA + OH^- \rightarrow A^- + H_2O$; this is the neutralization reaction that occurs when OH^- is added. We start off the titration with a beaker full of weak acid (beaker c). When some OH^- is added, we convert some weak acid HA into its conjugate base A^- (beaker a). At the halfway point to equivalence, we have converted exactly one-half of the initial amount of acid present into its conjugate base (beaker e). We finally reach the equivalence point when we have added just enough OH^- to convert all of the acid present initially into its conjugate base (beaker b). Past the equivalence point, we have added an excess of OH^-, so we have excess OH^- present as well as the conjugate base of the acid produced from the neutralization reaction (beaker d). The order of the beakers from start to finish is:

$$\text{beaker c} \rightarrow \text{beaker a} \rightarrow \text{beaker e} \rightarrow \text{beaker b} \rightarrow \text{beaker d}$$

c. pH = pK_a when a buffer solution is present that has equal concentrations of the weak acid and conjugate base. This is beaker e.

d. The equivalence point is when just enough OH^- has been added to exactly react with all of the acid present initially. This is beaker b.

e. Past the equivalence point, the pH is dictated by the concentration of excess OH^- added from the strong base. We can ignore the amount of hydroxide added by the weak conjugate base that is also present. This is beaker d.

14. Titration i is a strong acid titrated by a strong base. The pH is very acidic until just before the equivalence point; at the equivalence point, pH = 7.00, and past the equivalence the pH is very basic. Titration ii is a strong base titrated by a strong acid. Here, the pH is very basic until just before the equivalence point; at the equivalence point, pH = 7.00, and past the equivalence point the pH is very acidic. Titration iii is a weak base titrated by a strong acid. The pH starts out basic because a weak base is present. However, the pH will not be as basic as in titration ii, where a strong base is titrated. The pH drops as HCl is added; then at the halfway point to equivalence, pH = pK_a. Because $K_b = 4.4 \times 10^{-4}$ for CH_3NH_2, $CH_3NH_3^+$ has $K_a = K_w/K_b = 2.3 \times 10^{-11}$ and $pK_a = 10.64$. So, at the halfway point to equivalence for this weak base-strong acid titration, pH = 10.64. The pH continues to drop as HCl is added; then at the equivalence point the pH is acidic (pH < 7.00) because the only important major species present is a weak acid (the conjugate acid of the weak base). Past the equivalence point the pH becomes more acidic as excess HCl is added. Titration iv is a weak acid titrated by a strong base. The pH starts off acidic, but not nearly as acidic as the strong acid titration (i). The pH increases as NaOH is added; then at the halfway point to equivalence, pH = pK_a for HF = $-\log(7.2 \times 10^{-4}) = 3.14$. The pH continues to increase past the halfway point; then at the equivalence point the pH is basic (pH > 7.0) because the only important major species present is a weak base (the conjugate base of the weak acid). Past the equivalence point the pH becomes more basic as excess NaOH is added.

a. All require the same volume of titrant to reach the equivalence point. At the equivalence point for all these titrations, moles acid = moles base ($M_AV_A = M_BV_B$). Because all the molarities and volumes are the same in the titrations, the volume of titrant will be the same (50.0 mL titrant added to reach equivalence point).

b. Increasing initial pH: i < iv < iii < ii; the strong acid titration has the lowest pH, the weak acid titration is next, followed by the weak base titration, with the strong base titration having the highest pH.

c. i < iv < iii < ii; the strong acid titration has the lowest pH at the halfway point to equivalence, and the strong base titration has the highest halfway point pH. For the weak acid titration, pH = pK_a = 3.14, and for the weak base titration, pH = pK_a = 10.64.

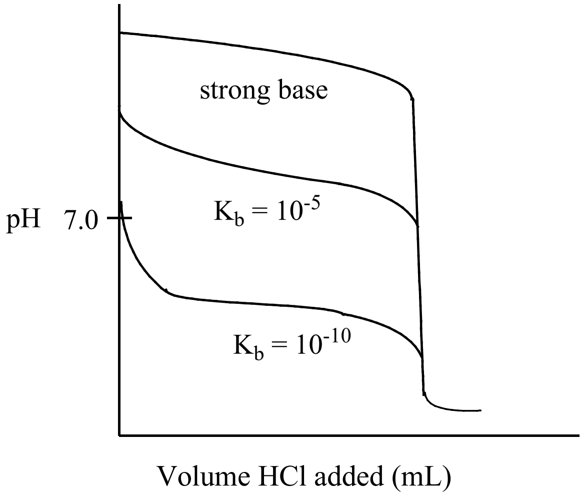
d. Equivalence point pH: iii < ii = i < iv; the strong-by-strong titrations have pH = 7.00 at the equivalence point. The weak base titration has an acidic pH at the equivalence point, and a weak acid titration has a basic equivalence point pH.
The only different answer when the weak acid and weak base are changed would be for part c. This is for the halfway point to equivalence, where pH = pK_a.

$$HOC_6H_5;\ K_a = 1.6 \times 10^{-10},\ pK_a = -\log(1.6 \times 10^{-10}) = 9.80$$

$$C_5H_5NH^+,\ K_a = \frac{K_w}{K_{b,\,C_5H_5N}} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6},\ pK_a = 5.23$$

From the pK_a values, the correct ordering at the halfway point to equivalence would be i < iii < iv < ii. Note that for the weak base-strong acid titration using C_5H_5N, the pH is acidic at the halfway point to equivalence, whereas the weak acid-strong base titration using HOC_6H_5 is basic at the halfway point to equivalence. This is fine; this will always happen when the weak base titrated has a $K_b < 1 \times 10^{-7}$ (so K_a of the conjugate acid is greater than 1×10^{-7}) and when the weak acid titrated has a $K_a < 1 \times 10^{-7}$ (so K_b of the conjugate base is greater than 1×10^{-7}).

15. The three key points to emphasize in your sketch are the initial pH, the pH at the halfway point to equivalence, and the pH at the equivalence point. For all the weak bases titrated, pH = pK_a at the halfway point to equivalence (50.0 mL HCl added) because [weak base] = [conjugate acid] at this point. Here, the weak base with $K_b = 1 \times 10^{-5}$ has a conjugate acid with $K_a = 1 \times 10^{-9}$, so pH = 9.0 at the halfway point. The weak base with $K_b = 1 \times 10^{-10}$ has a pH = 4.0 at the halfway point to equivalence. For the initial pH, the strong base has the highest pH (most basic), whereas the weakest base has the lowest pH (least basic). At the equivalence point (100.0 mL HCl added), the strong base titration has pH = 7.0. The weak bases titrated have acidic pH's because the conjugate acids of the weak bases titrated are the major species present. The weakest base has the strongest conjugate acid so its pH will be lowest (most acidic) at the equivalence point.



17. Only the third (lower) beaker represents a buffer solution. A weak acid and its conjugate base must both be present in large quantities in order to have a buffer solution. This is only the case in the third beaker. The first beaker represents a beaker full of strong acid which is 100% dissociated.

The second beaker represents a weak acid solution. In a weak acid solution, only a small fraction of the acid is dissociated. In this representation, 1/10 of the weak acid has dissociated. The only B^- present in this beaker is from the dissociation of the weak acid. A buffer solution has B^- added from another source.

18. A buffer solution is a solution containing a weak acid plus its conjugate base or a weak base plus its conjugate acid. Solution c contains a weak acid (HOCl) plus its conjugate base (OCl^-), so it is a buffer. Solution e is also a buffer solution. It contains a weak base (H_2NNH_2) plus its conjugate acid ($H_2NNH_3^+$).

Solution a contains a strong acid (HBr) and a weak acid (HOBr). Solution b contains a strong acid ($HClO_4$) and a strong base (RbOH). Solution d contains a strong base (KOH) and a weak base ($HONH_2$).

