Chapter 7

Mixtures of Acids and Bases

1. What is a common ion and what is the common-ion effect?

Common ions are involved in an equilibrium but have more than one source. The common-ion effect is the shift of the equilibrium away from the common ion so as to reduce the effect of the common ion.

3. What is a buffer and how does it function?

A buffer is a mixture of a weak acid and its conjugate base in comparable and appreciable amounts. Buffers convert strong acids and bases into the weak acids and bases, which minimizes the effect of the addition of a strong acid or base.

5. Explain why a solution that is 1.4 mM HF and 6.4 mM KF is not a good buffer.

The concentrations are fairly low, so this buffer would not have a very good buffer capacity.

7. Explain why a solution of a strong acid and its conjugate base is not a buffer. Use a solution of 0.1 M HCl and 0.1 M KCl as an example.

The solution is well protected against additional base because H_3O^{1+} would react with the strong base and convert it to water. However, there is no protection against additional acid because Cl^{1-} is too weak a base to react with H_3O^{1+}.

9. Of the acid-base pairs listed in the Appendix C, which would be the best to prepare buffers at the following pH's:

Choose the conjugate acid-base pair in which the pK_a of the acid is closest to the desired pH.

a) pH = 1.5 H_2SO_3/HSO_3^{1-} $pK_a = 1.82$ **b) pH = 7.0** HSO_3^{1-}/SO_3^{2-} $pK_a = 7.00$
c) pH = 12.0 HPO_4^{2-}/PO_4^{3-} $pK_a = 12.32$

11. What is the pH of a solution that is 0.16 M NH_3 and 0.43 M NH_4Cl?

Use Equation 7.2 and the pK_a of NH_4^{1+} from Appendix C: $pH = pK_a + \log\frac{C_b}{C_a} = 9.25 + \log\frac{0.16}{0.43} = 8.82$

13. What is the pH of a solution made by dissolving 7.6 g of KNO_2 to 750 mL of 0.11 M HNO_2?

Use Equation 7.2 and the pK_a of HNO_2 from Appendix C

$$n_b = 7.6\text{ g KNO}_2\times\frac{1\text{ mol KNO}_2}{85.1\text{ g KNO}_2} = 0.089\text{ mol base};\quad n_a = 0.75\text{ L solution}\times\frac{0.11\text{ mol HNO}_2}{\text{L solution}} = 0.082_5\text{ mol acid}$$

$$pH = pK_a + \log\frac{n_b}{n_a} = 3.40 + \log\frac{0.089}{0.82_5} = 3.43$$

15. How many grams of potassium acetate must be added to 2.5 L of 0.250 M acetic acid to prepare a pH = 4.26 buffer?

We employ the Henderson-Hasselbalch equation to a buffer solution with pH = 4.26. $K_a = 1.8 \times 10^{-5}$ for acetic acid (Appendix C), so $pK_a = 4.74$

$$pH = pK_a + \log\frac{n_b}{n_a} \quad\Rightarrow\quad \log\frac{n_b}{n_a} = pH - pK_a = 4.26 - 4.74 = -0.48 \quad\Rightarrow\quad \frac{n_b}{n_a} = 10^{-0.48} = 0.33$$

Thus, $n_b = 033\ n_a$. We are given that $n_a = 2.5 \times 0.250 = 0.63$ mol, so $n_b = (0.33)(0.63) = 0.21$ mol

Potassium acetate is CH_3COOK and has a molar mass of 98.1 g/mol.

Consequently, (0.21 mol)(98.1 g/mol) = 20. g of potassium acetate should be dissolved

17. How many milliliters of 6.0 M NaOH must be added to 0.50 L of 0.20 M HNO_2 to prepare a pH = 3.86 buffer?

(0.50 L)(0.20 M) = 0.10 mol HNO_2, so the reaction table for the mixing of the weak acid and strong base is

	HNO_2	+	OH^{1-}	→	NO_2^{1-}	+	H_2O
In	0.10		x		0	mol	
Δ	-x		-x		+x	mol	
Eq	0.10 – x		~0		x	mol	

