CHAPTER 15

ACID-BASE EQUILIBRIA

Questions

9. When an acid dissociates, ions are produced. The common ion effect is observed when one of the product ions in a particular equilibrium is added from an outside source. For a weak acid dissociating to its conjugate base and H^+, the common ion would be the conjugate base; this would be added by dissolving a soluble salt of the conjugate base into the acid solution. The presence of the conjugate base from an outside source shifts the equilibrium to the left so less acid dissociates.

10. $pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$; 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 $pH < pK_a$. When one has more acid than base in a buffer, the pH will be on the acidic side of the pK_a value; that is, the pH is at a value lower than the pK_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 $pH > pK_a$. When one has more base than acid in a buffer, the pH is on the basic side of the pK_a value; that is, the pH is at a value greater than the pK_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 $pH = pK_a$.

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 $pH = pK_a$), 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. 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 $pH = pK_a$.

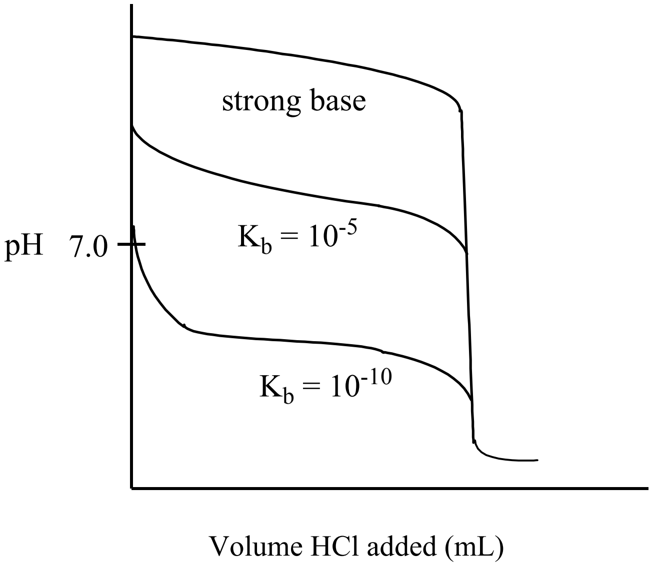
$$HOC_6H_5;\ K_a = 1.6 \times 10^{-10},\ pK_a = -\log(1.6 \times 10^{-10}) = 9.80$$

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

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}).

13. 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.



14. $HIn \rightleftharpoons H^+ + In^-$ $K_a = \dfrac{[H^+][In^-]}{[HIn]}$

Indicators are weak acids themselves. The special property they have is that the acid form of the indicator (HIn) has one distinct color, whereas the conjugate base form (In^-) has a different distinct color. Which form dominates and thus determines the color of the solution is determined by the pH. An indicator is chosen in order to match the pH of the color change at about the pH of the equivalence point.

Exercises

Buffers

15. 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:

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

16. Similar to the HCO_3^-/CO_3^{2-} buffer discussed in Exercise 15, the $HONH_3^+/HONH_2$ buffer absorbs added OH^- and H^+ in the same fashion.

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

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

17. a. This is a weak acid problem. Let $HC_3H_5O_2$ = HOPr and $C_3H_5O_2^-$ = OPr^-.

$$HOPr(aq) \rightleftharpoons H^+(aq) + OPr^-(aq) \qquad K_a = 1.3 \times 10^{-5}$$

Initial	$0.100\ M$		~ 0	0
	x mol/L HOPr dissociates to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.100 - x$		x	x

$$K_a = 1.3 \times 10^{-5} = \frac{[H^+][OPr^-]}{[HOPr]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = [H^+] = 1.1 \times 10^{-3}\ M$; pH = 2.96; assumptions good by the 5% rule.

b. This is a weak base problem.

$$OPr^-(aq) + H_2O(l) \rightleftharpoons HOPr(aq) + OH^-(aq) \quad K_b = \frac{K_w}{K_a} = 7.7 \times 10^{-10}$$

Initial	$0.100\ M$		0	~ 0
	x mol/L OPr^- reacts with H_2O to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.100 - x$		x	x

$$K_b = 7.7 \times 10^{-10} = \frac{[HOPr][OH^-]}{[OPr^-]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = [OH^-] = 8.8 \times 10^{-6}\ M$; pOH = 5.06; pH = 8.94; assumptions good.

c. Pure H_2O, $[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$; pH = 7.00

d. This solution contains a weak acid and its conjugate base. This is a buffer solution. We will solve for the pH through the weak acid equilibrium reaction.

$$HOPr(aq) \rightleftharpoons H^+(aq) + OPr^-(aq) \qquad K_a = 1.3 \times 10^{-5}$$

Initial	$0.100\ M$		~ 0	$0.100\ M$
	x mol/L HOPr dissociates to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.100 - x$		x	$0.100 + x$

$$1.3 \times 10^{-5} = \frac{(0.100 + x)(x)}{0.100 - x} \approx \frac{(0.100)(x)}{0.100} = x = [H^+]$$

$[H^+] = 1.3 \times 10^{-5}\ M$; pH = 4.89; assumptions good.

Alternately, we can use the Henderson-Hasselbalch equation to calculate the pH of buffer solutions.

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = pK_a + \log\left(\frac{0.100}{0.100}\right) = pK_a = -\log(1.3 \times 10^{-5}) = 4.89$$

The Henderson-Hasselbalch equation will be valid when an assumption of the type $0.1 + x \approx 0.1$ that we just made in this problem is valid. From a practical standpoint, this will almost always be true for useful buffer solutions. If the assumption is not valid, the solution will have such a low buffering capacity it will not be of any use to control the pH. *Note*: The Henderson-Hasselbalch equation can <u>only</u> be used to solve for the pH of buffer solutions.

18. a. Weak base problem:

	$HONH_2$	+	H_2O	$\rightleftharpoons$	$HONH_3^+$	+	OH^-	$K_b = 1.1 \times 10^{-8}$
Initial	$0.100\ M$				0		~0	
	x mol/L $HONH_2$ reacts with H_2O to reach equilibrium							
Change	$-x$			→	$+x$		$+x$	
Equil.	$0.100 - x$				x		x	

$$K_b = 1.1 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = [OH^-] = 3.3 \times 10^{-5}\ M$; pOH = 4.48; pH = 9.52; assumptions good.

b. Weak acid problem (Cl^- has no acidic/basic properties);

	$HONH_3^+$	$\rightleftharpoons$	$HONH_2$	+	H^+
Initial	$0.100\ M$		0		~0
	x mol/L $HONH_3^+$ dissociates to reach equilibrium				
Change	$-x$	→	$+x$		$+x$
Equil.	$0.100 - x$		x		x

$$K_a = \frac{K_w}{K_b} = 9.1 \times 10^{-7} = \frac{[HONH_2][H^+]}{[HONH_3^+]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = [H^+] = 3.0 \times 10^{-4}\ M$; pH = 3.52; assumptions good.

c. Pure H_2O, pH = 7.00

d. Buffer solution where $pK_a = -\log(9.1 \times 10^{-7}) = 6.04$. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 6.04 + \log\frac{[HONH_2]}{[HONH_3^+]} = 6.04 + \log\frac{(0.100)}{(0.100)} = 6.04$$

19. 0.100 M $HC_3H_5O_2$: Percent dissociation $= \frac{[H^+]}{[HC_3H_5O_2]_0} \times 100 = \frac{1.1 \times 10^{-3}\ M}{0.100\ M} \times 100 = 1.1\%$

0.100 M $HC_3H_5O_2$ + 0.100 M $NaC_3H_5O_2$: % dissociation $= \frac{1.3 \times 10^{-5}}{0.100} \times 100 = 1.3 \times 10^{-2}\ \%$

The percent dissociation of the acid decreases from 1.1% to 1.3×10^{-2} % when $C_3H_5O_2^-$ is present. This is known as the common ion effect. The presence of the conjugate base of the weak acid inhibits the acid dissociation reaction.

20. 0.100 M $HONH_2$: Percent ionization $\frac{[OH^-]}{[HONH_2]_0} \times 100 = \frac{3.3 \times 10^{-5}\ M}{0.100\ M} \times 100 = 3.3 \times 10^{-2}\ \%$

0.100 M $HONH_2$ + 0.100 M $HONH_3^+$: % ionization $= \frac{1.1 \times 10^{-8}}{0.100} \times 100 = 1.1 \times 10^{-5}\%$

The percent ionization decreases by a factor of 3000. The presence of the conjugate acid of the weak base inhibits the weak base reaction with water. This is known as the common ion effect.

21. a. We have a weak acid (HOPr = $HC_3H_5O_2$) and a strong acid (HCl) present. The amount of H^+ donated by the weak acid will be negligible. To prove it, consider the weak acid equilibrium reaction:

	HOPr	⇌	H^+	+	OPr^-	$K_a = 1.3 \times 10^{-5}$
Initial	0.100 M		0.020 M		0	
	x mol/L HOPr dissociates to reach equilibrium					
Change	$-x$	→	$+x$		$+x$	
Equil.	$0.100 - x$		$0.020 + x$		x	

$[H^+] = 0.020 + x \approx 0.020\ M$; pH = 1.70; assumption good ($x = 6.5 \times 10^{-5}$ is << 0.020).

Note: The H^+ contribution from the weak acid HOPr was negligible. The pH of the solution can be determined by only considering the amount of strong acid present.

b. Added H^+ reacts completely with the best base present, OPr^-.

	OPr^-	+	H^+	→	HOPr	
Before	0.100 M		0.020 M		0	
Change	−0.020		−0.020	→	+0.020	Reacts completely
After	0.080		0		0.020 M	

After reaction, a weak acid, HOPr , and its conjugate base, OPr^-, are present. This is a buffer solution. Using the Henderson-Hasselbalch equation where $pK_a = -\log(1.3 \times 10^{-5}) = 4.89$:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 4.89 + \log\frac{(0.080)}{(0.020)} = 5.49;\quad \text{assumptions good.}$$

c. This is a strong acid problem. $[H^+] = 0.020\ M$; pH = 1.70

d. Added H^+ reacts completely with the best base present, OPr^-.

	OPr^-	+	H^+	→	HOPr	
Before	0.100 *M*		0.020 *M*		0.100 *M*	
Change	–0.020		–0.020	→	+0.020	Reacts completely
After	0.080		0		0.120	

A buffer solution results (weak acid + conjugate base). Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 4.89 + \log\frac{(0.080)}{(0.120)} = 4.71; \text{ assumptions good.}$$

22. a. Added H^+ reacts completely with $HONH_2$ (the best base present) to form $HONH_3^+$.

	$HONH_2$	+	H^+	→	$HONH_3^+$	
Before	0.100 *M*		0.020 *M*		0	
Change	−0.020		−0.020	→	+0.020	Reacts completely
After	0.080		0		0.020	

After this reaction, a buffer solution exists; that is, a weak acid ($HONH_3^+$) and its conjugate base ($HONH_2$) are present at the same time. Using the Henderson-Hasselbalch equation to solve for the pH where $pK_a = -\log(K_w/K_b) = 6.04$:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 6.04 + \log\frac{(0.080)}{(0.020)} = 6.04 + 0.60 = 6.64$$

b. We have a weak acid and a strong acid present at the same time. The H^+ contribution from the weak acid, $HONH_3^+$, will be negligible. So we have to consider only the H^+ from HCl. $[H^+] = 0.020$ *M*; pH = 1.70

c. This is a strong acid in water. $[H^+] = 0.020$ *M*; pH = 1.70

d. Major species: H_2O, Cl^-, $HONH_2$, $HONH_3^+$, H^+

H^+ will react completely with $HONH_2$, the best base present.

	$HONH_2$	+	H^+	→	$HONH_3^+$	
Before	0.100 *M*		0.020 *M*		0.100 *M*	
Change	−0.020		−0.020	→	+0.020	Reacts completely
After	0.080		0		0.120	

A buffer solution results after reaction. Using the Henderson-Hasselbalch equation:

$$pH = 6.04 + \log\frac{[HONH_2]}{[HONH_3^+]} = 6.04 + \log\frac{(0.080)}{(0.120)} = 6.04 - 0.18 = 5.86$$

23. a. OH^- will react completely with the best acid present, HOPr.

$$HOPr + OH^- \rightarrow OPr^- + H_2O$$

	$HOPr$	OH^-		OPr^-	
Before	$0.100\ M$	$0.020\ M$		0	
Change	–0.020	–0.020	→	+0.020	Reacts completely
After	0.080	0		0.020	

A buffer solution results after the reaction. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 4.89 + \log\frac{(0.020)}{(0.080)} = 4.29;\ \text{assumptions good.}$$

b. We have a weak base and a strong base present at the same time. The amount of OH^- added by the weak base will be negligible. To prove it, let's consider the weak base equilibrium:

$$OPr^- + H_2O \rightleftharpoons HOPr + OH^- \qquad K_b = 7.7 \times 10^{-10}$$

	OPr^-		$HOPr$	OH^-
Initial	$0.100\ M$		0	$0.020\ M$
	x mol/L OPr^- reacts with H_2O to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.100 - x$		x	$0.020 + x$

$[OH^-] = 0.020 + x \approx 0.020\ M$; pOH = 1.70; pH = 12.30; assumption good.