19. When strong acid or strong base is added to a bicarbonate-carbonate mixture, the strong acid(base) is neutralized. The reaction goes to completion, resulting in the strong acid(base) being replaced with a weak acid(base), resulting in a new buffer solution. The reactions are:

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

20. Like the HCO_3^-/CO_3^{2-} buffer discussed in Exercise 19, the $HONH_3^+/HONH_2$ buffer absorbs added OH^- and H^+ in the same fashion.

$$HONH_2(aq) + H^+(aq) \rightarrow HONH_3^+(aq)$$

$$HONH_3^+(aq) + OH^-(aq) \rightarrow HONH_2(aq) + H_2O(l)$$

31. Major species: HNO_2, NO_2^- and Na^+. Na^+ has no acidic or basic properties. One appropriate equilibrium reaction you can use is the K_a reaction of HNO_2, which contains both HNO_2 and NO_2^-. However, you could also use the K_b reaction for NO_2^- and come up with the same answer. Solving the equilibrium problem (called a buffer problem):

	HNO_2	$\rightleftharpoons$	NO_2^-	+	H^+
Initial	1.00 M		1.00 M		~0
	x mol/L HNO_2 dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$1.00 - x$		$1.00 + x$		x

$$K_a = 4.0 \times 10^{-4} = \frac{[NO_2^-][H^+]}{[HNO_2]} = \frac{(1.00 + x)(x)}{1.00 - x} \approx \frac{(1.00)(x)}{1.00} \quad \text{(assuming } x << 1.00)$$

$x = 4.0 \times 10^{-4}\ M = [H^+]$; assumptions good ($x$ is 4.0×10^{-2}% of 1.00).

$pH = -\log(4.0 \times 10^{-4} = 3.40$

Note: We would get the same answer using the Henderson-Hasselbalch equation. Use whichever method you prefer.

32. Major species: HF, F^-, K^+, and H_2O. K^+ has no acidic or basic properties. This is a solution containing a weak acid and its conjugate base. This is a buffer solution. One appropriate equilibrium reaction you can use is the K_a reaction of HF, which contains both HF and F^-. However, you could also use the K_b reaction for F^- and come up with the same answer. Alternately, you could use the Henderson-Hasselblach equation to solve for the pH. For this problem, we will use the K_a reaction and set up an ICE table to solve for the pH.

	HF	$\rightleftharpoons$	F^-	+	H^+
Initial	0.60 *M*		1.00 *M*		~0
	x mol/L HF dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.60 - x$		$1.00 + x$		x

$$K_a = 7.2 \times 10^{-4} = \frac{[F^-][H^+]}{[HF]} = \frac{(1.00 + x)(x)}{0.60 - x} \approx \frac{(1.00)(x)}{0.60} \quad \text{(assuming } x << 0.60\text{)}$$

$x = [H^+] = 0.60 \times (7.2 \times 10^{-4}) = 4.3 \times 10^{-4}$ *M*; assumptions good.

$\text{pH} = -\log(4.3 \times 10^{-4}) = 3.37$

33. Major species after NaOH added: HNO_2, NO_2^-, Na^+, and OH^-. The OH^- from the strong base will react with the best acid present (HNO_2). Any reaction involving a strong base is assumed to go to completion. Because all species present are in the same volume of solution, we can use molarity units to do the stoichiometry part of the problem (instead of moles). The stoichiometry problem is:

	OH^-	+	HNO_2	$\rightarrow$	NO_2^- + H_2O	
Before	0.10 mol/1.00 L		1.00 *M*		1.00 *M*	
Change	–0.10 *M*		–0.10 *M*	$\rightarrow$	+0.10 *M*	Reacts completely
After	0		0.90		1.10	

After all the OH^- reacts, we are left with a solution containing a weak acid (HNO_2) and its conjugate base (NO_2^-). This is what we call a buffer problem. We will solve this buffer problem using the K_a equilibrium reaction. One could also use the K_b equilibrium reaction or use the Henderson-Hasselbalch equation to solve for the pH.

	HNO_2	$\rightleftharpoons$	NO_2^-	+	H^+
Initial	0.90 *M*		1.10 *M*		~0
	x mol/L HNO_2 dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.90 - x$		$1.10 + x$		x

$$K_a = 4.0 \times 10^{-4} = \frac{(1.10 + x)(x)}{0.90 - x} \approx \frac{(1.10)(x)}{0.90}, \quad x = [H^+] = 3.3 \times 10^{-4}\ M;\ \text{pH} = 3.48;$$

assumptions good.

Note: The added NaOH to this buffer solution changes the pH only from 3.40 to 3.48. If the NaOH were added to 1.0 L of pure water, the pH would change from 7.00 to 13.00.

Major species after HCl added: HNO_2, NO_2^-, H^+, Na^+, Cl^-; the added H^+ from the strong acid will react completely with the best base present (NO_2^-).

	H^+	+	NO_2^-		HNO_2	
Before	$\frac{0.20\text{ mol}}{1.00\text{ L}}$		1.00 *M*		1.00 *M*	
Change	–0.20 *M*		–0.20 *M*	→	+0.20 *M*	Reacts completely
After	0		0.80		1.20	

After all the H^+ has reacted, we have a buffer solution (a solution containing a weak acid and its conjugate base). Solving the buffer problem:

	HNO_2	$\rightleftharpoons$	NO_2^-	+	H^+
Initial	1.20 *M*		0.80 *M*		0
Equil.	$1.20 - x$		$0.80 + x$		$+x$

$$K_a = 4.0 \times 10^{-4} = \frac{(0.80 + x)(x)}{1.20 - x} \approx \frac{(0.80)(x)}{1.20}\text{, } x = [H^+] = 6.0 \times 10^{-4}\ M;\ \text{pH} = 3.22;$$

assumptions good.

Note: The added HCl to this buffer solution changes the pH only from 3.40 to 3.22. If the HCl were added to 1.0 L of pure water, the pH would change from 7.00 to 0.70.

34. Major species after NaOH added: HF, F^-, K^+, Na^+, OH^-, and H_2O. The OH^- from the strong base will react with the best acid present (HF). Any reaction involving a strong base is assumed to go to completion. Because all species present are in the same volume of solution, we can use molarity units to do the stoichiometry part of the problem (instead of moles). The stoichiometry problem is:

	OH^-	+	HF		F^-	+ H_2O	
Before	0.10 mol/1.00 L		0.60 *M*		1.00 *M*		
Change	–0.10 *M*		–0.10 *M*	→	+0.10 *M*		Reacts completely
After	0		0.50		1.10		

After all the OH^- reacts, we are left with a solution containing a weak acid (HF) and its conjugate base (F^-). This is what we call a buffer problem. We will solve this buffer problem using the K_a equilibrium reaction. One could also use the K_b equilibrium reaction or use the Henderson-Hasselbalch equation to solve for the pH.

	HF	$\rightleftharpoons$	F^-	+	H^+
Initial	0.50 *M*		1.10 *M*		~0
	x mol/L HF dissociates to reach equilibrium				
Change	$-x$	→	$+x$		$+x$
Equil.	$0.50 - x$		$1.10 + x$		x

$$K_a = 7.2 \times 10^{-4} = \frac{(1.10 + x)(x)}{0.50 - x} \approx \frac{(1.10)(x)}{0.50}\text{, } x = [H^+] = 3.3 \times 10^{-4}\ M;\ \text{pH} = 3.48;$$

assumptions good.

Note: The added NaOH to this buffer solution changes the pH only from 3.37 to 3.48. If the NaOH were added to 1.0 L of pure water, the pH would change from 7.00 to 13.00.
Major species after HCl added: HF, F^-, H^+, K^+, Cl^-, and H_2O; the added H^+ from the strong acid will react completely with the best base present (F^-).

	H^+	+	F^-	→	HF	
Before	$\frac{0.20\text{ mol}}{1.00\text{ L}}$		1.00 *M*		0.60 *M*	
Change	–0.20 *M*		–0.20 *M*	→	+0.20 *M*	Reacts completely
After	0		0.80		0.80	

After all the H^+ has reacted, we have a buffer solution (a solution containing a weak acid and its conjugate base). Solving the buffer problem:

	HF	⇌	F^-	+	H^+
Initial	0.80 *M*		0.80 *M*		0
Equil.	$0.80 - x$		$0.80 + x$		x

$$K_a = 7.2 \times 10^{-4} = \frac{(0.80 + x)(x)}{0.80 - x} \approx \frac{(0.80)(x)}{0.80},\ x = [H^+] = 7.2 \times 10^{-4}\ M;\ \text{pH} = 3.14;$$

assumptions good.

Note: The added HCl to this buffer solution changes the pH only from 3.37 to 3.14. If the HCl were added to 1.0 L of pure water, the pH would change from 7.00 to 0.70.