Solve Equation 7.2 for the n_b/n_a ratio

$$\log\frac{n_b}{n_a} = pH - pK_a = 3.86 - 3.40 = 0.46 \Rightarrow \frac{n_b}{n_a} = 10^{0.46} = 2.9$$

$$\frac{x}{0.1 - x} = 2.9 \quad\Rightarrow\quad x = 0.29 - 2.9x,\text{ so } x = \frac{0.29}{3.9} = 0.074\text{ mol} = 74\text{ mmol OH}^{1-}$$

19. Use the data in Appendix C to determine the equilibrium constants for the following reactions?

a) $NH_3(aq) + HCN(aq) \rightleftharpoons NH_4^{1+}(aq) + CN^{1-}(aq)$

The same procedure can be followed in all of these problems. First, identify the reacting acid and the produced acid. Second, find the K_a values for each acid from Appendix C. Finally, use Equation 7.3 to find the equilibrium constant for the overall reaction.

Reacting acid: HCN ($K_a = 4.0 \times 10^{-10}$) Produced acid: NH_4^{1+} ($K_a = 5.6 \times 10^{-10}$)

$$K_{rxn} = \frac{K_a(\text{reacting acid})}{K_a(\text{produced acid})} = \frac{4.0\times10^{-10}}{5.6\times10^{-10}} = 0.71$$

b) $S^{2-}(aq) + HCN(aq) \rightleftharpoons HS^{1-}(aq) + CN^{1-}(aq)$

Reacting acid: HCN ($K_a = 4.0 \times 10^{-10}$) Produced acid: HS^{1-} ($K_a = 1.3 \times 10^{-13}$)

$$K_{rxn} = \frac{4.0\times10^{-10}}{1.3\times10^{-3}} = 3.1\times10^{3}$$

c) $F^{1-}(aq) + HCN(aq) \rightleftharpoons HF(aq) + CN^{1-}(aq)$

Reacting acid: HCN ($K_a = 4.0 \times 10^{-10}$) Produced acid: HF ($K_a = 7.2 \times 10^{-4}$)

$$K_{rxn} = \frac{4.0\times10^{-10}}{7.2\times10^{-4}} = 5.6\times10^{-7}$$

21. What is the sulfite ion concentration in a solution prepared by mixing 25.0 mL of 0.100 M H_2CO_3 and 25.0 mL of 0.100 M K_2SO_3?

This is the reaction of a weak acid and a weak base. Refer to Appendix C for K_a values

Reacting acid is H_2CO_3, $K_a = 4.3 \times 10^{-7}$ Produced acid is HSO_3^{1-}, $K_a = 1.0 \times 10^{-7}$ so $K = \frac{4.3\times10^{-7}}{1.0\times10^{-7}} = 4.3$

K is neither very large nor very small, so the procedures used in Chapter 5 are used here.
The reaction table:

	H_2CO_3 +	SO_3^{2-}	$\rightleftharpoons$	HCO_3^{1-} +	HSO_3^{1-}	
In	0.050	0.050		0	0	M
Δ	-x	-x		x	x	M
eq	0.050-x	0.050-x		x	x	M

The concentrations reflect the dilution of mixing. Set up the equilibrium constant expression

$$K = 4.3 = \frac{(x)(x)}{(0.050 - x)(0.050 - x)} = \frac{x^2}{(0.050 - x)^2}$$

take the square root of both sides: $\sqrt{4.3} = 2.07 = \frac{x}{0.050 - x} \Rightarrow 0.10 - 2.07x = x$

solve for x: $x = \frac{0.10}{3.07} = 0.034$ M; $[SO_3^{2-}] = 0.050 - x = 0.050 - 0.034 = 0.016$ M

23. What is the $[F^{1-}]$ in a solution prepared by mixing 25 mL of 0.16 M HF and 42 mL of 0.086 M KCN?

Reacting acid: HF = 7.2×10^{-4} Produced acid: HCN = 4.0×10^{-10} $K = \frac{7.2\times10^{-4}}{4.0\times10^{-10}} = 1.8\times10^{6}$

K is very large, so this reaction is extensive. Stoichiometry alone can be used to obtain all concentrations other than that of the limiting reactant(s). We set up the reaction table in mmoles rather than concentrations to avoid dilution effects.