Note: The OH^- contribution from the weak base OPr^- was negligible ($x = 3.9 \times 10^{-9}\ M$ as compared to $0.020\ M$ OH^- from the strong base). The pH can be determined by only considering the amount of strong base present.

c. This is a strong base in water. $[OH^-] = 0.020\ M$; pOH = 1.70; pH = 12.30

d. OH^- will react completely with HOPr, the best acid present.

$$HOPr + OH^- \rightarrow OPr^- + H_2O$$

	$HOPr$	OH^-		OPr^-	
Before	$0.100\ M$	$0.020\ M$		$0.100\ M$	
Change	–0.020	–0.020	→	+0.020	Reacts completely
After	0.080	0		0.120	

Using the Henderson-Hasselbalch equation to solve for the pH of the resulting buffer solution:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 4.89 + \log\frac{(0.120)}{(0.080)} = 5.07;\ \text{assumptions good.}$$

24. a. We have a weak base and a strong base present at the same time. The OH^- contribution from the weak base, $HONH_2$, will be negligible. Consider only the added strong base as the primary source of OH^-.

$[OH^-] = 0.020\ M$; pOH = 1.70; pH = 12.30

b. Added strong base will react to completion with the best acid present, $HONH_3^+$.

	OH^-	+	$HONH_3^+$	→	$HONH_2$	+	H_2O	
Before	0.020 *M*		0.100 *M*		0			
Change	−0.020		−0.020	→	+0.020			Reacts completely
After	0		0.080		0.020			

The resulting solution is a buffer (a weak acid and its conjugate base). Using the Henderson-Hasselbalch equation:

$$pH = 6.04 + \log\frac{(0.020)}{(0.080)} = 6.04 - 0.60 = 5.44$$

c. This is a strong base in water. $[OH^-] = 0.020$ *M*; pOH = 1.70; pH = 12.30

d. Major species: H_2O, Cl^-, Na^+, $HONH_2$, $HONH_3^+$, OH^-; again, the added strong base reacts completely with the best acid present, $HONH_3^+$.

	$HONH_3^+$	+	OH^-	→	$HONH_2$	+	H_2O	
Before	0.100 *M*		0.020 *M*		0.100 *M*			
Change	−0.020		−0.020	→	+0.020			Reacts completely
After	0.080		0		0.120			

A buffer solution results. Using the Henderson-Hasselbalch equation:

$$pH = 6.04 + \log\frac{[HONH_2]}{[HONH_3^+]} = 6.04 + \log\frac{(0.120)}{(0.080)} = 6.04 + 0.18 = 6.22$$

25. Consider all the results to Exercises 17, 21, and 23:

Solution	Initial pH	After Added H^+	After Added OH^-
a	2.96	1.70	4.29
b	8.94	5.49	12.30
c	7.00	1.70	12.30
d	4.89	4.71	5.07

The solution in Exercise 17d is a buffer; it contains both a weak acid ($HC_3H_5O_2$) and a weak base ($C_3H_5O_2^-$). Solution d shows the greatest resistance to changes in pH when either a strong acid or a strong base is added, which is the primary property of buffers.

26. Consider all of the results to Exercises 18, 22, and 24.

Solution	Initial pH	After Added H^+	After Added OH^-
a	9.52	6.64	12.30
b	3.52	1.70	5.44
c	7.00	1.70	12.30
d	6.04	5.86	6.22

The solution in Exercise 18d is a buffer; it shows the greatest resistance to a change in pH when strong acid or base is added. The solution in Exercise 18d contains a weak acid ($HONH_3^+$) and a weak base ($HONH_2$), which constitutes a buffer solution.

27. 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

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

$x = 4.0 \times 10^{-4}\ M = [H^+]$; 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.

28. 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.

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

29. 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.

	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

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

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^-	$\rightarrow$	HNO_2	
Before	$\dfrac{0.20\ \text{mol}}{1.00\ \text{L}}$		1.00 M		1.00 M	
Change	−0.20 M		−0.20 M	$\rightarrow$	+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.	$1.20 - x$		$0.80 + x$		$+x$

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

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.

30. 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	$\rightarrow$	F^-	+ H_2O	
Before	0.10 mol/1.00 L		0.60 M		1.00 M		
Change	−0.10 M		−0.10 M	$\rightarrow$	+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	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.50 - x$		$1.10 + x$		x

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

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^-	$\rightarrow$	HF	
Before	$\frac{0.20\ \text{mol}}{1.00\ \text{L}}$		1.00 M		0.60 M	
Change	−0.20 M		−0.20 M	$\rightarrow$	+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	$\rightleftharpoons$	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.

31. a. $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$ $K_a = 1.8 \times 10^{-5}$

	$HC_2H_3O_2$		H^+	$C_2H_3O_2^-$
Initial	$0.10\ M$		~0	$0.25\ M$
	x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.10 - x$		x	$0.25 + x$

$$1.8 \times 10^{-5} = \frac{x(0.25 + x)}{(0.10 - x)} \approx \frac{x(0.25)}{0.10} \quad \text{(assuming } 0.25 + x \approx 0.25 \text{ and } 0.10 - x \approx 0.10\text{)}$$

$x = [H^+] = 7.2 \times 10^{-6}\ M$; pH = 5.14; assumptions good by the 5% rule.

Alternatively, we can use the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}, \text{ where } pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$pH = 4.74 + \log\frac{(0.25)}{(0.10)} = 4.74 + 0.40 = 5.14$$

The Henderson-Hasselbalch equation will be valid when assumptions of the type, $0.10 - x \approx 0.10$, that we just made are valid. From a practical standpoint, this will almost always be true for useful buffer solutions. *Note*: The Henderson-Hasselbalch equation can only be used to solve for the pH of buffer solutions.

b. $pH = 4.74 + \log\frac{(0.10)}{(0.25)} = 4.74 + (-0.40) = 4.34$

c. $pH = 4.74 + \log\frac{(0.20)}{(0.080)} = 4.74 + 0.40 = 5.14$

d. $pH = 4.74 + \log\frac{(0.080)}{(0.20)} = 4.74 + (-0.40) = 4.34$

32. We will use the Henderson-Hasselbalch equation to solve for the pH of these buffer solutions.

a. $pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$; $[\text{base}] = [C_2H_5NH_2] = 0.50\ M$; $[\text{acid}] = [C_2H_5NH_3^+] = 0.25\ M$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11}$$

$$pH = -\log(1.8 \times 10^{-11}) + \log\frac{(0.50\ M)}{(0.25\ M)} = 10.74 + 0.30 = 11.04$$

b. $pH = 10.74 + \log\frac{(0.25\ M)}{(0.50\ M)} = 10.74 + (-0.30) = 10.44$

c. $pH = 10.74 + \log\frac{(0.50\ M)}{(0.50\ M)} = 10.74 + 0 = 10.74$

33. $$[HC_7H_5O_2] = \frac{21.5\text{ g }HC_7H_5O_2 \times \dfrac{1\text{ mol }HC_7H_5O_2}{122.12\text{ g}}}{0.2000\text{ L}} = 0.880\ M$$

$$[C_7H_5O_2^-] = \frac{37.7\text{ g }NaC_7H_5O_2 \times \dfrac{1\text{ mol }NaC_7H_5O_2}{144.10\text{ g}} \times \dfrac{1\text{ mol }C_7H_5O_2^-}{\text{mol }NaC_7H_5O_2}}{0.2000\text{ L}} = 1.31\ M$$

We have a buffer solution since we have both a weak acid and its conjugate base present at the same time. One can use the K_a reaction or the K_b reaction to solve. We will use the K_a reaction for the acid component of the buffer.

	$HC_7H_5O_2$	$\rightleftharpoons$	H^+	+	$C_7H_5O_2^-$
Initial	$0.880\ M$		~0		$1.31\ M$
	x mol/L of $HC_7H_5O_2$ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.880 - x$		x		$1.31 + x$

$$K_a = 6.4 \times 10^{-5} = \frac{x(1.31 + x)}{0.880 - x} \approx \frac{x(1.31)}{0.880},\ x = [H^+] = 4.3 \times 10^{-5}\ M$$

$pH = -\log(4.3 \times 10^{-5}) = 4.37$; assumptions good.

Alternatively, we can use the Henderson-Hasselbalch equation to calculate the pH of buffer solutions.

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = pK_a + \log\frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]}$$

$$pH = -\log(6.4 \times 10^{-5}) + \log\left(\frac{1.31}{0.880}\right) = 4.19 + 0.173 = 4.36$$

Within round-off error, this is the same answer we calculated solving the equilibrium problem using the K_a reaction.

The Henderson-Hasselbalch equation will be valid when an assumption of the type $1.31 + x \approx 1.31$ that we just made in this problem is valid. From a practical standpoint, this will almost always be true for useful buffer solutions. If the assumption is not valid, the solution will have such a low buffering capacity that it will be of no use to control the pH. *Note*: The Henderson-Hasselbalch equation can only be used to solve for the pH of buffer solutions.

34. $50.0\text{ g }NH_4Cl \times \dfrac{1\text{ mol }NH_4Cl}{53.49\text{ g }NH_4Cl} = 0.935\text{ mol }NH_4Cl$ added to 1.00 L; $[NH_4^+] = 0.935\ M$

Using the Henderson Hasselbalch equation to solve for the pH of this buffer solution:

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.6 \times 10^{-10}) + \log\left(\frac{0.75}{0.935}\right) = 9.25 - 0.096 = 9.15$$

35. $[H^+]$ 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:

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

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. $\text{pH} = \text{pK}_a + \log\dfrac{[NH_3]}{[NH_4^+]}$, $9.25 + \log\left(\dfrac{0.46}{1.54}\right) = 8.73$

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^-.

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

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

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

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

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

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

37. $\text{pH} = \text{pK}_a + \log\dfrac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$; $\text{pK}_a = -\log(1.8 \times 10^{-5}) = 4.74$

Because the buffer components, $C_2H_3O_2^-$ and $HC_2H_3O_2$, are both in the same volume of solution, the concentration ratio of $[C_2H_3O_2^-] : [HC_2H_3O_2]$ will equal the mole ratio of mol $C_2H_3O_2^-$ to mol $HC_2H_3O_2$.

$$5.00 = 4.74 + \log\frac{\text{mol } C_2H_3O_2^-}{\text{mol } HC_2H_3O_2};\ \text{mol } HC_2H_3O_2 = 0.5000 \text{ L} \times \frac{0.200 \text{ mol}}{\text{L}} = 0.100 \text{ mol}$$

$$0.26 = \log\frac{\text{mol } C_2H_3O_2^-}{0.100 \text{ mol}},\ \frac{\text{mol } C_2H_3O_2^-}{0.100} = 10^{0.26} = 1.8,\ \text{mol } C_2H_3O_2^- = 0.18 \text{ mol}$$

$$\text{Mass } NaC_2H_3O_2 = 0.18 \text{ mol } NaC_2H_3O_2 \times \frac{82.03 \text{ g}}{\text{mol}} = 15 \text{ g } NaC_2H_3O_2$$

38. $\text{pH} = \text{pK}_a + \log\dfrac{[NO_2^-]}{[HNO_2]}$, $3.55 = -\log(4.0 \times 10^{-4}) + \log\dfrac{[NO_2^-]}{[HNO_2]}$

$$3.55 = 3.40 + \log\frac{[NO_2^-]}{[HNO_2]},\ \frac{[NO_2^-]}{[HNO_2]} = 10^{0.15} = 1.4 = \frac{\text{mol } NO_2^-}{\text{mol } HNO_2}$$

Let x = volume (L) of HNO_2 solution needed; then $1.00 - x$ = volume of $NaNO_2$ solution needed to form this buffer solution.

$$\frac{\text{Mol } NO_2^-}{\text{Mol } HNO_2} = 1.4 = \frac{(1.00 - x) \times \dfrac{0.50 \text{ mol } NaNO_2}{\text{L}}}{x \times \dfrac{0.50 \text{ mol } HNO_2}{\text{L}}} = \frac{0.50 - (0.50)x}{(0.50)x}$$

$$(0.70)x = 0.50 - (0.50)x,\ (1.20)x = 0.50,\ x = 0.42 \text{ L}$$

We need 0.42 L of 0.50 *M* HNO_2 and 1.00 – 0.42 = 0.58 L of 0.50 *M* $NaNO_2$ to form a pH = 3.55 buffer solution.