39. $[H^+]\text{ added} = \dfrac{0.010\text{ mol}}{0.2500\text{ L}} = 0.040\ M$; the added H^+ reacts completely with NH_3 to form NH_4^+.

a.

	NH_3	+	H^+	→	NH_4^+	
Before	0.050 *M*		0.040 *M*		0.15 *M*	
Change	–0.040		–0.040	→	+0.040	Reacts completely
After	0.010		0		0.19	

A buffer solution still exists after H^+ reacts completely. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.6 \times 10^{-10}) + \log\left(\frac{0.010}{0.19}\right) = 9.25 + (-1.28) = 7.97$$

b.

	NH_3	+	H^+	→	NH_4^+	
Before	0.50 *M*		0.040 *M*		1.50 *M*	
Change	–0.040		–0.040	→	+0.040	Reacts completely
After	0.46		0		1.54	

A buffer solution still exists. $\text{pH} = \text{p}K_a + \log\dfrac{[NH_3]}{[NH_4^+]},\ 9.25 + \log\left(\dfrac{0.46}{1.54}\right) = 8.73$

The two buffers differ in their capacity and not their initial pH (both buffers had an initial pH = 8.77). Solution b has the greatest capacity since it has the largest concentrations of weak acid and conjugate base. Buffers with greater capacities will be able to absorb more added H^+ or OH^- with little change to the pH.

40. a. pK_b for $C_6H_5NH_2 = -\log(3.8 \times 10^{-10}) = 9.42$; pK_a for $C_6H_5NH_3^+ = 14.00 - 9.42 = 4.58$

$$pH = pK_a + \log\frac{[C_6H_5NH_2]}{[C_6H_5NH_3^+]},\quad 4.20 = 4.58 + \log\frac{0.50\ M}{[C_6H_5NH_3^+]}$$

$$-0.38 = \log\frac{0.50\ M}{[C_6H_5NH_3^+]},\quad [C_6H_5NH_3^+] = [C_6H_5NH_3Cl] = 1.2\ M$$

b. $$4.0\text{ g NaOH} \times \frac{1\text{ mol NaOH}}{40.00\text{ g}} \times \frac{1\text{ mol OH}^-}{\text{mol NaOH}} = 0.10\text{ mol OH}^-;\ [OH^-] = \frac{0.10\text{ mol}}{1.0\text{ L}} = 0.10\ M$$

	$C_6H_5NH_3^+$	+	OH^-	$\rightarrow$	$C_6H_5NH_2$	+	H_2O	
Before	1.2 *M*		0.10 *M*		0.50 *M*			
Change	–0.10		–0.10	$\rightarrow$	+0.10			Reacts completely
After	1.1		0		0.60			

A buffer solution exists. $pH = 4.58 + \log\left(\frac{0.60}{1.1}\right) = 4.32$

47. A best buffer has large and equal quantities of weak acid and conjugate base. Because [acid] = [base] for a best buffer, $pH = pK_a + \log\frac{[base]}{[acid]} = pK_a + 0 = pK_a$ ($pH \approx pK_a$ for a best buffer).

The best acid choice for a pH = 7.00 buffer would be the weak acid with a pK_a close to 7.0 or $K_a \approx 1 \times 10^{-7}$. HOCl is the best choice in Table 13.2 ($K_a = 3.5 \times 10^{-8}$; $pK_a = 7.46$). To make this buffer, we need to calculate the [base] : [acid] ratio.

$$7.00 = 7.46 + \log\frac{[base]}{[acid]},\quad \frac{[OCl^-]}{[HOCl]} = 10^{-0.46} = 0.35$$

Any $OCl^-/HOCl$ buffer in a concentration ratio of 0.35 : 1 will have a pH = 7.00. One possibility is [NaOCl] = 0.35 *M* and [HOCl] = 1.0 *M*.

48. For a pH = 5.00 buffer, we want an acid with a pK_a close to 5.00. For a conjugate acid-base pair, $14.00 = pK_a + pK_b$. So, for a pH = 5.00 buffer, we want the base to have a pK_b close to (14.0 – 5.0 =) 9.0 or a K_b close to 1×10^{-9}. The best choice in Table 13.3 is pyridine (C_5H_5N) with $K_b = 1.7 \times 10^{-9}$.

$$pH = pK_a + \log\frac{[base]}{[acid]};\quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

$$5.00 = -\log(5.9 \times 10^{-6}) + \log\frac{[base]}{[acid]},\quad \frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{-0.23} = 0.59$$

There are many possibilities to make this buffer. One possibility is a solution of $[C_5H_5N]$ = 0.59 *M* and $[C_5H_5NHCl]$ = 1.0 *M*. The pH of this solution will be 5.00 because the base to acid concentration ratio is 0.59 : 1.

49. K_a for $H_2NNH_3^+ = K_w/K_{b,\,H_2NNH_2} = 1.0 \times 10^{-14}/3.0 \times 10^{-6} = 3.3 \times 10^{-9}$

$$pH = pK_a + \log\frac{[H_2NNH_2]}{[H_2NNH_3^+]} = -\log(3.3 \times 10^{-9}) + \log\left(\frac{0.40}{0.80}\right) = 8.48 + (-0.30) = 8.18$$

pH = pK_a for a buffer when [acid] = [base]. Here, the acid ($H_2NNH_3^+$) concentration needs to decrease, while the base (H_2NNH_2) concentration needs to increase for $[H_2NNH_3^+] = [H_2NNH_2]$. Both changes are accomplished by adding a strong base (like NaOH) to the original buffer. The added OH^- from the strong base converts the acid component of the buffer into the conjugate base. Here, the reaction is $H_2NNH_3^+ + OH^- \rightarrow H_2NNH_2 + H_2O$. Because a strong base is reacting, the reaction is assumed to go to completion. The following set-up determines the number of moles of OH^-(x) that must be added so that mol $H_2NNH_3^+$ = mol H_2NNH_2 . When mol acid = mol base in a buffer, then [acid] = [base] and pH = pK_a.

	$H_2NNH_3^+$	+	OH^-	$\rightarrow$	H_2NNH_2	+	H_2O	
Before	1.0 L × 0.80 mol/L		x		1.0 L × 0.40 mol/L			
Change	$-x$		$-x$	$\rightarrow$	$+x$			Reacts completely
After	$0.80 - x$		0		$0.40 + x$			

We want mol $H_2NNH_3^+$ = mol H_2NNH_2. Therefore:

$0.80 - x = 0.40 + x,\ 2x = 0.40,\ x = 0.20$ mol OH^-

When 0.20 mol OH^- is added to the initial buffer, mol $H_2NNH_3^+$ is decreased to 0.60 mol, while mol H_2NNH_2 is increased to 0.60 mol. Therefore, 0.20 mol of NaOH must be added to the initial buffer solution to produce a solution where pH = pK_a.

50. $$pH = pK_a + \log\frac{[OCl^-]}{[HOCl]} = -\log(3.5 \times 10^{-8}) + \log\left(\frac{0.90}{0.20}\right) = 7.46 + 0.65 = 8.11$$

pH = pK_a when $[HOCl] = [OCl^-]$ (or when mol HOCl = mol OCl^-). Here, the moles of the base component of the buffer must decrease, while the moles of the acid component of the buffer must increase to achieve a solution where pH = pK_a. Both changes occur when a strong acid (like HCl) is added. Let x = mol H^+ added from the strong acid HCl.