The reaction table:	HF	+	CN^{1-}	$\rightleftharpoons$	F^{1-}	+	CN^{1-}	
In	4.0		3.6		0		0	mmol
Δ	-3.6		-3.6		+3.6		+3.6	mmol
eq	0.4		~0		3.6		3.6	mmol

Thus, 3.6 mmol F^{1-} are present in 25+42 = 67 mL of solution, so $[F^{1-}] = \frac{3.6 \text{ mmol } F^{1-}}{67 \text{ mL}} = 0.054$ M

25. What is the pH of a solution made by mixing 5.0 mL of 1.2 M HCl and 3.0 mL of 0.88 M HBr?

Two strong acids and no base, so the hydronium ion concentration is determined as follows:

$$[H_3O^{1+}] = \frac{(5.0\text{ mL})(1.2\text{ mmol/mL}) + (3.0\text{ mL})(0.88\text{ mmol/mL})}{5.0\text{ mL} + 3.0\text{ mL}} = \frac{(6.0 + 2.6)\text{ mmol}}{8.0\text{ mL}} = 1.1\text{ M}$$

pH = -log (1.08) = -0.03 (Note that extra figures from the hydronium concentration were used.)

27. What is the pH of a solution prepared by mixing 5.00 mL of 1.20 M HCl and 4.60 mL of 0.840 M NaOH?

Reaction of a strong acid and a strong base. Initially: (5.0)(1.2) = 6.0 mmol H_3O^{1+} and (4.6)(0.84) = 3.9 mmol OH^{1-}

	H_3O^{1+}	+	OH^{1-}	→	$2H_2O$
In	6.00		3.86		
Δ	-3.86		-3.86		
Final	2.14		~0		⇒ A strong acid solution.

$$[H_3O^{1+}] = \frac{2.14\text{ mmol }H_3O^{1+}}{9.60\text{ mL}} = 0.222_5\text{ M} \Rightarrow \text{pH} = -\log 0.222_5 = 0.653$$

29. Calculate the pH change that results when 10. mL of 3.0 M NaOH is added to 500. mL of each of the following solutions:

Establish initial pH (pH_i) and final pH (pH_f). In each case, (10 mL)(3.0 mmol/mL) = 30 mmol OH^{1-} is added.

a) water

pH_i = 7.00. The dilution from 500. mL to 510. mL must be considered.

$$[OH^{1-}] = \frac{30\text{ mmol}}{(500 + 10)\text{ mL}} = 0.059\text{ M} \rightarrow \text{pOH} = 1.23\text{, so } pH_f = 12.77\text{, and } \Delta pH = pH_f - pH_i = 12.77 - 7.00 = +5.77$$

b) 0.10 M CH_3COO^{1-}

Acetate is the conjugate base of acetic acid, $HC_2H_3O_2$ its $K_b = 5.6 \times 10^{-10}$. Use this to find the initial $[OH^-]$.

$$[OH^{1-}] = \sqrt{K_b \times c_o} = \sqrt{5.6\times10^{-10}\times0.10} = 7.48\times10^{-6}\text{ M} \rightarrow \text{pOH} = 5.13\text{, so } pH_i = 8.87$$

The weak base can be ignored in a solution of a strong base and a weak base because the strong base suppresses the weak base action by the common-ion effect. Thus, the pH of the final solution is the same as in Part a.

$\Delta pH = pH_f - pH_i = 12.77 - 8.87 = +3.90$

c) 0.10 M CH_3COOH

The K_a of acetic acid is 1.8×10^{-5}. Use this to find the initial $[H_3O^+]$.

$$[H_3O^{1+}] = \sqrt{K_a \times c_o} = \sqrt{(1.8\times10^{-5})(0.10)} = 1.34\times10^{-3}\text{ M , so } pH_i = 2.87$$

The initial reaction with OH^{1-} is summarized below (values in mmols).

	$HC_2H_3O_2$	+	OH^{1-}	→	H_2O	+	$C_2H_3O_2^{1-}$	
Initial	50		30				0	
Δ	-30		-30				+30	
Final	20		0				30	⇒ A buffer solution

$$pH_f = pK_a + \log\frac{[C_2H_3O_2^{1-}]}{[HC_2H_3O_2]} = 4.74 + \log\frac{30}{20} = 4.92 \qquad \Delta pH = pH_f - pH_i = 4.92 - 2.87 = +2.05$$

d) a solution that is 0.10 M in each acetate ion and acetic acid.