39. $C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N \quad K_a = \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$

$\text{pK}_a = -\log(5.9 \times 10^{-6}) = 5.23$

We will use the Henderson-Hasselbalch equation to calculate the concentration ratio necessary for each buffer.

$$\text{pH} = \text{pK}_a + \log\frac{[\text{base}]}{[\text{acid}]},\ \text{pH} = 5.23 + \log\frac{[C_5H_5N]}{[C_5H_5NH^+]}$$

a. $4.50 = 5.23 + \log\dfrac{[C_5H_5N]}{[C_5H_5NH^+]}$, $\dfrac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{-0.73} = 0.19$

b. $5.00 = 5.23 + \log\frac{[C_5H_5N]}{[C_5H_5NH^+]}$, $\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{-0.23} = 0.59$

c. $5.23 = 5.23 + \log\frac{[C_5H_5N]}{[C_5H_5NH^+]}$, $\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{0.0} = 1.0$

d. $5.50 = 5.23 + \log\frac{[C_5H_5N]}{[C_5H_5NH^+]}$, $\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{0.27} = 1.9$

40. $NH_4^+ \rightleftharpoons H^+ + NH_3$ $K_a = K_w/K_b = 5.6 \times 10^{-10}$; $pK_a = -\log(5.6 \times 10^{-10}) = 9.25$; we will use the Henderson-Hasselbalch equation to calculate the concentration ratio necessary for each buffer.

$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$, $pH = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}$

a. $9.00 = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}$, $\frac{[NH_3]}{[NH_4^+]} = 10^{-0.25} = 0.56$

b. $8.80 = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}$, $\frac{[NH_3]}{[NH_4^+]} = 10^{-0.45} = 0.35$

c. $10.00 = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}$, $\frac{[NH_3]}{[NH_4^+]} = 10^{0.75} = 5.6$

d. $9.60 = 9.25 + \log\frac{[NH_3]}{[NH_4^+]}$, $\frac{[NH_3]}{[NH_4^+]} = 10^{0.35} = 2.2$

41. A best buffer has large and equal quantities of weak acid and conjugate base. Because [acid] = [base] for a best buffer, $pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = pK_a + 0 = pK_a$ ($pH \approx pK_a$ 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 14.2 ($K_a = 3.5 \times 10^{-8}$; $pK_a = 7.46$). To make this buffer, we need to calculate the [base] : [acid] ratio.

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

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*.

42. 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 14.3 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.

43. 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 in order for $[H_2NNH_3^+] = [H_2NNH_2]$. Both of these 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. So:

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

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 in order to produce a solution where pH = pK_a.

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

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 in order to achieve a solution where pH = pK_a. Both of these 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^-.

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

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 in order to produce a solution where pH = pK_a.

45. The reaction $OH^- + CH_3NH_3^+ \rightarrow CH_3NH_2 + H_2O$ goes to completion for solutions a, c, and d (no reaction occurs between the species in solution b because both species are bases). After the OH^- reacts completely, there must be both $CH_3NH_3^+$ and CH_3NH_2 in solution for it to be a buffer. The important components of each solution (after the OH^- reacts completely) is(are):

    a. 0.05 *M* CH_3NH_2 (no $CH_3NH_3^+$ remains, no buffer)
    b. 0.05 *M* OH^- and 0.1 *M* CH_3NH_2 (two bases present, no buffer)
    c. 0.05 *M* OH^- and 0.05 *M* CH_3NH_2 (too much OH^- added, no $CH_3NH_3^+$ remains, no buffer)
    d. 0.05 *M* CH_3NH_2 and 0.05 *M* $CH_3NH_3^+$ (a buffer solution results)

    Only the combination in mixture d results in a buffer. Note that the concentrations are halved from the initial values. This is so because equal volumes of two solutions were added together, which halves the concentrations.

46. a. No; a solution of a strong acid (HNO_3) and its conjugate base (NO_3^-) is not generally considered a buffer solution.

    b. No; two acids are present (HNO_3 and HF), so it is not a buffer solution.

    c. H^+ reacts completely with F^-. Since equal volumes are mixed, the initial concentrations in the mixture are 0.10 *M* HNO_3 and 0.20 *M* NaF.

	H^+	+	F^-	$\rightarrow$	HF	
Before	0.10 *M*		0.20 *M*		0	
Change	−0.10		−0.10	$\rightarrow$	+0.10	Reacts completely
After	0		0.10		0.10	

After H^+ reacts completely, a buffer solution results; that is, a weak acid (HF) and its conjugate base (F^-) are both present in solution in large quantities.

d. No; a strong acid (HNO_3) and a strong base (NaOH) do not form buffer solutions. They will neutralize each other to form H_2O.

47. Added OH^- converts $HC_2H_3O_2$ into $C_2H_3O_2^-$: $HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$

    From this reaction, the moles of $C_2H_3O_2^-$ produced equal the moles of OH^- added. Also, the total concentration of acetic acid plus acetate ion must equal 2.0 *M* (assuming no volume change on addition of NaOH). Summarizing for each solution:

$[C_2H_3O_2^-] + [HC_2H_3O] = 2.0\ M$ and $[C_2H_3O_2^-]$ produced = $[OH^-]$ added

a. $pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$; for $pH = pK_a$, $\log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 0$

Therefore, $\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.0$ and $[C_2H_3O_2^-] = [HC_2H_3O_2]$.

Because $[C_2H_3O_2^-] + [HC_2H_3O_2] = 2.0\ M$:

$[C_2H_3O_2^-] = [HC_2H_3O_2] = 1.0\ M = [OH^-]$ added

To produce a 1.0 M $C_2H_3O_2^-$ solution, we need to add 1.0 mol of NaOH to 1.0 L of the 2.0 M $HC_2H_3O_2$ solution. The resulting solution will have $pH = pK_a = 4.74$.

b. $4.00 = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$, $\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{-0.74} = 0.18$

$[C_2H_3O_2^-] = 0.18[HC_2H_3O_2]$ or $[HC_2H_3O_2] = 5.6[C_2H_3O_2^-]$

Because $[C_2H_3O_2^-] + [HC_2H_3O_2] = 2.0\ M$:

$[C_2H_3O_2^-] + 5.6[C_2H_3O_2^-] = 2.0\ M$, $[C_2H_3O_2^-] = \frac{2.0}{6.6} = 0.30\ M = [OH^-]$ added

We need to add 0.30 mol of NaOH to 1.0 L of 2.0 M $HC_2H_3O_2$ solution to produce 0.30 M $C_2H_3O_2^-$. The resulting solution will have pH = 4.00.

c. $5.00 = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$, $\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{0.26} = 1.8$

$1.8[HC_2H_3O_2] = [C_2H_3O_2^-]$ or $[HC_2H_3O_2] = 0.56[C_2H_3O_2^-]$

$1.56[C_2H_3O_2^-] = 2.0\ M$, $[C_2H_3O_2^-] = 1.3\ M = [OH^-]$ added

We need to add 1.3 mol of NaOH to 1.0 L of 2.0 M $HC_2H_3O_2$ to produce a solution with pH = 5.00.

48. When H^+ is added, it converts $C_2H_3O_2^-$ into $HC_2H_3O_2$: $C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$. From this reaction, the moles of $HC_2H_3O_2$ produced must equal the moles of H^+ added and the total concentration of acetate ion + acetic acid must equal 1.0 M (assuming no volume change). Summarizing for each solution:

$[C_2H_3O_2^-] + [HC_2H_3O_2] = 1.0\ M$ and $[HC_2H_3O_2] = [H^+]$ added

a. $pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$; for $pH = pK_a$, $[C_2H_3O_2^-] = [HC_2H_3O_2]$.

For this to be true, $[C_2H_3O_2^-] = [HC_2H_3O_2] = 0.50\ M = [H^+]$ added, which means that 0.50 mol of HCl must be added to 1.0 L of the initial solution to produce a solution with $pH = pK_a$.

b. $4.20 = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}, \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{-0.54} = 0.29$

$[C_2H_3O_2^-] = 0.29[HC_2H_3O_2]$; $0.29[HC_2H_3O_2] + [HC_2H_3O_2] = 1.0\ M$

$[HC_2H_3O_2] = 0.78\ M = [H^+]$ added

0.78 mol of HCl must be added to produce a solution with pH = 4.20.

c. $5.00 = 4.74 + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}, \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{0.26} = 1.8$

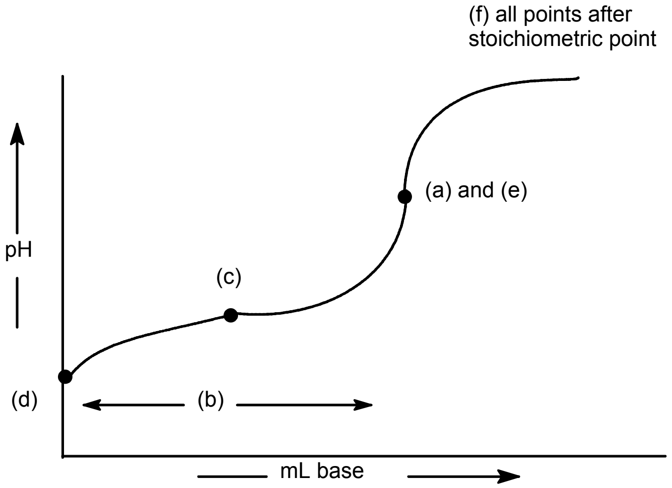
$[C_2H_3O_2^-] = 1.8[HC_2H_3O_2]$; $1.8[HC_2H_3O_2] + [HC_2H_3O_2] = 1.0\ M$

$[HC_2H_3O_2] = 0.36\ M = [H^+]$ added

0.36 mol of HCl must be added to produce a solution with pH = 5.00.

Acid-Base Titrations

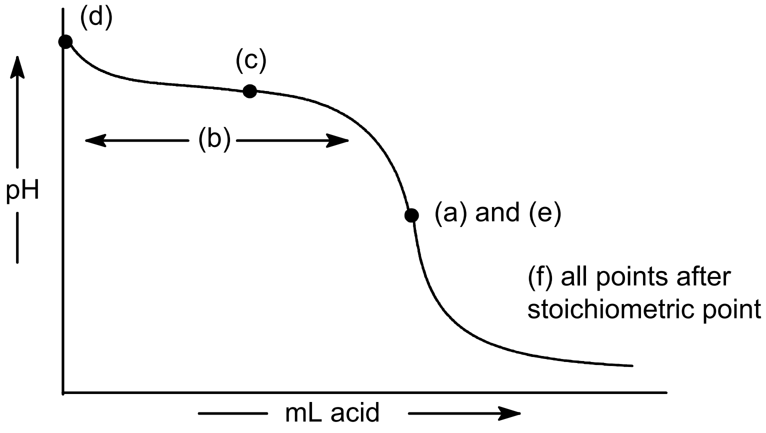
49.



$HA + OH^- \rightarrow A^- + H_2O$; 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.

50.



$B + H^+ \rightarrow BH^+$; 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.

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

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

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^-	$\rightarrow$	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. $[H^+]_{\text{excess}} = \dfrac{7.00\ \text{mmol H}^+}{40.0\ \text{mL} + 10.0\ \text{mL}} = 0.140\ M$

pH = −log(0.140) = 0.854

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

	H^+	+	OH^-	$\rightarrow$	H_2O
Before	8.00 mmol		4.00 mmol		
After	4.00 mmol		0		

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

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^-	$\rightarrow$	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.