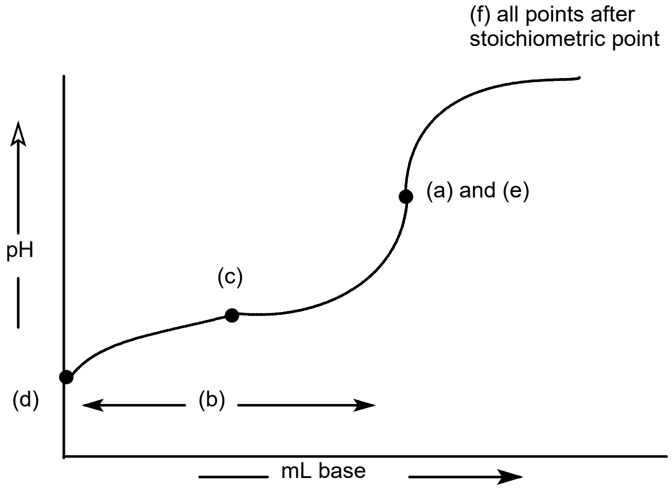
	H^+	+	OCl^-	$\rightarrow$	HOCl	
Before	x		1.0 L × 0.90 mol/L		1.0 L × 0.20 mol/L	
Change	$-x$		$-x$	$\rightarrow$	$+x$	Reacts completely
After	0		$0.90 - x$		$0.20 + x$	

We want mol HOCl = mol OCl^-. Therefore:

$0.90 - x = 0.20 + x,\ 2x = 0.70,\ x = 0.35$ mol H^+

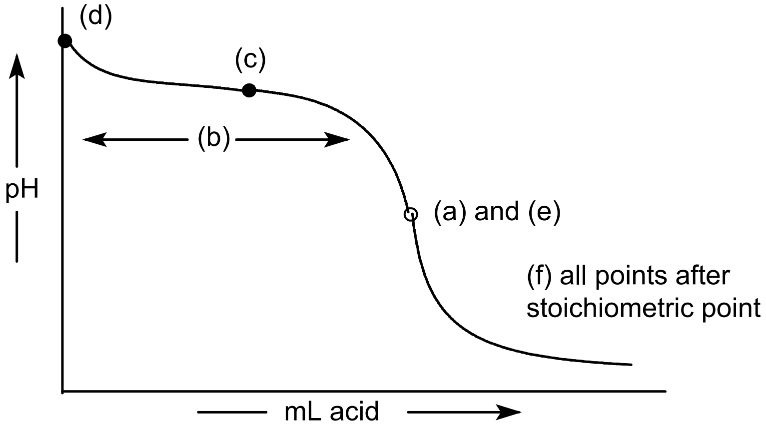
When 0.35 mol H^+ is added, mol OCl^- is decreased to 0.55 mol, while the mol HOCl is increased to 0.55 mol Therefore, 0.35 mol of HCl must be added to the original buffer solution to produce a solution where pH = pK_a.

55.



$HA + OH^- \rightarrow A^- + H_2O$; added OH^- from the strong base converts the weak acid HA into its conjugate base A^-. Initially, before any OH^- is added (point d), HA is the dominant species present. After OH^- is added, both HA and A^- are present, and a buffer solution results (region b). At the equivalence point (points a and e), exactly enough OH^- has been added to convert all the weak acid HA into its conjugate base A^-. Past the equivalence point (region f), excess OH^- is present. For the answer to part b, we included almost the entire buffer region. The maximum buffer region (or the region which is the best buffer solution) is around the halfway point to equivalence (point c). At this point, enough OH^- has been added to convert exactly one-half of the weak acid present initially into its conjugate base, so $[HA] = [A^-]$ and $pH = pK_a$. A "best" buffer has about equal concentrations of weak acid and conjugate base present.

56.



$B + H^+ \rightarrow BH^+$; added H^+ from the strong acid converts the weak base B into its conjugate acid BH^+. Initially, before any H^+ is added (point d), B is the dominant species present. After H^+ is added, both B and BH^+ are present, and a buffered solution results (region b). At the equivalence point (points a and e), exactly enough H^+ has been added to convert all the weak base present initially into its conjugate acid BH^+. Past the equivalence point (region f), excess H^+ is present. For the answer to b, we included almost the entire buffer region. The maximum buffer region is around the halfway point to equivalence (point c), where $[B] = [BH^+]$. Here, $pH = pK_a$, which is a characteristic of a best buffer.

57. This is a strong acid ($HClO_4$) titrated by a strong base (KOH). Added OH^- from the strong base will react completely with the H^+ present from the strong acid to produce H_2O.

a. Only strong acid present. $[H^+] = 0.200\ M$; pH = 0.699

b. $$\text{mmol OH}^- \text{ added} = 10.0\ \text{mL} \times \frac{0.100\ \text{mmol OH}^-}{\text{mL}} = 1.00\ \text{mmol OH}^-$$

$$\text{mmol H}^+ \text{ present} = 40.0\ \text{mL} \times \frac{0.200\ \text{mmol H}^+}{\text{mL}} = 8.0\ \text{mmol H}^+$$

Note: The units millimoles are usually easier numbers to work with. The units for molarity are moles per liter but are also equal to millimoles per milliliter.

	H^+	+	OH^-	→	H_2O
Before	8.00 mmol		1.00 mmol		
Change	−1.00 mmol		−1.00 mmol		Reacts completely
After	7.00 mmol		0		

The excess H^+ determines the pH. $$[H^+]_{excess} = \frac{7.00\ \text{mmol H}^+}{40.0\ \text{mL} + 10.0\ \text{mL}} = 0.140\ M$$

pH = −log(0.140) = 0.854

c. mmol OH^- added = 40.0 mL × 0.100 M = 4.00 mmol OH^-

	H^+	+	OH^-	→	H_2O
Before	8.00 mmol		4.00 mmol		
After	4.00 mmol		0		

$$[H^+]_{excess} = \frac{4.00\ \text{mmol}}{(40.0 + 40.0)\ \text{mL}} = 0.0500\ M;\ \ \text{pH} = 1.301$$

d. mmol OH^- added = 80.0 mL × 0.100 M = 8.00 mmol OH^-; this is the equivalence point because we have added just enough OH^- to react with all the acid present. For a strong acid-strong base titration, pH = 7.00 at the equivalence point because only neutral species are present (K^+, ClO_4^-, H_2O).

e. mmol OH^- added = 100.0 mL × 0.100 M = 10.0 mmol OH^-

	H^+	+	OH^-	→	H_2O
Before	8.00 mmol		10.0 mmol		
After	0		2.0 mmol		

Past the equivalence point, the pH is determined by the excess OH^- present.

$$[OH^-]_{excess} = \frac{2.0\ \text{mmol}}{(40.0 + 100.0)\ \text{mL}} = 0.014\ M;\ \ \text{pOH} = 1.85;\ \ \text{pH} = 12.15$$

58. This is a strong base, $Ba(OH)_2$, titrated by a strong acid, HCl. The added strong acid will neutralize the OH^- from the strong base. As is always the case when a strong acid and/or strong base reacts, the reaction is assumed to go to completion.

a. Only a strong base is present, but it breaks up into 2 moles of OH^- ions for every mole of $Ba(OH)_2$. $[OH^-] = 2 \times 0.100\ M = 0.200\ M$; pOH = 0.699; pH = 13.301

b. $$\text{mmol OH}^- \text{ present} = 80.0\ \text{mL} \times \frac{0.100\ \text{mmol Ba(OH)}_2}{\text{mL}} \times \frac{2\ \text{mmol OH}^-}{\text{mmol Ba(OH)}_2}$$

$$= 16.0\ \text{mmol OH}^-$$

$$\text{mmol H}^+ \text{ added} = 20.0\ \text{mL} \times \frac{0.400\ \text{mmol H}^+}{\text{mL}} = 8.00\ \text{mmol H}^+$$

	OH^-	+	H^+	→	H_2O	
Before	16.0 mmol		8.00 mmol			
Change	–8.00 mmol		–8.00 mmol			Reacts completely
After	8.0 mmol		0			

$$[OH^-]_{\text{excess}} = \frac{8.0\ \text{mmol OH}^-}{80.0\ \text{mL} + 20.0\ \text{mL}} = 0.080\ M;\ \text{pOH} = 1.10;\ \ \text{pH} = 12.90$$

c. mmol H^+ added = 30.0 mL × 0.400 M = 12.0 mmol H^+

	OH^-	+	H^+	→	H_2O
Before	16.0 mmol		12.0 mmol		
After	4.0 mmol		0		

$$[OH^-]_{\text{excess}} = \frac{4.0\ \text{mmol OH}^-}{(80.0 + 30.0)\ \text{mL}} = 0.036\ M;\ \text{pOH} = 1.44;\ \text{pH} = 12.56$$

d. mmol H^+ added = 40.0 mL × 0.400 M = 16.0 mmol H^+; this is the equivalence point. Because the H^+ will exactly neutralize the OH^- from the strong base, all we have in solution is Ba^{2+}, Cl^-, and H_2O. All are neutral species, so pH = 7.00.