Buffers are solution that contain both acidic and basic species and resist changes to pH. Initial pH can be determined using the Henderson-Hasselbalch equation (Eq. 7.2).

$$pH_i = pK_a + \log\frac{[C_2H_3O_2^{1-}]}{[HC_2H_3O_2]} = 4.74 + \log\frac{0.10\text{ M}}{0.10\text{ M}} = 4.74$$

The initial reaction with OH^{1-} is summarized below.

	$HC_2H_3O_2$	+	OH^{1-}	→	H_2O	+	$C_2H_3O_2^{1-}$	
Initial	50		30				50	
Δ	- 30		- 30				+ 30	
After Rxn	20		0				80	⇒ A buffer solution

$$pH_i = pK_a + \log\frac{[C_2H_3O_2^{1-}]}{[HC_2H_3O_2]} = 4.74 + \log\frac{80}{20} = 5.34 \text{ and } \Delta pH = pH_f - pH_i = 5.34 - 4.74 = +0.60$$

Mixtures of Acids and Bases

31. Calculate the pH change that results when 10. mL of 6.0 M HCl is added to 750. mL of each of the following solutions:

a) water

The initial solution is pure water, which has a pH = 7.00. Addition of (10 mL)(6.0 mmol/mL) = 60 mmol to 750 mL results in 760 mL of solution in which $[H_3O^{1+}] = \dfrac{60 \text{ mmol } H_3O^{1+}}{760 \text{ mL soluton}} = 0.079 \text{ M}$

This part of the problem is the dilution of the original 1.0 M HCl solution. The pH after the addition of the HCl is pH = -log(0.079) = 1.10. Therefore, the pH change can be calculated to be $\Delta pH = pH_f - pH_i = 1.10 - 7.0 = -5.90$

b) 0.10 M ammonium chloride

In this problem, we must calculate the pH of the ammonium solution before the addition of the HCl.

$NH_4^{1+} + H_2O$ Í $NH_3 + H_3O^{1+}$ $K_a = 5.6 \times 10^{-10}$

$K_a = \dfrac{[H_3O^{1+}][NH_3]}{[NH_4^{1+}]}$, so $[H_3O^{1+}] = \sqrt{K_a[NH_4^{1+}]} = \sqrt{(5.6\times10^{-10})(0.10)} = 7.5\times10^{-6}$ M and pH = -log(7.5 x 10^{-6}) = 5.13

Addition of a strong acid to a weak acid results in a solution with the same pH as the addition of the acid to water (common ion effect, see Section 7.1). So the final pH is 1.10 as in Part a.

$\Delta pH = 1.10 – 5.13 = -4.03$

c) 0.10 M NH_3

First, calculate the pH of the original ammonia solution: $NH_3 + H_2O$ Í $NH_4^{1+} + OH^{1-}$ $K_b = 1.8 \times 10^{-5}$

$[OH^{1-}] = \sqrt{(1.8 \times 10^{-5})(0.10)} = 0.0013$ M

pH = 14 – pOH = 14 – 2.87 = 11.13

The final solution is prepared by mixing (750 mL)(0.10 M) = 75 mmol NH_3 with 60 mmol H_3O^{1+}, so the acid-base reaction table is

	NH_3	+	H_3O^{1+}	$\rightarrow$	NH_4^{1+}	+	H_2O	
Initial:	75		60		0		-	
Δ	-60		-60		60		-	
Final:	15		small		60		-	$\Rightarrow$ A buffer solution

$pH = pK_a + \log\dfrac{n_b}{n_a} = 9.25 + \log\dfrac{15}{60} = 8.65$. Finally, $\Delta pH = 8.65 – 11.13 = -2.48$

d) a solution that is 0.10 M in each ammonium ion and NH_3.