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

52. 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^+	$\rightarrow$	H_2O	
Before	16.0 mmol		8.00 mmol			
Change	–8.00 mmol		–8.00 mmol			Reacts completely
After	8.0 mmol		0			

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

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

	OH^-	+	H^+	$\rightarrow$	H_2O
Before	16.0 mmol		12.0 mmol		
After	4.0 mmol		0		

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

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^+	$\rightarrow$	H_2O
Before	16.0 mmol		32.0 mmol		
After	0		16.0 mmol		

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

53. 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:

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	+	$C_2H_3O_2^-$
Initial	0.200 M		~0		0
	x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
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 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.

$$\text{pH} = \text{pK}_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = -\log(1.8\times10^{-5}) + \log\left(\frac{5.00\text{ mmol}/V_T}{15.0\text{ mmol}/V_T}\right),\ \text{where } V_T = \text{total volume}$$

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

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^-	→	$C_2H_3O_2^-$	+	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.

$$\text{pH} = -\log(1.8\times10^{-5}) = 4.74$$

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:

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

$$\text{pH} = 4.74 + 0.48 = 5.22$$

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.

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \qquad K_b = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

	$C_2H_3O_2^-$		$HC_2H_3O_2$	OH^-	
Initial	20.0 mmol/300.0 mL		0	0	$K_b = 5.6 \times 10^{-9}$
	x mol/L $C_2H_3O_2^-$ reacts with H_2O to reach equilibrium				
Change	$-x$	→	$+x$	$+x$	
Equil.	$0.0667 - x$		x	x	

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

pOH = 5.21; pH = 8.79; assumptions good.

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

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

	$HC_2H_3O_2$	OH^-	$C_2H_3O_2^-$
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.

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

54. 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.

$$H_2NNH_2 + H_2O \rightleftharpoons H_2NNH_3^+ + OH^-$$

	H_2NNH_2	$H_2NNH_3^+$	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. mmol H_2NNH_2 present = 100.0 mL × $\frac{0.100\ \text{mmol}\ H_2NNH_2}{\text{mL}}$ = 10.0 mmol H_2NNH_2

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

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

$$pH = -\log(3.3 \times 10^{-9}) + \log\left(\frac{6.0\ \text{mmol}/V_T}{4.00\ \text{mmol}/V_T}\right),$$ where V_T = total volume, which 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^+	$\rightarrow$	$H_2NNH_3^+$
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:

	$H_2NNH_3^+$	$\rightleftharpoons$	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^+	$\rightarrow$	$H_2NNH_3^+$
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.

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

55. We will do sample calculations for the various parts of the titration. All results are summarized in Table 15.1 at the end of Exercise 58.

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

$$HLac \rightleftharpoons H^+ + Lac^- \qquad K_a = 10^{-3.86} = 1.4 \times 10^{-4}$$

	HLac	$\rightleftharpoons$	H^+	+	Lac^-
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

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

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.

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 $pK_a = 3.86$:

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

(Total volume cancels, so we can use use the ratio of moles or millimoles.)

$pH = 3.86 - 0.72 = 3.14$

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 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.

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

$$Lac^- + H_2O \rightleftharpoons HLac + OH^- \qquad K_b = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.1 \times 10^{-11}$$

	$Lac^- + H_2O$		$HLac$	OH^-
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.

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

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^-

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

All results are listed in Table 15.1 at the end of the solution to Exercise 58.

56. Results for all points are summarized in Table 15.1 at the end of the solution to Exercise 58. At the beginning of the titration, we have a weak acid problem:

	HOPr	⇌	H^+	+	OPr^-	
						HOPr = $HC_3H_5O_2$ $OPr^- = C_3H_5O_2^-$
Initial	0.100 M		~0		0	
	x mol/L HOPr acid dissociates to reach equilibrium					
Change	$-x$	→	$+x$		$+x$	
Equil.	$0.100 - x$		x		x	

$$K_a = \frac{[H^+][OPr^-]}{[HOPr]} = 1.3 \times 10^{-5} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$x = [H^+] = 1.1 \times 10^{-3}\ M$; pH = 2.96; assumptions good.

The buffer region is from 4.0 to 24.9 mL of OH^- added. We will do a sample calculation at 24.0 mL OH^- added.

$$\text{Initial mmol HOPr present} = 25.0\ \text{mL} \times \frac{0.100\ \text{mmol}}{\text{mL}} = 2.50\ \text{mmol HOPr}$$

$$\text{mmol } OH^- \text{ added} = 24.0\ \text{mL} \times \frac{0.100\ \text{mmol}}{\text{mL}} = 2.40\ \text{mmol } OH^-$$

The added strong base converts HOPr into OPr^-.

	HOPr	+	OH^-	→	OPr^-	+	H_2O	
Before	2.50 mmol		2.40 mmol		0			
Change	−2.40		−2.40	→	+2.40			Reacts completely
After	0.10 mmol		0		2.40 mmol			

A buffer solution results. Using the Henderson-Hasselbalch equation where $pK_a = -\log(1.3 \times 10^{-5}) = 4.89$:

$$\text{pH} = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 4.89 + \log\frac{[OPr^-]}{[HOPr]}$$

$$\text{pH} = 4.89 + \log\left(\frac{2.40}{0.10}\right) = 4.89 + 1.38 = 6.27$$ (Volume cancels, so we can use the millimole ratio in the log term.)

All points in the buffer region 4.0 mL to 24.9 mL are calculated this way. See Table 15.1 at the end of Exercise 58 for all the results.

At the stoichiometric point, only a weak base (OPr^-) is present:

	OPr^- + H_2O	$\rightleftharpoons$	OH^-	+ HOPr
Initial	$\frac{2.50\text{ mmol}}{50.0\text{ mL}} = 0.0500\ M$		0	0
	x mol/L OPr^- reacts with H_2O to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.0500 - x$		x	x

$$K_b = \frac{[OH^-][HOPr]}{[OPr^-]} = \frac{K_w}{K_a} = 7.7 \times 10^{-10} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500}$$

$x = 6.2 \times 10^{-6}\ M = [OH^-]$, pOH = 5.21, pH = 8.79; assumptions good.

Beyond the stoichiometric point, the pH is determined by the excess strong base added. The results are the same as those in Exercise 55 (see Table 15.1).

For example, at 26.0 mL NaOH added:

$$[OH^-] = \frac{2.60\text{ mmol} - 2.50\text{ mmol}}{(25.0 + 26.0)\text{ mL}} = 2.0 \times 10^{-3}\ M;\quad \text{pOH} = 2.70;\quad \text{pH} = 11.30$$

57. 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:

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

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

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

Other points in the buffer region are calculated in similar fashion. Results are summarized in Table 15.1 at the end of Exercise 58.

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 mmol/50.0 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	

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

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 Table 15.1.

58. Initially, a weak base problem:

	py + H_2O	$\rightleftharpoons$	Hpy^+	+	OH^-	py is pyridine.
Initial	0.100 *M*		0		~0	
Equil.	0.100 – x		x		x	

$$K_b = \frac{[Hpy^+][OH^-]}{[py]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100} \approx 1.7 \times 10^{-9}$$

$x = [OH^-] = 1.3 \times 10^{-5}$ *M*; pOH = 4.89; pH = 9.11; assumptions good.

Buffer region (4.0 – 24.5 mL): Added H^+ reacts completely with py: $py + H^+ \rightarrow Hpy^+$. Determine the moles (or millimoles) of py and Hpy^+ after reaction, then use the Henderson-Hasselbalch equation to solve for the pH.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6};\ pK_a = 5.23;\ pH = 5.23 + \log\frac{[py]}{[Hpy^+]}$$

Results in the buffer region are summarized in Table 15.1, which follows this problem. See Exercise 57 for a similar sample calculation.

At the stoichiometric point (25.0 mL H^+ added), this is a weak acid problem since just enough H^+ has been added to convert all the weak base into its conjugate acid. The initial concentration of $[Hpy^+] = 0.0500\ M$.

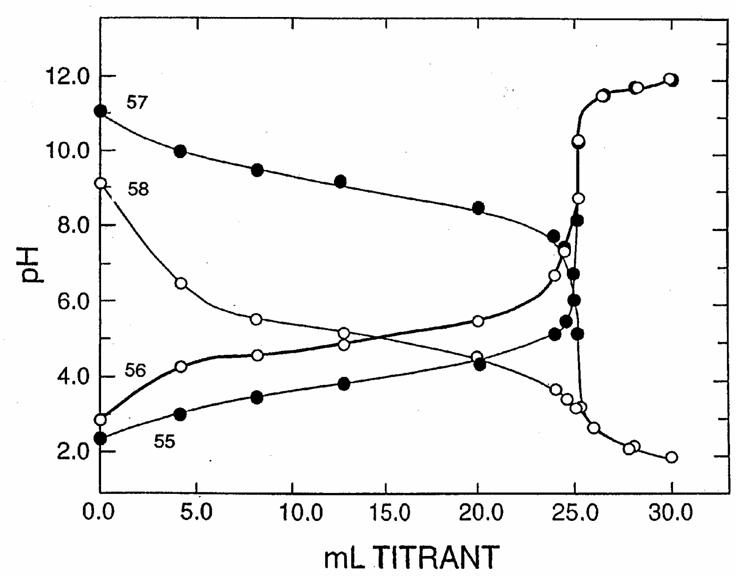
	Hpy^+	$\rightleftharpoons$	py	+	H^+	$K_a = 5.9 \times 10^{-6}$
Initial	0.0500 M		0		0	
Equil.	$0.0500 - x$		x		x	

$$5.9 \times 10^{-6} = \frac{x^2}{0.0500 - x} \approx \frac{x^2}{0.0500},\ x = [H^+] = 5.4 \times 10^{-4}\ M;\ pH = 3.27;\ \text{asumptions good.}$$

Beyond the equivalence point, the pH determination is made by calculating the concentration of excess H^+. See Exercise 57 for an example. All results are summarized in Table 15.1.

Table 15.1 Summary of pH Results for Exercises 55 – 58 (Graph follows)

Titrant mL	Exercise 55	Exercise 56	Exercise 57	Exercise 58
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	2.25
30.0	11.96	11.96	2.04	2.04



59. 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 mL + 1.0 × 10^2 mL = 2.0 × 10^2 mL. Solving the weak base equilibrium problem:

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

	$C_7H_5O_2^-$	$HC_7H_5O_2$	OH^-
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. mmol/(100.0 + 50.) mL = 0.067 *M*. Solving the weak acid equilibrium problem:

$$C_2H_5NH_3^+ \rightleftharpoons H^+ + C_2H_5NH_2$$

	$C_2H_5NH_3^+$	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^+

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

$$H^+ + OH^- \rightarrow H_2O$$

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

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

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.

60. 50.0 mL × 1.0 *M* = 50. mmol CH_3NH_2 present initially; $CH_3NH_2 + H^+ \rightarrow CH_3NH_3^+$

a. 50.0 mL × 0.50 *M* = 25. mmol HCl added. The added H^+ will convert one-half of the CH_3NH_2 into $CH_3NH_3^+$. This is the halfway point to equivalence, where $[CH_3NH_2]$ = $[CH_3NH_3^+]$.

$$pH = pK_a + \log\frac{[CH_3NH_2]}{[CH_3NH_3^+]} = pK_a;\quad K_a = \frac{1.0\times10^{-14}}{4.4\times10^{-4}} = 2.3\times10^{-11}$$

$$pH = pK_a = -\log(2.3\times10^{-11}) = 10.64$$

b. It will take 100. mL of HCl solution to reach the stoichiometric (equivalence) point. Here the added H^+ will convert all of the CH_3NH_2 into its conjugate acid, $CH_3NH_3^+$.

$$[CH_3NH_3^+]_0 = \frac{50.\text{ mmol}}{150.\text{ mL}} = 0.33\ M$$

	$CH_3NH_3^+$	$\rightleftharpoons$	H^+	+	CH_3NH_2
Initial	0.33 M		0		0
Equil.	$0.33 - x$		x		x

$$K_a = \frac{K_w}{K_b} = 2.3\times10^{-11}$$

$$2.3\times10^{-11} = \frac{x^2}{0.33-x} \approx \frac{x^2}{0.33},\quad x = [H^+] = 2.8\times10^{-6}\ M;\ pH = 5.55;$$ assumptions good.