e. mmol H^+ added = 80.0 mL × 0.400 M = 32.0 mmol H^+

	OH^-	+	H^+	→	H_2O
Before	16.0 mmol		32.0 mmol		
After	0		16.0 mmol		

$$[H^+]_{\text{excess}} = \frac{16.0\ \text{mmol H}^+}{(80.0 + 80.0)\ \text{mL}} = 0.100\ M;\ \text{pH} = 1.000$$

59. This is a weak acid ($HC_2H_3O_2$) titrated by a strong base (KOH).

a. Only weak acid is present. Solving the weak acid problem:

	$HC_2H_3O_2$	⇌	H^+	+	$C_2H_3O_2^-$
Initial	0.200 M		~0		0
	x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium				
Change	$-x$	→	$+x$		$+x$

Equil.	$0.200 - x$	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.200 - x} \approx \frac{x^2}{0.200},\ x = [H^+] = 1.9 \times 10^{-3}\ M$$

pH = 2.72; assumptions good.

b. The added OH^- will react completely with the best acid present, $HC_2H_3O_2$.

$$\text{mmol } HC_2H_3O_2 \text{ present} = 100.0 \text{ mL} \times \frac{0.200 \text{ mmol } HC_2H_3O_2}{\text{mL}} = 20.0 \text{ mmol } HC_2H_3O_2$$

$$\text{mmol } OH^- \text{ added} = 50.0 \text{ mL} \times \frac{0.100 \text{ mmol } OH^-}{\text{mL}} = 5.00 \text{ mmol } OH^-$$

	$HC_2H_3O_2$	+ OH^-	$\rightarrow$	$C_2H_3O_2^-$ + H_2O	
Before	20.0 mmol	5.00 mmol		0	
Change	−5.00 mmol	−5.00 mmol	$\rightarrow$	+5.00 mmol	Reacts Completely
After	15.0 mmol	0		5.00 mmol	

After reaction of all of the strong base, we have a buffer solution containing a weak acid ($HC_2H_3O_2$) and its conjugate base ($C_2H_3O_2^-$). We will use the Henderson-Hasselbalch equation to solve for the pH.

$$pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = -\log(1.8 \times 10^{-5}) + \log\left(\frac{5.00 \text{ mmol}/V_T}{15.0 \text{ mmol}/V_T}\right),\ \text{where } V_T = \text{total volume}$$

$$pH = 4.74 + \log\left(\frac{5.00}{15.0}\right) = 4.74 + (-0.477) = 4.26$$

Note that the total volume cancels in the Henderson-Hasselbalch equation. For the [base]/[acid] term, the mole ratio equals the concentration ratio because the components of the buffer are always in the same volume of solution.

c. mmol OH^- added = 100.0 mL × (0.100 mmol OH^-/mL) = 10.0 mmol OH^-; the same amount (20.0 mmol) of $HC_2H_3O_2$ is present as before (it doesn't change). As before, let the OH^- react to completion, then see what is remaining in solution after this reaction.

	$HC_2H_3O_2$	+ OH^-	$\rightarrow$	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol	10.0 mmol		0
After	10.0 mmol	0		10.0 mmol

A buffer solution results after reaction. Because $[C_2H_3O_2^-] = [HC_2H_3O_2]$ = 10.0 mmol/total volume, pH = pK_a. This is always true at the halfway point to equivalence for a weak acid-strong base titration, pH = pK_a.

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

d. mmol OH^- added = 150.0 mL × 0.100 M = 15.0 mmol OH^-. Added OH^- reacts completely with the weak acid.

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		15.0 mmol		0
After	5.0 mmol		0		15.0 mmol

We have a buffer solution after all the OH^- reacts to completion. Using the Henderson-Hasselbalch equation:

$$pH = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.74 + \log\left(\frac{15.0\text{ mmol}}{5.0\text{ mmol}}\right)$$

$$pH = 4.74 + 0.48 = 5.22$$

e. mmol OH^- added = 200.00 mL × 0.100 M = 20.0 mmol OH^-; as before, let the added OH^- react to completion with the weak acid; then see what is in solution after this reaction.

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		20.0 mmol		0
After	0		0		20.0 mmol

This is the equivalence point. Enough OH^- has been added to exactly neutralize all the weak acid present initially. All that remains that affects the pH at the equivalence point is the conjugate base of the weak acid ($C_2H_3O_2^-$). This is a weak base equilibrium problem.

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \qquad K_b = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}}$$

	$C_2H_3O_2^-$		$HC_2H_3O_2$	OH^-	
Initial	20.0 mmol/300.0 mL		0	0	$K_b = 5.6\times10^{-9}$
	x mol/L $C_2H_3O_2^-$ reacts with H_2O to reach equilibrium				
Change	$-x$	→	$+x$	$+x$	
Equil.	$0.0667 - x$		x	x	

$$K_b = 5.6\times10^{-10} = \frac{x^2}{0.0667 - x} \approx \frac{x^2}{0.0667}, \quad x = [OH^-] = 6.1\times10^{-6}\ M$$

pOH = 5.21; pH = 8.79; assumptions good.

f. mmol OH^- added = 250.0 mL × 0.100 M = 25.0 mmol OH^-

	$HC_2H_3O_2$	+	OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	20.0 mmol		25.0 mmol		0
After	0		5.0 mmol		20.0 mmol

After the titration reaction, we have a solution containing excess OH^- and a weak base $C_2H_3O_2^-$. When a strong base and a weak base are both present, assume that the amount of OH^- added from the weak base will be minimal; that is, the pH past the equivalence point is determined by the amount of excess strong base.

$$[OH^-]_{excess} = \frac{5.0\text{ mmol}}{100.0\text{ mL} + 250.0\text{ mL}} = 0.014\ M;\ \ pOH = 1.85;\ \ pH = 12.15$$

60. This is a weak base (H_2NNH_2) titrated by a strong acid (HNO_3). To calculate the pH at the various points, let the strong acid react completely with the weak base present; then see what is in solution.

a. Only a weak base is present. Solve the weak base equilibrium problem.

	H_2NNH_2 + H_2O ⇌	$H_2NNH_3^+$ +	OH^-
Initial	$0.100\ M$	0	~0
Equil.	$0.100 - x$	x	x

$$K_b = 3.0 \times 10^{-6} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100},\ x = [OH^-] = 5.5 \times 10^{-4}\ M$$

pOH = 3.26; pH = 10.74; assumptions good.

b. $$\text{mmol } H_2NNH_2 \text{ present} = 100.0\text{ mL} \times \frac{0.100\text{ mmol } H_2NNH_2}{\text{mL}} = 10.0\text{ mmol } H_2NNH_2$$

$$\text{mmol } H^+ \text{ added} = 20.0\text{ mL} \times \frac{0.200\text{ mmol } H^+}{\text{mL}} = 4.00\text{ mmol } H^+$$

	H_2NNH_2	+ H^+	→	$H_2NNH_3^+$	
Before	10.0 mmol	4.00 mmol		0	
Change	−4.00 mmol	−4.00 mmol	→	+4.00 mmol	Reacts completely
After	6.0 mmol	0		4.00 mmol	

A buffer solution results after the titration reaction. Solving using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]};\quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-6}} = 3.3 \times 10^{-9}$$

$$pH = -\log(3.3 \times 10^{-9}) + \log\left(\frac{6.0\text{ mmol}/V_T}{4.00\text{ mmol}/V_T}\right),\ \text{where } V_T = \text{total volume, cancels.}$$

$$pH = 8.48 + \log(1.5) = 8.48 + 0.18 = 8.66$$

c. mmol H^+ added = 25.0 mL × 0.200 M = 5.00 mmol H^+

	H_2NNH_2	+ H^+	→ $H_2NNH_3^+$
Before	10.0 mmol	5.00 mmol	0
After	5.0 mmol	0	5.00 mmol

This is the halfway point to equivalence, where $[H_2NNH_3^+] = [H_2NNH_2]$. At this point, $pH = pK_a$ (which is characteristic of the halfway point for any weak base-strong acid titration).

$pH = -\log(3.3 \times 10^{-9}) = 8.48$

d. mmol H^+ added = 40.0 mL × 0.200 *M* = 8.00 mmol H^+

	H_2NNH_2	+	H^+	→	$H_2NNH_3^+$
Before	10.0 mmol		8.00 mmol		0
After	2.0 mmol		0		8.00 mmol

A buffer solution results.