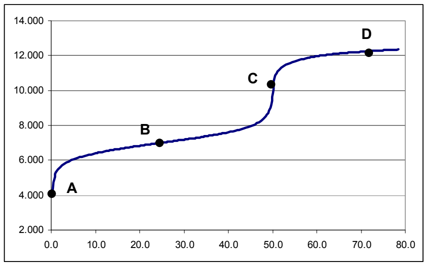
The initial solution is a buffer in which $n_a = n_b$, so $pH = pK_a = 9.25$

In this problem, the 60. mmol of H_3O^{1+} is added to a buffer solution that contains 75 mmoles each of the acid and the base.

	NH_3	+	H_3O^{1+}	$\rightarrow$	NH_4^{1+}	+	H_2O	
Initial:	75		60		75		-	
Δ	-60		-60		+60		-	
Final:	15		-		135		-	$\Rightarrow$ A buffer solution

$pH = pK_a + \log\dfrac{n_b}{n_a} = 9.25 + \log\dfrac{15}{135} =$ 8.30 , and $\Delta pH = 8.30 – 9.25 = -0.95$

33. Sketch the titration curve for the titration of 50 mL of 0.1 M HA ($K_a = 10^{-7}$) with 0.1 M NaOH.



Point A: pH: $[H_3O^{1+}] = \sqrt{(10^{-7})(0.1)} = 10^{-4}$ M $\Rightarrow$ pH = 4

Point B: $pH = pK_a = 7$

Point C: Equivalence point: a solution of the weak base A^{1-}.

$[A^{1-}] = \dfrac{5 \text{ mmol}}{100 \text{ mL}} = 0.05 \text{ M}; K_b = \dfrac{10^{-14}}{10^{-7}} = 10^{-7};$

$[OH^{1-}] = \sqrt{(10^{-7})(0.05)} = 7\times10^{-5}$; pOH = 4.1; pH = 9.9

Point D: Excess hydroxide (7 mmol added – 5 mmol reacted)

$[OH^{1-}] = \dfrac{2 \text{ mmol}}{120 \text{ mL}} = 0.017$ M; pOH = 1.8; pH = 12.2

35. What are the pH's of the first and second equivalence points in the titration of 25 mL of 0.080 M H_3PO_4 with 0.065 M NaOH?

The first equivalence point consists of a solution of the amphiprotic substance $H_2PO_4^{1-}$. The pH of the solution is obtained from Equation 6.12 to be pH = ½(pK$_1$ + pK$_2$) = ½(2.12+7.21) = 4.67. The second equivalence point is a solution of $H_2PO_4^{1-}$, which is also amphiprotic, so pH = = ½(pK$_2$ + pK$_3$) = ½(7.21 + 12.32) = 9.77.

37. Consider the titration of 35.0 mL of 0.122 M ammonia with 0.0774 M HCl.

a) How many mL of HCl are required to reach the equivalence point?

The reaction is a 1:1 acid-base reaction, so we can use $M_AV_A = M_BV_B$ for this part of the problem.

(0.0774 M)(V_A) = (0.122 M)(35.0 mL) = 4.27 mmol, so $V_A = \dfrac{(0.122\text{ M})(35.00\text{ mL})}{0.0774\text{ M}} = 55.2\text{ mL HCl}$.

b) What is the pH at the equivalence point? What indicator should be used for this titration?

As discussed in Example 7.9, the equivalence point is the point at which the number of moles of H_3O^{1+} added equals the number of moles of NH_3 in the original solution. In this problem, 4.27 mmol NH_3 have been added to 4.27 mmol H_3O^{1+} to produce 4.27 mmol NH_4^{1+}. The total volume of the solution is 35.0 + 55.2 = 90.2 mL, so the ammonium ion concentration at the equivalence point is $\dfrac{4.27\text{ mmol}}{90.2\text{ mL}} = 0.0473\text{ M }NH_4^{1+}$

From Equation 6.5 and the dissociation expression, $[H_3O^{1+}]=\sqrt{K_a\left[NH_4^{1+}\right]} = \sqrt{(5.6\times10^{-10})(0.0473)} = 5.1\times10^{-6}\text{ M}$

pH = -log(5.1 x 10^{-6}) = 5.29; A useful indicator for this pH is bromocresol green.

c) What is the pH of the solution after addition of 15.0 mL of acid?