61. $$75.0\text{ mL}\times\frac{0.10\text{ mmol}}{\text{mL}} = 7.5\text{ mmol HA};\quad 30.0\text{ mL}\times\frac{0.10\text{ mmol}}{\text{mL}} = 3.0\text{ mmol OH}^-\text{ added}$$

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

	HA	+	OH^-	$\rightarrow$	A^-	+	H_2O
Before	7.5 mmol		3.0 mmol		0		
After	4.5 mmol		0		3.0 mmol		

A buffer results after the OH^- reacts to completion. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[A^-]}{[HA]},\quad 5.50 = pK_a + \log\left(\frac{3.0\text{ mmol}/105.0\text{ mL}}{4.5\text{ mmol}/105.0\text{ mL}}\right)$$

$$pK_a = 5.50 - \log(3.0/4.5) = 5.50 - (-0.18) = 5.68;\quad K_a = 10^{-5.68} = 2.1\times10^{-6}$$

62. 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^+	$\rightarrow$	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:

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

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

For a conjugate acid-base pair, $pK_a + pK_b = 14{,}00$, so:

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

Indicators

63. $HIn \rightleftharpoons In^- + H^+ \quad K_a = \dfrac{[In^-][H^+]}{[HIn]} = 1.0 \times 10^{-9}$

a. In a very acid solution, the HIn form dominates, so the solution will be yellow.

b. The color change occurs when the concentration of the more dominant form is approximately ten times as great as the less dominant form of the indicator.

$$\frac{[HIn]}{[In^-]} = \frac{10}{1};\ \ K_a = 1.0 \times 10^{-9} = \left(\frac{1}{10}\right)[H^+],\ \ [H^+] = 1 \times 10^{-8}\,M;\ \ pH = 8.0 \text{ at color change}$$

c. This is way past the equivalence point (100.0 mL OH^- added), so the solution is very basic, and the In^- form of the indicator dominates. The solution will be blue.

64. The color of the indicator will change over the approximate range of $pH = pK_a \pm 1 = 5.3 \pm 1$. Therefore, the useful pH range of methyl red where it changes color would be about 4.3 (red) to 6.3 (yellow). Note that at $pH < 4.3$, the HIn form of the indicator dominates, and the color of the solution is the color of HIn (red). At $pH > 6.3$, the In^- form of the indicator dominates, and the color of the solution is the color of In^- (yellow). In titrating a weak acid with base, we start off with an acidic solution with $pH < 4.3$, so the color would change from red to reddish orange at $pH \approx 4.3$. In titrating a weak base with acid, the color change would be from yellow to yellowish orange at $pH \approx 6.3$. Only a weak base-strong acid titration would have an acidic pH at the equivalence point, so only in this type of titration would the color change of methyl red indicate the approximate endpoint.

65. At the equivalence point, P^{2-} is the major species. P^{2-} is a weak base in water because it is the conjugate base of a weak acid.

	P^{2-}	+	H_2O	$\rightleftharpoons$	HP^-	+	OH^-
Initial	$\dfrac{0.5\text{ g}}{0.1\text{ L}} \times \dfrac{1\text{ mol}}{204.2\text{ g}} = 0.024\,M$				0		~0 (carry extra sig. fig.)
Equil.	$0.024 - x$				x		x

$$K_b = \frac{[HP^-][OH^-]}{P^{2-}} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{10^{-5.51}},\ \ 3.2 \times 10^{-9} = \frac{x^2}{0.024 - x} \approx \frac{x^2}{0.024}$$

$x = [OH^-] = 8.8 \times 10^{-6}\ M$; pOH = 5.1; pH = 8.9; assumptions good.

Phenolphthalein would be the best indicator for this titration because it changes color at pH ≈ 9 (from acid color to base color).

66. $HIn \rightleftharpoons In^- + H^+ \quad K_a = \dfrac{[In^-][H^+]}{[HIn]} = 10^{-3.00} = 1.0 \times 10^{-3}$

At 7.00% conversion of HIn into In^-, $[In^-]/[HIn] = 7.00/93.00$.

$$K_a = 1.0 \times 10^{-3} = \frac{[In^-]}{[HIn]} \times [H^+] = \frac{7.00}{93.00} \times [H^+],\ \ [H^+] = 1.3 \times 10^{-2}\ M,\ \ pH = 1.89$$

The color of the base form will start to show when the pH is increased to 1.89.

67. When choosing an indicator, we want the color change of the indicator to occur approximately at the pH of the equivalence point. Because the pH generally changes very rapidly at the equivalence point, we don't have to be exact. This is especially true for strong acid-strong base titrations. The following are some indicators where the color change occurs at about the pH of the equivalence point:

Exercise	pH at Eq. Pt.	Indicator
51	7.00	bromthymol blue or phenol red
53	8.79	o-cresolphthalein or phenolphthalein

68.

Exercise	pH at Eq. Pt.	Indicator
52	7.00	bromthymol blue or phenol red
54	4.82	bromcresol green

69.

Exercise	pH at Eq. Pt.	Indicator
55	8.28	o-cresolphthalein or phenolphthalein
57	5.28	bromcresol green

70.

Exercise	pH at Eq. Pt.	Indicator
56	8.79	o-cresolphthalein or phenolphthalein
58	3.27	2,4-dinitrophenol

In the titration in Exercise 58, it will be very difficult to mark the equivalence point. The pH break at the equivalence point is too small.

71. pH > 5 for bromcresol green to be blue. pH < 8 for thymol blue to be yellow. The pH is between 5 and 8.

72. The pH will be less than about 0.5 because crystal violet is yellow at a pH less than about 0.5. The methyl orange result only tells us that the pH is less than about 3.5.

73. a. yellow b. green (Both yellow and blue forms are present.) c. yellow d. blue

74. a. yellow b. yellow

c. green (Both yellow and blue forms are present.) d. colorless

Connecting to Biochemistry

75. a. The optimum pH for a buffer is when pH = pK_a. At this pH a buffer will have equal neutralization capacity for both added acid and base. As shown next, because the pK_a for $TRISH^+$ is 8.1, the optimal buffer pH is about 8.1.

$K_b = 1.19 \times 10^{-6}$; $K_a = K_w/K_b = 8.40 \times 10^{-9}$; $pK_a = -\log(8.40 \times 10^{-9}) = 8.076$

b. $\text{pH} = pK_a + \log\dfrac{[\text{TRIS}]}{[\text{TRISH}^+]}$, $7.00 = 8.076 + \log\dfrac{[\text{TRIS}]}{[\text{TRISH}^+]}$

$$\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 10^{-1.08} = 0.083 \quad (\text{at pH} = 7.00)$$

$$9.00 = 8.076 + \log\frac{[\text{TRIS}]}{[\text{TRISH}^+]},\ \frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 10^{0.92} = 8.3 \quad (\text{at pH} = 9.00)$$

c. $\dfrac{50.0\ \text{g TRIS}}{2.0\ \text{L}} \times \dfrac{1\ \text{mol}}{121.14\ \text{g}} = 0.206\ M = 0.21\ M = [\text{TRIS}]$

$$\frac{65.0\ \text{g TRISHCl}}{2.0\ \text{L}} \times \frac{1\ \text{mol}}{157.60\ \text{g}} = 0.206\ M = 0.21\ M = [\text{TRISHCl}] = [\text{TRISH}^+]$$

$$\text{pH} = pK_a + \log\frac{[\text{TRIS}]}{[\text{TRISH}^+]} = 8.076 + \log\frac{(0.21)}{(0.21)} = 8.08$$

The amount of H^+ added from HCl is: $(0.50 \times 10^{-3}\ \text{L}) \times 12\ \text{mol/L} = 6.0 \times 10^{-3}\ \text{mol H}^+$

The H^+ from HCl will convert TRIS into $TRISH^+$. The reaction is:

	TRIS	+	H^+	→	$TRISH^+$	
Before	0.21 M		$\dfrac{6.0 \times 10^{-3}}{0.2005} = 0.030\ M$		0.21 M	
Change	–0.030		–0.030	→	+0.030	Reacts completely
After	0.18		0		0.24	

Now use the Henderson-Hasselbalch equation to solve this buffer problem.

$$\text{pH} = 8.076 + \log\left(\frac{0.18}{0.24}\right) = 7.95$$

76. a. $\text{pH} = pK_a + \log\dfrac{[\text{base}]}{[\text{acid}]}$, $7.15 = -\log(6.2 \times 10^{-8}) + \log\dfrac{[\text{HPO}_4^{\ 2-}]}{[\text{H}_2\text{PO}_4^{\ -}]}$

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

b. A best buffer has approximately equal concentrations of weak acid and conjugate base, so pH ≈ pK_a for a best buffer. The pK_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.

77. $\text{pH} = pK_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$, $7.40 = -\log(4.3 \times 10^{-7}) + \log\frac{[HCO_3^-]}{0.0012}$

$$\log\frac{[HCO_3^-]}{0.0012} = 7.40 - 6.37 = 1.03, \frac{[HCO_3^-]}{0.0012} = 10^{1.03}, [HCO_3^-] = 1.3 \times 10^{-2}\ M$$

78. At pH = 7.40: $7.40 = -\log(4.3 \times 10^{-7}) + \log\frac{[HCO_3^-]}{[H_2CO_3]}$

$$\log\frac{[HCO_3^-]}{[H_2CO_3]} = 7.40 - 6.37 = 1.03, \frac{[HCO_3^-]}{[H_2CO_3]} = 10^{1.03}, \frac{[H_2CO_3]}{[HCO_3^-]} = 10^{-1.03} = 0.093$$

At pH = 7.35: $\log\frac{[HCO_3^-]}{[H_2CO_3]} = 7.35 - 6.37 = 0.98$, $\frac{[HCO_3^-]}{[H_2CO_3]} = 10^{0.98}$

$$\frac{[H_2CO_3]}{[HCO_3^-]} = 10^{-0.98} = 0.10$$

The $[H_2CO_3] : [HCO_3^-]$ concentration ratio must increase from 0.093 to 0.10 in order for the onset of acidosis to occur.

79. $HA + OH^- \rightarrow A^- + H_2O$, where HA = acetylsalicylic acid (assuming it is a monoprotic acid).

$$\text{mmol HA present} = 27.36\ \text{mL OH}^- \times \frac{0.5106\ \text{mmol OH}^-}{\text{mL OH}^-} \times \frac{1\ \text{mmol HA}}{\text{mmol OH}^-} = 13.97\ \text{mmol HA}$$

$$\text{Molar mass of HA} = \frac{2.51\ \text{g HA}}{13.97 \times 10^{-3}\ \text{mol HA}} = 180.\ \text{g/mol}$$

To determine the K_a value, use the pH data. After complete neutralization of acetylsalicylic acid by OH^-, we have 13.97 mmol of A^- produced from the neutralization reaction. A^- will react completely with the added H^+ and re-form acetylsalicylic acid HA.

$$\text{mmol H}^+ \text{ added} = 13.68\text{ mL} \times \frac{0.5106\text{ mmol H}^+}{\text{mL}} = 6.985\text{ mmol H}^+$$

	A^-	+ H^+	$\rightarrow$	HA	
Before	13.97 mmol	6.985 mmol		0	
Change	–6.985	–6.985	$\rightarrow$	+6.985	Reacts completely
After	6.985 mmol	0		6.985 mmol	

We have back titrated this solution to the halfway point to equivalence, where pH = pK_a (assuming HA is a weak acid). This is true because after H^+ reacts completely, equal millimoles of HA and A^- are present, which only occurs at the halfway point to equivalence. Assuming acetylsalicylic acid is a weak monoprotic acid, then pH = pK_a = 3.48. $K_a = 10^{-3.48} = 3.3 \times 10^{-4}$.

80. $$\text{NaOH added} = 50.0\text{ mL} \times \frac{0.500\text{ mmol}}{\text{mL}} = 25.0\text{ mmol NaOH}$$

$$\text{NaOH left unreacted} = 31.92\text{ mL HCl} \times \frac{0.289\text{ mmol}}{\text{mL}} \times \frac{1\text{ mmol NaOH}}{\text{mmol HCl}} = 9.22\text{ mmol NaOH}$$

NaOH reacted with aspirin = 25.0 – 9.22 = 15.8 mmol NaOH

$$15.8\text{ mmol NaOH} \times \frac{1\text{ mmol aspirin}}{2\text{ mmol NaOH}} \times \frac{180.2\text{ mg}}{\text{mmol}} = 1420\text{ mg} = 1.42\text{ g aspirin}$$

$$\text{Purity} = \frac{1.42\text{ g}}{1.427\text{ g}} \times 100 = 99.5\%$$

Here, a strong base is titrated by a strong acid. The equivalence point will be at pH = 7.0. Bromthymol blue would be the best indicator since it changes color at pH ≈ 7 (from base color to acid color), although phenolphthalein is commonly used for the indicator. See Fig. 15.8 of the text.

81. $pK_a = -\log(1.3 \times 10^{-7}) = 6.89$; the color of an indicator changes over the approximate pH range of pH = $pK_a \pm 1 = 6.89 \pm 1$. For cyanidin aglycone, the useful pH range where this indicator changes color is from approximately 5.9 to 7.9.