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 8.48 + \log\left(\frac{2.0\ \text{mmol}/V_T}{8.00\ \text{mmol}/V_T}\right) = 8.48 + (-0.60) = 7.88$$

e. mmol H^+ added = 50.0 mL × 0.200 *M* = 10.0 mmol H^+

	H_2NNH_2	+	H^+	→	$H_2NNH_3^+$
Before	10.0 mmol		10.0 mmol		0
After	0		0		10.0 mmol

As is always the case in a weak base-strong acid titration, the pH at the equivalence point is acidic because only a weak acid ($H_2NNH_3^+$) is present. Solving the weak acid equilibrium problem:

	$H_2NNH_3^+$	⇌	H^+	+	H_2NNH_2
Initial	10.0 mmol/150.0 mL		0		0
Equil.	$0.0667 - x$		x		x

$$K_a = 3.3 \times 10^{-9} = \frac{x^2}{0.0667 - x} \approx \frac{x^2}{0.0667}, \quad x = [H^+] = 1.5 \times 10^{-5}\ M$$

pH = 4.82; assumptions good.

f. mmol H^+ added = 100.0 mL × 0.200 *M* = 20.0 mmol H^+

	H_2NNH_2	+	H^+	→	$H_2NNH_3^+$
Before	10.0 mmol		20.0 mmol		0
After	0		10.0 mmol		10.0 mmol

Two acids are present past the equivalence point, but the excess H^+ will determine the pH of the solution since $H_2NNH_3^+$ is a weak acid.

$$[H^+]_{\text{excess}} = \frac{10.0\ \text{mmol}}{100.0\ \text{mL} + 100.0\ \text{mL}} = 0.0500\ M;\ \ pH = 1.301$$

61. We will do sample calculations for the various parts of the titration. All results are summarized in Table 14.1 at the end of Exercise 63.

At the beginning of the titration, only the weak acid $HC_3H_5O_3$ is present. Let HLac = $HC_3H_5O_3$ and $Lac^- = C_3H_5O_3^-$.

	HLac	$\rightleftharpoons$	H^+	+	Lac^-	$K_a = 10^{-3.86} = 1.4 \times 10^{-4}$
Initial	$0.100\ M$		~0		0	
	x mol/L HLac dissociates to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$0.100 - x$		x		x	

$$1.4 \times 10^{-4} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100},\ x = [H^+] = 3.7 \times 10^{-3}\ M;\ \text{pH} = 2.43;\quad \text{assumptions good.}$$

Up to the stoichiometric point, we calculate the pH using the Henderson-Hasselbalch equation. This is the buffer region. For example, at 4.0 mL of NaOH added:

$$\text{initial mmol HLac present} = 25.0\ \text{mL} \times \frac{0.100\ \text{mmol}}{\text{mL}} = 2.50\ \text{mmol HLac}$$

$$\text{mmol OH}^-\ \text{added} = 4.0\ \text{mL} \times \frac{0.100\ \text{mmol}}{\text{mL}} = 0.40\ \text{mmol OH}^-$$

Note: The units millimoles are usually easier numbers to work with. The units for molarity are moles per liter but are also equal to millimoles per milliliter.

The 0.40 mmol of added OH^- converts 0.40 mmol HLac to 0.40 mmol Lac^- according to the equation:

$HLac + OH^- \rightarrow Lac^- + H_2O$ Reacts completely since a strong base is added.

mmol HLac remaining = 2.50 – 0.40 = 2.10 mmol; mmol Lac^- produced = 0.40 mmol
We have a buffer solution. Using the Henderson-Hasselbalch equation where $pK_a = 3.86$:

$$\text{pH} = pK_a + \log\frac{[Lac^-]}{[HLac]} = 3.86 + \log\frac{(0.40)}{(2.10)}$$

Note: total volume cancels, so we can use the ratio of moles or millimoles in place of the concentration ratio in the Henderson-Hasselbalch equation.

$$\text{pH} = 3.86 - 0.72 = 3.14$$

Other points in the buffer region are calculated in a similar fashion. Perform a stoichiometry problem first, followed by a buffer problem. The buffer region includes all points up to and including 24.9 mL OH^- added.

At the stoichiometric point (25.0 mL OH^- added), we have added enough OH^- to convert all of the HLac (2.50 mmol) into its conjugate base (Lac^-). All that is present is a weak base. To determine the pH, we perform a weak base calculation.

$$[Lac^-]_0 = \frac{2.50\ \text{mmol}}{25.0\ \text{mL} + 25.0\ \text{mL}} = 0.0500\ M$$

	$Lac^- + H_2O$	$\rightleftharpoons$	HLac	+	OH^-	$K_b = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.1 \times 10^{-11}$
Initial	$0.0500\ M$		0		0	
	x mol/L Lac^- reacts with H_2O to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$0.0500 - x$		x		x	

$$K_b = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500} = 7.1 \times 10^{-11}$$

$x = [OH^-] = 1.9 \times 10^{-6}\ M$; pOH = 5.72; pH = 8.28; assumptions good.

Past the stoichiometric point, we have added more than 2.50 mmol of NaOH. The pH will be determined by the excess OH^- ion present. An example of this calculation follows.

At 25.1 mL: OH^- added $= 25.1\ \text{mL} \times \frac{0.100\ \text{mmol}}{\text{mL}} = 2.51$ mmol OH^-

2.50 mmol OH^- neutralizes all the weak acid present. The remainder is excess OH^-.

Excess $OH^- = 2.51 - 2.50 = 0.01$ mmol OH^-

$$[OH^-]_{\text{excess}} = \frac{0.01\ \text{mmol}}{(25.0 + 25.1)\ \text{mL}} = 2 \times 10^{-4}\ M;\ \text{pOH} = 3.7;\ \text{pH} = 10.3$$

All results are listed in Table 14.1 at the end of the solution to Exercise 63.

63. At beginning of the titration, only the weak base NH_3 is present. As always, solve for the pH using the K_b reaction for NH_3.

	$NH_3 + H_2O$	$\rightleftharpoons$	NH_4^+	+	OH^-	$K_b = 1.8 \times 10^{-5}$
Initial	$0.100\ M$		0		~0	
Equil.	$0.100 - x$		x		x	

$$K_b = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$x = [OH^-] = 1.3 \times 10^{-3}\ M$; pOH = 2.89; pH = 11.11; assumptions good.

In the buffer region (4.0 – 24.9 mL), we can use the Henderson-Hasselbalch equation:

$$K_a = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10};\ pK_a = 9.25;\ \text{pH} = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}$$

We must determine the amounts of NH_3 and NH_4^+ present after the added H^+ reacts completely with the NH_3. For example, after 8.0 mL HCl added:

$$\text{initial mmol } NH_3 \text{ present} = 25.0\ \text{mL} \times \frac{0.100\ \text{mmol}}{\text{mL}} = 2.50\ \text{mmol } NH_3$$

$$\text{mmol H}^+ \text{ added} = 8.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 0.80 \text{ mmol H}^+$$

Added H^+ reacts with NH_3 to completion: $NH_3 + H^+ \rightarrow NH_4^+$

mmol NH_3 remaining = 2.50 – 0.80 = 1.70 mmol; mmol NH_4^+ produced = 0.80 mmol

$\text{pH} = 9.25 + \log\frac{1.70}{0.80} = 9.58$ (Mole ratios can be used since the total volume cancels.)

Other points in the buffer region are calculated in similar fashion. Results are summarized in Table 14.1 at the end of Exercise 63.

At the stoichiometric point (25.0 mL H^+ added), just enough HCl has been added to convert all the weak base (NH_3) into its conjugate acid (NH_4^+). Perform a weak acid calculation.

$[NH_4^+]_0 = 2.50 \text{ mmol}/50.0 \text{ mL} = 0.0500\ M$

	NH_4^+	$\rightleftharpoons$	H^+	+	NH_3	$K_a = 5.6 \times 10^{-10}$
Initial	0.0500 *M*		0		0	
Equil.	0.0500 - *x*		*x*		*x*	

$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$, $x = [H^+] = 5.3 \times 10^{-6}\ M$; pH = 5.28; assumptions good.