First, construct the Reaction Table. 15.0 mL of acid contains (15.0 mL)(0.0774 mmol/mL) = 1.16 mmol H_3O^{1+}

	H_3O^{1+} +	NH_3 →	NH_4^{1+} +	H_2O
Initial	1.16	4.27	0	
Δ	-1.16	-1.16	+1.16	
Eq	~0	3.11	1.16	⇒ A buffer solution

$\text{pH} = \text{p}K_a + \log\dfrac{n_b}{n_a} = 9.25 + \log\dfrac{3.11}{1.16} = 9.68$, where 9.25 is the p$K_a$ of NH_4^{1+}.

d) What is the pH of the solution after the addition of 65.0 mL of acid?

First, construct the Reaction Table

65.0 mL of acid contains (15.0 mL)(0.0774 mmol/mL) = 5.03 mmol H_3O^{1+}

	H_3O^{1+} +	NH_3 →	NH_4^{1+} +	H_2O
Initial	5.03	4.27	0	
Δ	-4.27	-4.27	+4.27	
Eq	0.76	~0	4.27	

The resulting solution is a solution of a strong acid. The NH_4^{1+} can be ignored in the presence of the strong acid due to the common ion effect. Thus, $[H_3O^{1+}]=\dfrac{0.76\text{ mmol}}{(65.0 + 35.0)} = 0.0076\text{ M}$ and pH = -log 0.0076 = 2.12

39. 50.0 ml of 0.10 M HCl are required to titrate 10.0 ml of ammonia window cleaner to the end point.

a) What is the concentration of ammonia in the window cleaner?

$$H_3O^{1+} + NH_3 \rightarrow NH_4^{1+} + H_2O$$

The mole to mole ratio between H_3O^{1+} and NH_3 is 1 to 1. Apply the equation $C_A V_A = C_B V_B$

$$C_{NH_3} = \frac{C_{HCl}\times V_{HCl}}{V_{NH_3}} = \frac{0.10\text{ M HCl}\times 50.0\text{ mL HCl}}{10.0\text{ mL }NH_3} = 0.50\text{ M }NH_3$$

b) What is the pH of the window cleaner given that $K_b = 1.8 \times 10^{-5}$?

Ammonia is a weak base, so Eq. 6.7 can be used to solve for $[OH^{1-}]$ and pH can be calculated.

$\left[OH^{1-}\right]=\sqrt{K_bc_o} = \sqrt{1.8\times10^{-5}\times0.50} = 3.0\times10^{-3}\text{ M}$ pOH = 2.5 and pH = 14.0 – 2.5 = 11.5

c) What is the pH at the equivalence point?

The solution is a solution of the weak acid NH_4^{1+} ($K_a = 5.6 \times 10^{-10}$) at the equivalence point. (50.0 mL)(0.10 mmol/mL) = 5.0 mmol of acid was required to reach the equivalence point so there are 5.0 mmol NH_4^{1+} produced. The total volume is 50.0 + 10.0 – 60.0 mL. Thus, $[NH_4^{1+}]$ = 5 mmol/60 mL = 0.083 M. The hydronium ion concentration is this weak acid solution is determined as follows : $[H_3O^{1+}] = \sqrt{(5.6\times10^{10})(0.083)} = 6.8\times10^{-6}$ M, so pH = 5.17

d) Which indicator would be best to use in this titration?

Bromocresol green with a pH range of 3.8 – 5.4 would be the best indicator listed.

b) What is the molar mass of the acid?

There are 4.641 mmol in 25.00 mL, so there are 4(4.641) = 18.56 mmol in the 100 mL sample, which contained 5.182 g of acid. Consequently, the molar mass of the acid is $M_m = \dfrac{5.182\text{ g}}{0.01856\text{ mol}} = 279.1\text{ g}\cdot\text{mol}^{-1}$

c) What is the pK_a of the acid?