82. Let's abbreviate the carboxylic acid group in alanine as RCOOH and the amino group in alanine as RNH_2. The K_a reaction for the carboxylic acid group is:

$$\text{RCOOH} \rightleftharpoons \text{RCOO}^- + \text{H}^+ \qquad K_a = 4.5 \times 10^{-7}$$

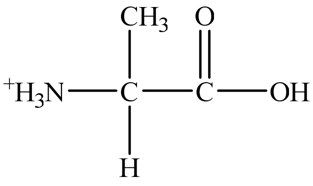
From Le Chatelier's principle, if we have a very acidic solution, a lot of H^+ is present. This drives the K_a reaction to the left, and the dominant form of the carboxylic acid group will be RCOOH (an overall neutral charge). If we have a very basic solution, the excess OH^- will remove H^+ from solution. As H^+ is removed, the K_a reaction shifts right, and the dominant form of the carboxylic acid group will be $RCOO^-$ (an overall 1– charged ion).

The K_b reaction for the amino group is:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

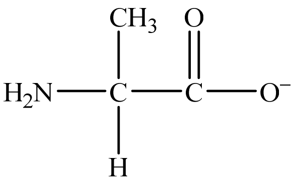
If we have a very acidic solution, the excess protons present will remove OH^- from solution, and the dominant form of the amino group will be RNH_3^+ (an overall 1+ charged ion). If we have a very basic solution, a lot of OH^- is present, and the dominant form of the amino group will be RNH_2 (an overall neutral charge).

In alanine, both an RCOOH group and an RNH_2 group are present. The dominant form of alanine in a very acidic solution will be the form with the protons attached to the two groups that have acid-base properties. This form of alanine is:



$$^+H_3N-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

which has an overall harge of 1+. The dominant form of alanine in a very basic solution will be in the form with the protons removed from the two groups that have acid-base properties. This form of alanine is:



$$H_2N-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-O^-$$

which has an overall charge of 1−.

Additional Exercises

83. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$; taking the −log of the K_b expression:

$$-\log K_b = -\log[OH^-] - \log\frac{[NH_4^+]}{[NH_3]}, \quad -\log[OH^-] = -\log K_b + \log\frac{[NH_4^+]}{[NH_3]}$$

$$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_3]} \text{ or } pOH = pK_b + \log\frac{[acid]}{[base]}$$

84. a. $pH = pK_a = -\log(6.4 \times 10^{-5}) = 4.19$ since $[HBz] = [Bz^-]$, where $HBz = C_6H_5CO_2H$ and $[Bz^-] = C_6H_5CO_2^-$.

b. $[Bz^-]$ will increase to 0.120 *M* and [HBz] will decrease to 0.080 *M* after OH^- reacts completely with HBz. The Henderson-Hasselbalch equation is derived from the K_a dissociation reaction.

$$pH = pK_a + \log\frac{[Bz^-]}{[HBz]},\ pH = 4.19 + \log\frac{(0.120)}{(0.080)} = 4.37;\ \text{assumptions good.}$$

c.

	Bz^-	+	H_2O	$\rightleftharpoons$	HBz	+	OH^-
Initial	$0.120\ M$				$0.080\ M$		0
Equil.	$0.120 - x$				$0.080 + x$		x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-5}} = \frac{(0.080 + x)(x)}{(0.120 - x)} \approx \frac{(0.080)(x)}{0.120}$$

$x = [OH^-] = 2.34 \times 10^{-10}\ M$ (carrying extra sig. fig.); assumptions good.

pOH = 9.63; pH = 4.37

d. We get the same answer. Both equilibria involve the two major species, benzoic acid and benzoate anion. Both equilibria must hold true. K_b is related to K_a by K_w and $[OH^-]$ is related to $[H^+]$ by K_w, so all constants are interrelated.

85. a. $C_2H_5NH_3^+ \rightleftharpoons H^+ + C_2H_5NH_2 \quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11};\ pK_a = 10.74$

$$pH = pK_a + \log\frac{[C_2H_5NH_2]}{[C_2H_5NH_3^+]} = 10.74 + \log\frac{0.10}{0.20} = 10.74 - 0.30 = 10.44$$

b. $C_2H_5NH_3^+ + OH^- \rightleftharpoons C_2H_5NH_2$; after $0.050\ M\ OH^-$ reacts to completion (converting $0.050\ M\ C_2H_5NH_3^+$ into $0.050\ M\ C_2H_5NH_2$), a buffer solution still exists where $[C_2H_5NH_3^+] = [C_2H_5NH_2] = 0.15\ M$. Here $pH = pK_a + \log(1.0) = 10.74$ ($pH = pK_a$).

86. $$pH = pK_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]},\ 4.00 = -\log(1.8 \times 10^{-5}) + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 0.18$; this is also equal to the mole ratio between $C_2H_3O_2^-$ and $HC_2H_3O_2$.

Let x = volume of $1.00\ M\ HC_2H_3O_2$ and y = volume of $1.00\ M\ NaC_2H_3O_2$

$x + y = 1.00$ L, $x = 1.00 - y$

$x(1.00$ mol/L$)$ = mol $HC_2H_3O_2$; $y(1.00$ mol/L$)$ = mol $NaC_2H_3O_2$ = mol $C_2H_3O_2^-$

Thus: $\frac{y}{x} = 0.18$ or $\frac{y}{1.00 - y} = 0.18$; solving: $y = 0.15$ L, so $x = 1.00 - 0.15 = 0.85$ L.

We need 850 mL of $1.00\ M\ HC_2H_3O_2$ and 150 mL of $1.00\ M\ NaC_2H_3O_2$ to produce a buffer solution at pH = 4.00.

87. A best buffer is when pH ≈ pK_a; these solutions have about equal concentrations of weak acid and conjugate base. Therefore, choose combinations that yield a buffer where pH ≈ pK_a; that is, look for acids whose pK_a is closest to the pH.

a. Potassium fluoride + HCl will yield a buffer consisting of HF (pK_a = 3.14) and F^-.

b. Benzoic acid + NaOH will yield a buffer consisting of benzoic acid (pK_a = 4.19) and benzoate anion.

c. Sodium acetate + acetic acid (pK_a = 4.74) is the best choice for pH = 5.0 buffer since acetic acid has a pK_a value closest to 5.0.

d. HOCl and NaOH: This is the best choice to produce a conjugate acid-base pair with pH = 7.0. This mixture would yield a buffer consisting of HOCl (pK_a = 7.46) and OCl^-. Actually, the best choice for a pH = 7.0 buffer is an equimolar mixture of ammonium chloride and sodium acetate. NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$), and $C_2H_3O_2^-$ is a weak base ($K_b = 5.6 \times 10^{-10}$). A mixture of the two will give a buffer at pH = 7.0 because the weak acid and weak base are the same strengths (K_a for NH_4^+ = K_b for $C_2H_3O_2^-$). $NH_4C_2H_3O_2$ is commercially available, and its solutions are used for pH = 7.0 buffers.

e. Ammonium chloride + NaOH will yield a buffer consisting of NH_4^+ (pK_a = 9.26) and NH_3.

88. At pH = 0.00, $[H^+] = 10^{-0.00} = 1.0\ M$. We begin with 1.0 L × 2.0 mol/L OH^- = 2.0 mol OH^-. We will need 2.0 mol HCl to neutralize the OH^-, plus an additional 1.0 mol excess H^+ to reduce the pH to 0.00. We need 3.0 mol HCl total assuming 1.0 L of solution.

89. a. $HC_2H_3O_2 + OH^- \rightleftharpoons C_2H_3O_2^- + H_2O$

$$K_{eq} = \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2][OH^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_{a,\,HC_2H_3O_2}}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^9$$

b. $C_2H_3O_2^- + H^+ \rightleftharpoons HC_2H_3O_2$ $K_{eq} = \dfrac{[HC_2H_3O_2]}{[H^+][C_2H_3O_2^-]} = \dfrac{1}{K_{a,\,HC_2H_3O_2}} = 5.6 \times 10^4$

c. $HCl + NaOH \rightarrow NaCl + H_2O$

Net ionic equation is $H^+ + OH^- \rightleftharpoons H_2O$; $K_{eq} = \dfrac{1}{K_w} = 1.0 \times 10^{14}$

90. 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 $K_a \approx 1 \times 10^{-6}$.

91. 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

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

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

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

92. For a titration of a strong acid with a strong base, the added OH^- reacts completely with the H^+ present. To determine the pH, we calculate the concentration of excess H^+ or OH^- after the neutralization reaction, and then calculate the pH.

0 mL: $[H^+] = 0.100\ M$ from HNO_3; pH = 1.000

4.0 mL: Initial mmol H^+ present = 25.0 mL × $\frac{0.100\ \text{mmol H}^+}{\text{mL}}$ = 2.50 mmol H^+

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

0.40 mmol OH^- reacts completely with 0.40 mmol H^+: $OH^- + H^+ \rightarrow H_2O$

$$[H^+]_{\text{excess}} = \frac{(2.50 - 0.40)\ \text{mmol}}{(25.0 + 4.0)\ \text{mL}} = 7.24 \times 10^{-2}\ M;\ \text{pH} = 1.140$$

We follow the same procedure for the remaining calculations.

8.0 mL: $$[H^+]_{\text{excess}} = \frac{(2.50 - 0.80)\ \text{mmol}}{33.0\ \text{mL}} = 5.15 \times 10^{-2}\ M;\ \text{pH} = 1.288$$

12.5 mL: $[\mathrm{H}^+]_{\text{excess}} = \dfrac{(2.50 - 1.25)\ \text{mmol}}{37.5\ \text{mL}} = 3.33 \times 10^{-2}\ M$; pH = 1.478

20.0 mL: $[\mathrm{H}^+]_{\text{excess}} = \dfrac{(2.50 - 2.00)\ \text{mmol}}{45.0\ \text{mL}} = 1.1 \times 10^{-2}\ M$; pH = 1.96

24.0 mL: $[\mathrm{H}^+]_{\text{excess}} = \dfrac{(2.50 - 2.40)\ \text{mmol}}{49.0\ \text{mL}} = 2.0 \times 10^{-3}\ M$; pH = 2.70

24.5 mL: $[\mathrm{H}^+]_{\text{excess}} = \dfrac{(2.50 - 2.45)\ \text{mmol}}{49.5\ \text{mL}} = 1 \times 10^{-3}\ M$; pH = 3.0

24.9 mL: $[\mathrm{H}^+]_{\text{excess}} = \dfrac{(2.50 - 2.49)\ \text{mmol}}{49.9\ \text{mL}} = 2 \times 10^{-4}\ M$; pH = 3.7

25.0 mL: Equivalence point; we have a neutral solution because there is no excess H^+ or OH^- remaining after the neutralization reaction. pH = 7.00

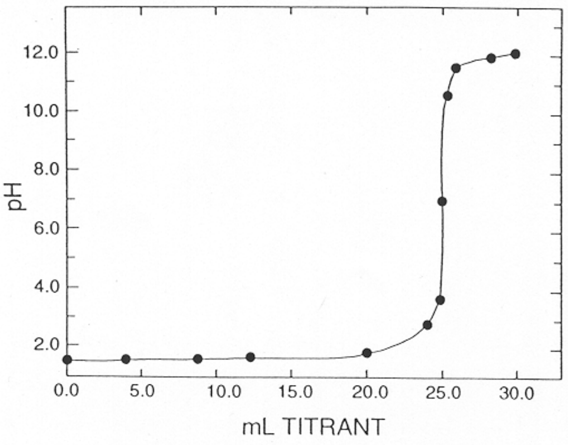
25.1 mL: Base in excess; $[\mathrm{OH}^-]_{\text{excess}} = \dfrac{(2.51 - 2.50)\ \text{mmol}}{50.1\ \text{mL}} = 2 \times 10^{-4}\ M$; pOH = 3.7

pH = 14.00 – 3.7 = 10.3

26.0 mL: $[\mathrm{OH}^-]_{\text{excess}} = \dfrac{(2.60 - 2.50)\ \text{mmol}}{51.0\ \text{mL}} = 2.0 \times 10^{-3}\ M$; pOH = 2.70; pH = 11.30

28.0 mL: $[\mathrm{OH}^-]_{\text{excess}} = \dfrac{(2.80 - 2.50)\ \text{mmol}}{53.0\ \text{mL}} = 5.7 \times 10^{-3}\ M$; pOH = 2.24; pH = 11.76

30.0 mL: $[\mathrm{OH}^-]_{\text{excess}} = \dfrac{(3.00 - 2.50)\ \text{mmol}}{55.0\ \text{mL}} = 9.1 \times 10^{-3}\ M$; pOH = 2.04; pH = 11.96



93. $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$; let C_0 = initial concentration of $HC_2H_3O_2$

From normal weak acid setup: $K_a = 1.8 \times 10^{-5} = \dfrac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \dfrac{[H^+]^2}{C_0 - [H^+]}$

$$[H^+] = 10^{-2.68} = 2.1 \times 10^{-3}\ M;\ 1.8 \times 10^{-5} = \frac{(2.1 \times 10^{-3})^2}{C_0 - (2.1 \times 10^{-3})},\ C_0 = 0.25\ M$$

25.0 mL × 0.25 mmol/mL = 6.3 mmol $HC_2H_3O_2$

Need 6.3 mmol KOH = V_{KOH} × 0.0975 mmol/mL, V_{KOH} = 65 mL

94. Mol acid = $0.210\ g \times \dfrac{1\ mol}{192\ g} = 0.00109$ mol

Mol OH^- added = $0.0305\ L \times \dfrac{0.108\ mol\ NaOH}{L} \times \dfrac{1\ mol\ OH^-}{mol\ NaOH} = 0.00329$ mol OH^-

$$\frac{Mol\ OH^-}{Mol\ acid} = \frac{0.00329}{0.00109} = 3.02$$

The acid is triprotic (H_3A) because 3 mol of OH^- are required to react with 1 mol of the acid; that is, the acid must have 3 mol H^+ in the formula to react with 3 mol of OH^-.