Beyond the stoichiometric point, the pH is determined by the excess H^+. For example, at 28.0 mL of H^+ added:

$$H^+ \text{ added} = 28.0 \text{ mL} \times \frac{0.100 \text{ mmol}}{\text{mL}} = 2.80 \text{ mmol H}^+$$

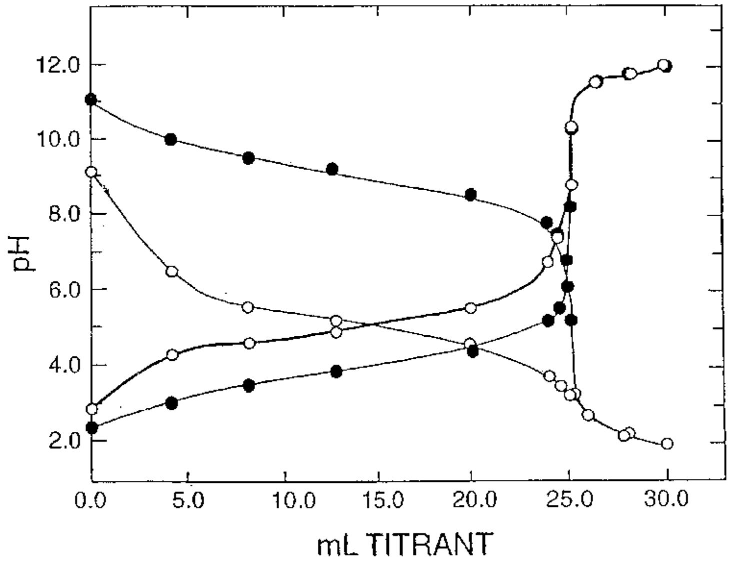
Excess H^+ = 2.80 mmol – 2.50 mmol = 0.30 mmol excess H^+

$$[H^+]_{\text{excess}} = \frac{0.30 \text{ mmol}}{(25.0 + 28.0) \text{ mL}} = 5.7 \times 10^{-3}\ M;\ \text{pH} = 2.24$$

All results are summarized in the following Table.

Table 14.1 Summary of pH Results for Exercises 61-64 (Plot below)

Titrant mL	Exercise 61	Exercise 62	Exercise 63	Exercise 64
0.0	2.43	2.96	11.11	9.11
4.0	3.14	4.17	9.97	5.95
8.0	3.53	4.56	9.58	5.56
12.5	3.86	4.89	9.25	5.23
20.0	4.46	5.49	8.65	4.63
24.0	5.24	6.27	7.87	3.85
24.5	5.6	6.6	7.6	3.5
24.9	6.3	7.3	6.9	–
25.0	8.28	8.79	5.28	3.27
25.1	10.3	10.3	3.7	–
26.0	11.30	11.30	2.71	2.71
28.0	11.75	11.75	2.24	2.24
30.0	11.96	11.96	2.04	2.04



65. a. This is a weak acid-strong base titration. At the halfway point to equivalence, [weak acid] = [conjugate base], so pH = pK_a (always for a weak acid-strong base titration).

$$pH = -\log(6.4 \times 10^{-5}) = 4.19$$

mmol $HC_7H_5O_2$ present = 100.0 mL × 0.10 M = 10. mmol $HC_7H_5O_2$. For the equivalence point, 10. mmol of OH^- must be added. The volume of OH^- added to reach the equivalence point is:

$$10.\ \text{mmol OH}^- \times \frac{1\ \text{mL}}{0.10\ \text{mmol OH}^-} = 1.0 \times 10^2\ \text{mL OH}^-$$

At the equivalence point, 10. mmol of $HC_7H_5O_2$ is neutralized by 10. mmol of OH^- to produce 10. mmol of $C_7H_5O_2^-$. This is a weak base. The total volume of the solution is $100.0\text{ mL} + 1.0 \times 10^2\text{ mL} = 2.0 \times 10^2\text{ mL}$. Solving the weak base equilibrium problem:

$$C_7H_5O_2^- + H_2O \rightleftharpoons HC_7H_5O_2 + OH^- \qquad K_b = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = 1.6 \times 10^{-10}$$

Initial	10. mmol/2.0×10^2 mL	0	0
Equil.	$0.050 - x$	x	x

$$K_b = 1.6 \times 10^{-10} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050},\ x = [OH^-] = 2.8 \times 10^{-6}\ M$$

pOH = 5.55; pH = 8.45; assumptions good.

b. At the halfway point to equivalence for a weak base-strong acid titration, pH = pK_a because [weak base] = [conjugate acid].

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11};\ pH = pK_a = -\log(1.8 \times 10^{-11}) = 10.74$$

For the equivalence point (mmol acid added = mmol base present):

mmol $C_2H_5NH_2$ present = 100.0 mL × 0.10 *M* = 10. mmol $C_2H_5NH_2$

$$\text{mL } H^+ \text{ added} = 10.\text{ mmol } H^+ \times \frac{1\text{ mL}}{0.20\text{ mmol } H^+} = 50.\text{ mL } H^+$$

The strong acid added completely converts the weak base into its conjugate acid. Therefore, at the equivalence point, $[C_2H_5NH_3^+]_0 = 10.\text{ mmol}/(100.0 + 50.)\text{ mL} = 0.067\ M$. Solving the weak acid equilibrium problem:

	$C_2H_5NH_3^+$	$\rightleftharpoons$	H^+	+	$C_2H_5NH_2$
Initial	0.067 *M*		0		0
Equil.	$0.067 - x$		x		x

$$K_a = 1.8 \times 10^{-11} = \frac{x^2}{0.067 - x} \approx \frac{x^2}{0.067},\ x = [H^+] = 1.1 \times 10^{-6}\ M$$

pH = 5.96; assumptions good.

c. In a strong acid-strong base titration, the halfway point has no special significance other than that exactly one-half of the original amount of acid present has been neutralized.

mmol H^+ present = 100.0 mL × 0.50 *M* = 50. mmol H^+

$$\text{mL } OH^- \text{ added} = 25\text{ mmol } OH^- \times \frac{1\text{ mL}}{0.25\text{ mmol}} = 1.0 \times 10^2\text{ mL } OH^-$$

	H^+	+	OH^-	→	H_2O
Before	50. mmol		25 mmol		
After	25 mmol		0		

$$[H^+]_{\text{excess}} = \frac{25\text{ mmol}}{(100.0 + 1.0 \times 10^2)\text{ mL}} = 0.13\ M;\ \text{pH} = 0.89$$

At the equivalence point of a strong acid-strong base titration, only neutral species are present (Na^+, Cl^-, and H_2O), so the pH = 7.00.

68. Mol H^+ added = 0.0400 L × 0.100 mol/L = 0.00400 mol H^+

The added strong acid reacts to completion with the weak base to form the conjugate acid of the weak base and H_2O. Let B = weak base:

	B	+	H^+	→	BH^+
Before	0.0100 mol		0.00400 mol		0
After	0.0060		0		0.0400 mol

After the H^+ reacts to completion, we have a buffer solution. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]},\ 8.00 = \text{p}K_a + \log\frac{(0.0060/V_T)}{(0.00400/V_T)},\ \text{where } V_T = \text{total volume of soln}$$

$$\text{p}K_a = 8.00 - \log\frac{(0.0060)}{(0.00400)} = 8.00 - 0.18,\ \text{p}K_a = 7.82$$

For a conjugate acid-base pair, $\text{p}K_a + \text{p}K_b = 14,00$, so:

$$\text{p}K_b = 14.00 - 7.82 = 6.18;\ K_b = 10^{-6.18} = 6.6 \times 10^{-7}$$

90. a. $\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]},\ 7.15 = -\log(6.2 \times 10^{-8}) + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$

$$7.15 = 7.21 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]},\ \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 10^{-0.06} = 0.9,\ \frac{[H_2PO_4^-]}{[HPO_4^{2-}]} = \frac{1}{0.9} = 1.1 \approx 1$$

b. A best buffer has approximately equal concentrations of weak acid and conjugate base, so pH ≈ $\text{p}K_a$ for a best buffer. The $\text{p}K_a$ value for a $H_3PO_4/H_2PO_4^-$ buffer is $-\log(7.5 \times 10^{-3}) = 2.12$. A pH of 7.15 is too high for a $H_3PO_4/H_2PO_4^-$ buffer to be effective. At this high of pH, there would be so little H_3PO_4 present that we could hardly consider it a buffer; this solution would not be effective in resisting pH changes, especially when a strong base is added.