95. 50.0 mL × 0.100 *M* = 5.00 mmol NaOH initially

At pH = 10.50, pOH = 3.50, $[OH^-] = 10^{-3.50} = 3.2 \times 10^{-4}$ *M*

mmol OH^- remaining = 3.2×10^{-4} mmol/mL × 73.75 mL = 2.4×10^{-2} mmol

mmol OH^- that reacted = 5.00 − 0.024 = 4.98 mmol

Because the weak acid is monoprotic, 23.75 mL of the weak acid solution contains 4.98 mmol HA.

$$[HA]_0 = \frac{4.98\ mmol}{23.75\ mL} = 0.210\ M$$

96. $HA + OH^- \rightarrow A^- + H_2O$; 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^-	→	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.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]},\quad 4.7 = \text{p}K_a + \log\left(\frac{1.2\ \text{mmol}/V_T}{1.3\ \text{mmol}/V_T}\right),\ \text{where } V_T = \text{total volume}$$

Because the log term will be negative [log(1.2/1.3) = −0.035)], the $\text{p}K_a$ value of the acid must be greater than 4.7.

97. At equivalence point: 16.00 mL × 0.125 mmol/mL = 2.00 mmol OH^- added; there must be 2.00 mmol HX present initially.

$HX + OH^- \rightarrow X^- + H_2O$ (neutralization rection)

2.00 mL NaOH added = 2.00 mL × 0.125 mmol/mL = 0.250 mmol OH^-; 0.250 mmol of OH^- added will convert 0.250 mmol HX into 0.250 mmol X^-. Remaining HX = 2.00 − 0.250 = 1.75 mmol HX; this is a buffer solution where $[H^+] = 10^{-6.912} = 1.22 \times 10^{-7}\ M$. Because total volume cancels:

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{1.22 \times 10^{-7}(0.250/V_T)}{1.75/V_T} = \frac{1.22 \times 10^{-7}(0.250)}{1.75} = 1.74 \times 10^{-8}$$

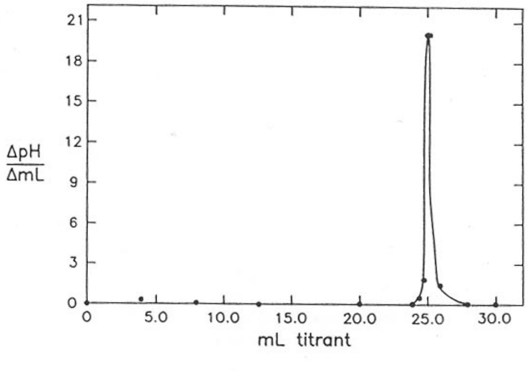
Note: We could solve for K_a using the Henderson-Hasselbalch equation.

Challenge Problems

98. At 4.0 mL NaOH added: $\left|\frac{\Delta\text{pH}}{\Delta\text{mL}}\right| = \left|\frac{2.43 - 3.14}{0 - 4.0}\right| = 0.18$

The other points are calculated in a similar fashion. The results are summarized and plotted below. As can be seen from the plot, the advantage of this approach is that it is much easier to accurately determine the location of the equivalence point.

mL	pH	|ΔpH/ΔmL|
0	2.43	–
4.0	3.14	0.18
8.0	3.53	0.098
12.5	3.86	0.073
20.0	4.46	0.080
24.0	5.24	0.20
24.5	5.6	0.7
24.9	6.3	2
25.0	8.28	20
25.1	10.3	20
26.0	11.30	1
28.0	11.75	0.23
30.0	11.96	0.11



99. mmol $HC_3H_5O_2$ present initially = 45.0 mL × $\frac{0.750\text{ mmol}}{\text{mL}}$ = 33.8 mmol $HC_3H_5O_2$

mmol $C_3H_5O_2^-$ present initially = 55.0 mL × $\frac{0.700\text{ mmol}}{\text{mL}}$ = 38.5 mmol $C_3H_5O_2^-$

The initial pH of the buffer is:

$$\text{pH} = \text{pK}_a + \log\frac{[C_3H_5O_2^-]}{[HC_3H_5O_2]} = -\log(1.3 \times 10^{-5}) + \log\frac{\frac{38.5\text{ mmol}}{100.0\text{ mL}}}{\frac{33.8\text{ mmol}}{100.0\text{ mL}}} = 4.89 + \log\frac{38.5}{33.8} = 4.95$$

Note: Because the buffer components are in the same volume of solution, we can use the mole (or millimole) ratio in the Henderson-Hasselbalch equation to solve for pH instead of using the concentration ratio of $[C_3H_5O_2^-]$: $[HC_3H_5O_2]$.

When NaOH is added, the pH will increase, and the added OH^- will convert $HC_3H_5O_2$ into $C_3H_5O_2^-$. The pH after addition of OH^- increases by 2.5%, so the resulting pH is:

$$4.95 + 0.025(4.95) = 5.07$$

At this pH, a buffer solution still exists, and the millimole ratio between $C_3H_5O_2^-$ and $HC_3H_5O_2$ is:

$$\text{pH} = \text{pK}_a + \log\frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2}, \quad 5.07 = 4.89 + \log\frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2}$$

$$\frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2} = 10^{0.18} = 1.5$$

Let x = mmol OH^- added to increase pH to 5.07. Because OH^- will essentially react to completion with $HC_3H_5O_2$, the setup to the problem using millimoles is:

	$HC_3H_5O_2$	+	OH^-	→	$C_3H_5O_2^-$	
Before	33.8 mmol		x mmol		38.5 mmol	
Change	$-x$		$-x$	→	$+x$	Reacts completely
After	$33.8 - x$		0		$38.5 + x$	

$$\frac{\text{mmol } C_3H_5O_2^-}{\text{mmol } HC_3H_5O_2} = 1.5 = \frac{38.5 + x}{33.8 - x}, \quad 1.5(33.8 - x) = 38.5 + x, \quad x = 4.9 \text{ mmol } OH^- \text{ added}$$

The volume of NaOH necessary to raise the pH by 2.5% is:

$$4.9 \text{ mmol NaOH} \times \frac{1\text{ mL}}{0.10\text{ mmol NaOH}} = 49\text{ mL}$$

49 mL of 0.10 *M* NaOH must be added to increase the pH by 2.5%.

100. 0.400 mol/L × V_{NH_3} = mol NH_3 = mol NH_4^+ after reaction with HCl at the equivalence point.

At the equivalence point: $[NH_4^+]_0 = \dfrac{\text{mol } NH_4^+}{\text{total volume}} = \dfrac{0.400 \times V_{NH_3}}{1.50 \times V_{NH_3}} = 0.267\ M$

	NH_4^+	$\rightleftharpoons$	H^+	+	NH_3
Initial	0.267 M		0		0
Equil.	$0.267 - x$		x		x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}},\ 5.6 \times 10^{-10} = \frac{x^2}{0.267 - x} \approx \frac{x^2}{0.267}$$

$x = [H^+] = 1.2 \times 10^{-5}\ M$; pH = 4.92; assumption good.

101. For HOCl, $K_a = 3.5 \times 10^{-8}$ and $pK_a = -\log(3.5 \times 10^{-8}) = 7.46$. This will be a buffer solution because the pH is close to the pK_a value.

$$pH = pK_a + \log\frac{[OCl^-]}{[HOCl]},\quad 8.00 = 7.46 + \log\frac{[OCl^-]}{[HOCl]},\quad \frac{[OCl^-]}{[HOCl]} = 10^{0.54} = 3.5$$

1.00 L × 0.0500 M = 0.0500 mol HOCl initially. Added OH^- converts HOCl into OCl^-. The total moles of OCl^- and HOCl must equal 0.0500 mol. Solving where n = moles:

$n_{OCl^-} + n_{HOCl} = 0.0500$ and $n_{OCl^-} = (3.5)n_{HOCl}$

$(4.5)n_{HOCl} = 0.0500$, $n_{HOCl} = 0.011$ mol; $n_{OCl^-} = 0.039$ mol

Need to add 0.039 mol NaOH to produce 0.039 mol OCl^-.

0.039 mol = V × 0.0100 M, V = 3.9 L NaOH

Note: Normal buffer assumptions hold.

102. 50.0 mL × 0.100 M = 5.00 mmol H_2SO_4; 30.0 mL × 0.100 M = 3.00 mmol HOCl

25.0 mL × 0.200 M = 5.00 mmol NaOH; 10.0 mL × 0.150 M = 1.50 mmol KOH

25.0 mL × 0.100 M = 2.50 mmol $Ba(OH)_2$ = 5.00 mmol OH^-; we've added 11.50 mmol OH^- total.

Let OH^- react completely with the best acid present (H_2SO_4).

10.00 mmol OH^- + 5.00 mmol H_2SO_4 → 0.00 mmol H_2O + 5.00 mmol SO_4^{2-}

OH^- still remains after reacting completely with H_2SO_4. OH^- will then react with the next best acid (HOCl). The remaining 1.50 mmol OH^- will convert 1.50 mmol HOCl into 1.50

mmol OCl^-, resulting in a solution with 1.50 mmol OCl^- and (3.00 – 1.50 =) 1.50 mmol HOCl. The major species at this point are HOCl, OCl^-, SO_4^{2-}, and H_2O plus cations that don't affect pH. SO_4^{2-} is an extremely weak base ($K_b = 8.3 \times 10^{-13}$). We have a buffer solution composed of HOCl and OCl^-. Because $[HOCl] = [OCl^-]$:

$[H^+] = K_a = 3.5 \times 10^{-8}$ *M*; pH = 7.46; assumptions good.

103. 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 of 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 of 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.

   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 up to 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 of 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 $K_{a_1} = 4.0$ 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.

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

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 $K_{a_2} = 10^{-8.0} = 1 \times 10^{-8}$.

104. We will see only the first stoichiometric point in the titration of salicylic acid because K_{a_2} is so small. For adipic acid, the K_a values are fairly close to each other. Both protons will be titrated almost simultaneously, giving us only one break. The stoichiometric points will occur when 1 mol of OH^- is added per mole of salicylic acid present and when 2 mol of OH^- is added per mole of adipic acid present. Thus the 25.00-mL volume corresponded to the titration of salicylic acid, and the 50.00-mL volume corresponded to the titration of adipic acid.

105. a. Na^+ is present in all solutions. The added H^+ from HCl reacts completely with CO_3^{2-} to convert it into HCO_3^- (points A-C). After all of the CO_3^{2-} is reacted (after point C, the first equivalence point), H^+ then reacts completely with the next best base present, HCO_3^- (points C-E). Point E represents the second equivalence point. The major species present at the various points after H^+ reacts completely follow.

A. CO_3^{2-}, H_2O, Na^+

B. CO_3^{2-}, HCO_3^-, H_2O, Cl^-, Na^+

C. HCO_3^-, H_2O, Cl^-, Na^+

D. HCO_3^-, CO_2 (H_2CO_3), H_2O, Cl^-, Na^+

E. CO_2 (H_2CO_3), H_2O, Cl^-, Na^+

F. H^+ (excess), CO_2 (H_2CO_3), H_2O, Cl^-. Na^+

b. $H_2CO_3 \rightleftharpoons HCO_3^- + H^+, Na^+$ $\quad K_{a_1} = 4.3 \times 10^{-7}$

$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+, Na^+$ $\quad K_{a_2} = 5.6 \times 10^{-11}$

The first titration reaction occurring between points A and C is:

$$H^+ + CO_3^{2-} \rightarrow HCO_3^-$$

At point B, enough H^+ has been added to convert one-half of the CO_3^{2-} into its conjugate acid. At this halfway point to equivalence, $[CO_3^{2-}] = [HCO_3^-]$. For this buffer solution,

$$pH = pK_{a_2} = -\log(5.6 \times 10^{-11}) = 10.25$$

The second titration reaction occurring between points C and E is:

$$H^+ + HCO_3^- \rightarrow H_2CO_3$$

Point D is the second halfway point to equivalence, where $[HCO_3^-] = [H_2CO_3]$. Here, $pH = pK_{a_1} = -\log(4.3 \times 10^{-7}) = 6.37$.

106. a. V_1 corresponds to the titration reaction of $CO_3^{2-} + H^+ \rightarrow HCO_3^-$; V_2 corresponds to the titration reaction of $HCO_3^- + H^+ \rightarrow H_2CO_3$.

Here, there are two sources of HCO_3^-: $NaHCO_3$ and the titration of Na_2CO_3, so $V_2 > V_1$.

b. V_1 corresponds to two titration reactions: $OH^- + H^+ \rightarrow H_2O$ and $CO_3^{2-} + H^+ \rightarrow HCO_3^-$. V_2 corresponds to just one titration reaction: $HCO_3^- + H^+ \rightarrow H_2CO_3$.

Here, $V_1 > V_2$ due to the presence of OH^- , which is titrated in the V_1 region.

c. 0.100 mmol HCl/mL × 18.9 mL = 1.89 mmol H^+; Because the first stoichiometric point only involves the titration of Na_2CO_3 by H^+, 1.89 mmol of CO_3^{2-} has been converted into HCO_3^-. The sample contains 1.89 mmol Na_2CO_3 × 105.99 mg/mmol = 2.00×10^2 mg = 0.200 g Na_2CO_3.

The second stoichiometric point involves the titration of HCO_3^- by H^+.

$$\frac{0.100 \text{ mmol H}^+}{\text{mL}} \times 36.7 \text{ mL} = 3.67 \text{ mmol H}^+ = 3.67 \text{ mmol HCO}_3^-$$

1.89 mmol $NaHCO_3$ came from the first stoichiometric point of the Na_2CO_3 titration.

3.67 − 1.89 = 1.78 mmol HCO_3^- came from $NaHCO_3$ in the original mixture.

1.78 mmol $NaHCO_3$ × 84.01 mg $NaHCO_3$/mmol = 1.50×10^2 mg $NaHCO_3$ = 0.150 g $NaHCO_3$

$$\text{Mass \% Na}_2\text{CO}_3 = \frac{0.200 \text{ g}}{(0.200 + 0.150) \text{ g}} \times 100 = 57.1\% \text{ Na}_2\text{CO}_3$$

$$\text{Mass \% NaHCO}_3 = \frac{0.150 \text{ g}}{0.350 \text{ g}} \times 100 = 42.9\% \text{ NaHCO}_3$$

107. An indicator changes color at $pH \approx pK_a \pm 1$.The results from each indicator tells us something about the pH. The conclusions are summarized below:

Results from	pH
bromphenol blue	$\geq \approx 5.0$
bromcresol purple	$\leq \approx 5.0$
bromcresol green *	$pH \approx pK_a \approx 4.8$
alizarin	$\leq \approx 5.5$

*For bromcresol green, the resultant color is green.
This is a combination of the extremes (yellow and blue).
This occurs when $pH \approx pK_a$ of the indicator.

From the indicator results, the pH of the solution is about 5.0. We solve for K_a by setting up the typical weak acid problem.

	HX	$\rightleftharpoons$	H^+	+	X^-
Initial	1.0 *M*		~0		0
Equil.	$1.0 - x$		x		x

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{x^2}{1.0 - x}\text{; because pH} \approx 5.0,\ [H^+] = x \approx 1 \times 10^{-5}\ M.$$

$$K_a \approx \frac{(1 \times 10^{-5})^2}{1.0 - 1 \times 10^{-5}} \approx 1 \times 10^{-10}$$

108. Phenolphthalein will change color at pH ≈ 9. Phenolphthalein will mark the second end point of the titration. Therefore, we have titrated both protons on malonic acid.

$H_2Mal + 2\ OH^- \rightarrow 2\ H_2O + Mal^{2-}$ where H_2Mal = malonic acid

$$31.50\text{ mL} \times \frac{0.0984\text{ mmol NaOH}}{\text{mL}} \times \frac{1\text{ mmol }H_2Mal}{2\text{ mol NaOH}} = 1.55\text{ mmol }H_2Mal$$

$$[H_2Mal] = \frac{1.55\text{ mmol}}{25.00\text{ mL}} = 0.0620\ M$$

Integrative Problems

109. $$pH = pK_a + \log\frac{[C_7H_4O_2F^-]}{[C_7H_5O_2F]} = 2.90 + \log\left[\frac{(55.0\text{ mL} \times 0.472\ M)/130.0\text{ mL}}{(75.0\text{ mL} \times 0.275\ M)/130.0\text{ mL}}\right]$$

$$pH = 2.90 + \log\left(\frac{26.0}{20.6}\right) = 2.90 + 0.101 = 3.00$$

110. a. 1.00 L × 0.100 mol/L = 0.100 mol HCl added to reach stoichiometric point.

The 10.00-g sample must have contained 0.100 mol of NaA. $\frac{10.00\text{ g}}{0.100\text{ mol}}$ = 100. g/mol

b. 500.0 mL of HCl added represents the halfway point to equivalence. Thus $pH = pK_a$ = 5.00 and $K_a = 1.0 \times 10^{-5}$. At the equivalence point, enough H^+ has been added to convert all the A^- present initially into HA. The concentration of HA at the equivalence point is:

$$[HA]_0 = \frac{0.100\text{ mol}}{1.10\text{ L}} = 0.0909\ M$$

	HA	$\rightleftharpoons$	H^+	+	A^-	$K_a = 1.0 \times 10^{-5}$
Initial	0.0909 *M*		0		0	
Equil.	0.0909 - x		x		x	

$$K_a = 1.0 \times 10^{-5} = \frac{x^2}{0.0909 - x} \approx \frac{x^2}{0.0909}$$

$x = 9.5 \times 10^{-4}\ M = [H^+]$; pH = 3.02; assumptions good.

111. The added OH^- from the strong base reacts to completion with the best acid present, HF. To determine the pH, see what is in solution after the OH^- reacts to completion.

$$OH^- \text{ added} = 38.7 \text{ g soln} \times \frac{1.50 \text{ g NaOH}}{100.0 \text{ g soln}} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g}} \times \frac{1 \text{ mol } OH^-}{\text{mol NaOH}} = 0.0145 \text{ mol } OH^-$$

For the 0.174 *m* HF solution, if we had exactly 1 kg of H_2O, then the solution would contain 0.174 mol HF.

$$0.174 \text{ mol HF} \times \frac{20.01 \text{ g}}{\text{mol HF}} = 3.48 \text{ g HF}$$

Mass of solution = 1000.00 g H_2O + 3.48 g HF = 1003.48 g

$$\text{Volume of solution} = 1003.48 \text{ g} \times \frac{1 \text{ mL}}{1.10 \text{ g}} = 912 \text{ mL}$$

$$\text{Mol HF} = 250. \text{ mL} \times \frac{0.174 \text{ mol HF}}{912 \text{ mL}} = 4.77 \times 10^{-2} \text{ mol HF}$$

	OH^-	+	HF	$\rightarrow$	F^-	+	H_2O
Before	0.0145 mol		0.0477 mol		0		
Change	−0.0145		−0.0145		+0.0145		
After	0		0.0332 mol		0.0145 mol		

After reaction, a buffer solution results containing HF, a weak acid, and F^-, its conjugate base. Let V_T = total volume of solution.

$$pH = pK_a + \log\frac{[F^-]}{[HF]} = -\log(7.2 \times 10^{-4}) + \log\left(\frac{0.0145/V_T}{0.0332/V_T}\right)$$

$$pH = 3.14 + \log\left(\frac{0.0145}{0.0332}\right) = 3.14 + (-0.360),\ pH = 2.78$$

Marathon Problem

112. a. Because $K_{a_1} >> K_{a_2}$, the amount of H^+ contributed by the K_{a_2} reaction will be negligible. The $[H^+]$ donated by the K_{a_1} reaction is $10^{-2.06} = 8.7 \times 10^{-3}\ M\ H^+$.

	H_2A	$\rightleftharpoons$	H^+	+	HA^-	$K_{a_1} = 5.90 \times 10^{-2}$
Initial	$[H_2A]_0$		~0		0	$[H_2A]_0$ = initial concentration
Equil.	$[H_2A]_0 - x$		x		x	

$$K_{a_1} = 5.90 \times 10^{-2} = \frac{x^2}{[H_2A]_0 - x} = \frac{(8.7 \times 10^{-3})^2}{[H_2A]_0 - 8.7 \times 10^{-3}}, \ [H_2A]_0 = 1.0 \times 10^{-2}\ M$$

$$\text{Mol } H_2A \text{ present initially} = 0.250\ L \times \frac{1.0 \times 10^{-2}\ \text{mol } H_2A}{L} = 2.5 \times 10^{-3}\ \text{mol } H_2A$$

$$\text{Molar mass } H_2A = \frac{0.225\ g\ H_2A}{2.5 \times 10^{-3}\ \text{mol } H_2A} = 90.\ g/mol$$

b. $H_2A + 2\ OH^- \rightarrow A^{2-} + H_2O$; at the second equivalence point, the added OH^- has converted all the H_2A into A^{2-}, so A^{2-} is the major species present that determines the pH. The millimoles of A^{2-} present at the equivalence point equal the millimoles of H_2A present initially (2.5 mmol), and the millimoles of OH^- added to reach the second equivalence point are 2(2.5 mmol) = 5.0 mmol OH^-added. The only information we need now in order to calculate the K_{a_2} value is the volume of $Ca(OH)_2$ added in order to reach the second equivalent point. The volume of $Ca(OH)_2$ required to deliver 5.0 mmol OH^- (the amount of OH^- necessary to reach the second equivalence point) is:

$$5.0\ \text{mmol } OH^- \times \frac{1\ \text{mmol } Ca(OH)_2}{2\ \text{mmol } OH^-} \times \frac{1\ mL}{6.9 \times 10^{-3}\ \text{mmol } Ca(OH)_2}$$

$$= 362\ mL = 360\ mL\ Ca(OH)_2$$

At the second equivalence point, the total volume of solution is:

250. mL + 360 mL = 610 mL

Now we can solve for K_{a_2} using the pH data at the second equivalence point. Because the only species present that has any effect on pH is the weak base A^{2-}, the setup to the problem requires the K_b reaction for A^{2-}.

$$A^{2-} + H_2O \rightleftharpoons HA^- + OH^- \qquad K_b = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{K_{a_2}}$$

	A^{2-}	HA^-	OH^-
Initial	$\frac{2.5\ \text{mmol}}{610\ \text{mmol}}$	0	0
Equil.	$4.1 \times 10^{-3}\ M - x$	x	x

$$K_b = \frac{1.0 \times 10^{-14}}{K_{a_2}} = \frac{x^2}{4.1 \times 10^{-3} - x}$$

From the problem: pH = 7.96, so $[OH^-] = 10^{-6.04} = 9.1 \times 10^{-7}\ M = x$

$$K_b = \frac{1.0 \times 10^{-14}}{K_{a_2}} = \frac{(9.1 \times 10^{-7})^2}{(4.1 \times 10^{-3}) - (9.1 \times 10^{-7})} = 2.0 \times 10^{-10};\ K_{a_2} = 5.0 \times 10^{-5}$$

Note: The amount of OH^- donated by the weak base HA^- will be negligible because the K_b value for A^{2-} is more than a 1000 times the K_b value for HA^-.