94. a. Because all acids are the same initial concentration, the pH curve with the highest pH at 0 mL of NaOH added will correspond to the titration of the weakest acid. This is pH curve f.

b. The pH curve with the lowest pH at 0 mL of NaOH added will correspond to the titration of the strongest acid. This is pH curve a.

The best point to look at to differentiate a strong acid from a weak acid titration (if initial concentrations are not known) is the equivalence point pH. If the pH = 7.00, the acid titrated is a strong acid; if the pH is greater than 7.00, the acid titrated is a weak acid.

c. For a weak acid-strong base titration, the pH at the halfway point to equivalence is equal to the pK_a value. The pH curve, which represents the titration of an acid with $K_a = 1.0 \times 10^{-6}$, will have a $pH = -\log(1 \times 10^{-6}) = 6.0$ at the halfway point. The equivalence point, from the plots, occurs at 50 mL NaOH added, so the halfway point is 25 mL. Plot d has a pH ≈ 6.0 at 25 mL of NaOH added, so the acid titrated in this pH curve (plot d) has $K_a \approx 1 \times 10^{-6}$.

95. In the final solution: $[H^+] = 10^{-2.15} = 7.1 \times 10^{-3}\ M$

Beginning mmol HCl = 500.0 mL × 0.200 mmol/mL = 100. mmol HCl

Amount of HCl that reacts with NaOH = 1.50×10^{-2} mmol/mL × V

$$\frac{7.1 \times 10^{-3}\ \text{mmol}}{\text{mL}} = \frac{\text{final mmol H}^+}{\text{total volume}} = \frac{100. - (0.0150)\text{V}}{500.0\ + \text{V}}$$

$3.6 + (7.1 \times 10^{-3})V = 100. - (1.50 \times 10^{-2})V$, $(2.21 \times 10^{-2})V = 100. - 3.6$

$V = 4.36 \times 10^3$ mL = 4.36 L = 4.4 L NaOH

97. a. This is a strong acid (HI) titrated by a strong base (NaOH). Added OH^- from the strong base will react completely with the H^+ present from the strong acid to produce H_2O.

$$\text{mmol OH}^- \text{ added} = 20.0\ \text{mL} \times \frac{0.250\ \text{mmol OH}^-}{\text{mL}} = 5.00\ \text{mmol OH}^-$$

$$\text{mmol H}^+ \text{ present} = 150.0\ \text{mL} \times \frac{0.100\ \text{mmol H}^+}{\text{mL}} = 15.0\ \text{mmol H}^+$$

Note: The units millimoles are usually easier numbers to work with. The units for molarity are moles per liter but are also equal to millimoles per milliliter.

	H^+	+	OH^-	→ H_2O	
Before	15.0 mmol		5.00 mmol		
Change	−5.00 mmol		−5.00 mmol		Reacts completely
After	10.0 mmol		0		

$$\text{The excess H}^+ \text{ determines the pH.}\ [\text{H}^+]_{\text{excess}} = \frac{10.0\ \text{mmol H}^+}{150.0\ \text{mL} + 20.0\ \text{mL}} = 0.0588\ M$$

$pH = -\log(0.0588) = 1.231$

b. For a strong acid-strong base titration, pH = 7.00 at the equivalence point. Because we have 15.0 mmol of H^+, we need 15.0 mmol of OH^- to reach the equivalence point.

$$15.0 \text{ mmol OH}^- \times \frac{1 \text{ mL OH}^-}{0.250 \text{ mmol OH}^-} = 60.0 \text{ mL OH}^-$$

To reach the equivalence point where pH = 7.00, 60.0 mL of NaOH must be added.

106. $HA + OH^- \rightarrow A^- + H_2O$; it takes 25.0 mL of 0.100 *M* NaOH to reach the equivalence point, where mmol HA = mmol OH^- = 25.0 mL(0.100 *M*) = 2.50 mmol. At the equivalence point, some HCl is added. The H^+ from the strong acid reacts to completion with the best base present, A^-.

	H^+	+	A^-	$\rightarrow$	HA
Before	13.0 mL × 0.100 *M*		2.5 mmol		0
Change	−1.3 mmol		−1.3 mmol		+1.3 mmol
After	0		1.2 mmol		1.3 mmol

A buffer solution is present after the H^+ has reacted completely.

$$pH = pK_a + \log\frac{[A^-]}{[HA]}, \quad 4.70 = pK_a + \log\left(\frac{1.2 \text{ mmol}/V_T}{1.3 \text{ mmol}/V_T}\right), \text{ where } V_T = \text{total volume}$$

Because the log term will be negative [log(1.2/1.3) = –0.035)], the pK_a value of the acid must be greater than 4.70 (pK_a = 4.70 + 0.035 = 4.74).

115. The first titration plot (from 0 – 100.0 mL) corresponds to the titration of H_2A by OH^-. The reaction is $H_2A + OH^- \rightarrow HA^- + H_2O$. After all the H_2A has been reacted, the second titration (from 100.0 – 200.0 mL) corresponds to the titration of HA^- by OH^-. The reaction is $HA^- + OH^- \rightarrow A^{2-} + H_2O$.

a. At 100.0 mL of NaOH, just enough OH^- has been added to react completely with all the H_2A present (mol OH^- added = mol H_2A present initially). From the balanced equation, the mol of HA^- produced will equal the mol of H_2A present initially. Because mol of HA^- present at 100.0 mL OH^- added equals the mol of H_2A present initially, exactly 100.0 mL more of NaOH must be added to react with all the HA^-. The volume of NaOH added to reach the second equivalence point equals 100.0 mL + 100.0 mL = 200.0 mL.

b. $H_2A + OH^- \rightarrow HA^- + H_2O$ is the reaction occurring from 0 – 100.0 mL NaOH added.

$HA^- + OH^- \rightarrow A^{2-} + H_2O$ is the reaction occurring from 100.0 – 200.0 mL NaOH added.

i. No reaction has taken place, so H_2A and H_2O are the major species.

ii. Adding OH^- converts H_2A into HA^-. The major species between 0 and 100.0 mL NaOH added are H_2A, HA^-, H_2O, and Na^+.

iii. At 100.0 mL NaOH added, mol of OH^- = mol H_2A, so all of the H_2A present initially has been converted into HA^-. The major species are HA^-, H_2O, and Na^+.

iv. Between 100.0 and 200.0 mL NaOH added, the OH^- converts HA^- into A^{2-}. The major species are HA^-, A^{2-}, H_2O, and Na^+.

v. At the second equivalence point (200.0 mL), just enough OH^- has been added to convert all the HA^- into A^{2-}. The major species are A^{2-}, H_2O, and Na^+.

vi. Past 200.0 mL NaOH added, excess OH^- is present. The major species are OH^-, A^{2-}, H_2O, and Na^+.

c. 50.0 mL of NaOH added corresponds to the first halfway point to equivalence. Exactly one-half of the H_2A present initially has been converted into its conjugate base HA^-, so $[H_2A] = [HA^-]$ in this buffer solution.

$$H_2A \rightleftharpoons HA^- + H^+ \qquad K_{a_1} = \frac{[HA^-][H^+]}{[H_2A]}$$

When $[HA^-] = [H_2A]$, then $K_{a_1} = [H^+]$ or $pK_{a_1} = pH$.

Here, pH = 4.0, so $pK_{a_1} = 4.0$ and $K_{a_1} = 10^{-4.0} = 1 \times 10^{-4}$.

150.0 mL of NaOH added correspond to the second halfway point to equivalence, where $[HA^-] = [A^{2-}]$ in this buffer solution.

$$HA^- \rightleftharpoons A^{2-} + H^+ \qquad K_{a_2} = \frac{[A^{2-}][H^+]}{[HA^-]}$$

When $[A^{2-}] = [HA^-]$, then $K_{a_2} = [H^+]$ or $pK_{a_2} = pH$.

Here, pH = 8.0, so $pK_{a_2} = 8.0$ and $K_{a_2} = 10^{-8.0} = 1 \times 10^{-8}$.