Consider the composition after the addition of 20.00 mL of base

n_b = (20.00 mL)(0.09685 mmol/mL) = 1.937 mmol

	HA	+	OH^{1-}	→	A^{1-}	+	H_2O
In	4.641		1.937		0		
Δ	-1.937		-1.937		+1.937		
Eq	2.704		~0		1.937		

The solution is a buffer, so we use the given pH and Equation 7.2 to get the pK_a

$$pK_a = pH - \log\frac{n_b}{n_a} = 5.58 - \log\frac{1.937}{2.704} = 5.72$$

41. What is the percent purity of a benzoic acid (C_6H_5COOH) if 406.2 mg of the weak monoprotic acid dissolved in 50 mL of water required 38.62 mL of 0.06642 M NaOH solution to reach the equivalence point?

a) What is the percent purity of the benzoic acid?

Moles of acid = moles of base added at equivalence point = (38.62 mL)(0.06642 M) = 2.565 mmol

M_m = 7(12.011) + 6(1.0079) + 2(15.999) = 122.122 g/mol. The sample contained (2.565 mmol)(122.122 mg/mmol) = 313.2 mg, so % = $\dfrac{\text{mass of acid}}{\text{mass of sample}}\times100\% = \dfrac{313.2\text{ mg}}{406.2\text{ mg}}\times100\%$ = 77.12%

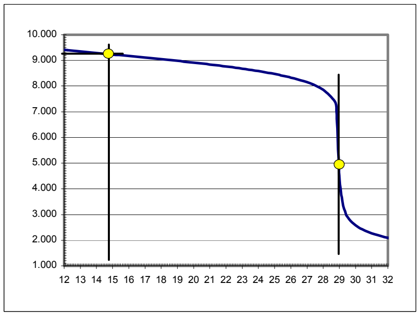
b) What is the pK_a of benzoic acid if the pH of the solution after the addition of 25.00 mL of base was 4.46?

Consider the composition after the addition of 25.00 mL of base. n_b = (25.00 mL)(0.06642 mmol/mL) = 1.661 mmol

	$HC_6H_5O_2$	+	OH^{1-}	→	$C_6H_5O_2^{1-}$	+	H_2O
In	2.565		1.661		0		
Δ	-1.661		-1.661		+1.661		
Eq	0.904		~0		1.661		

The solution is a buffer, Equation 7.2 can be used to get the pK_a : $pK_a = pH - \log\dfrac{n_b}{n_a} = 4.46 - \log\dfrac{1.661}{0.904} = 4.20$

43. Use the portion of the titration curve for the titration of 20.00 mL of a weak base with 0.143 M HCl shown above right to determine the concentration and pK_b of the weak base.



The equivalence point occurs at V = 29 mL, so the concentration of the acid is $c_b = \dfrac{(29)(0.143)\text{ mmol}}{20.00\text{ mL}}$ =0.21 M

The pH at the midpoint of the titration (29/2 = 14.5 mL) is 9.3, so pK_a = 9.3 for the conjugate acid. pK_b = 14.0 – 9.3 = 4.7 for the base.

45. What are the concentrations of H_2S, HS^{1-}, and S^{2-} in a solution prepared by adjusting a 0.10 M H_2S acid solution to the following pH's? $K_1 = 1.0\text{x}10^{-7}$ and $K_2 = 1.3\text{x}10^{-13}$; $pK_1 = 7.00$ and $pK_2 = 12.89$

a) pH = 5.0

The pH is more than 2 units lower than K_1, so $[H_2S] = 0.10$ M.

$$[HS^{1-}] = \frac{K_1[H_2S]}{[H_3O^{1+}]} = \frac{(1.00\times10^{-7})(0.10)}{1.0\times10^{-5}} = 0.0010\text{ M} \;\;\&\;\; [S^{2-}] = \frac{K_2[HS^{1-}]}{[H_3O^{1+}]} = \frac{(1.3\times10^{-13})(0.0010)}{1.0\times10^{-5}} = 1.3\times10^{-11}\text{ M}$$

b) pH = 7.0

The pH is within 2 units of pK_1, so both H_2S and HS^{1-} are important. In addition, $pH = pK_a$, so $[H_2S] = [HS^{1-}] = 0.050$ M.

$$[S^{2-}] = \frac{K_2[HS^{1-}]}{[H_3O^{1+}]} = \frac{(1.3\times10^{-13})(0.05)}{1.0\times10^{-7}} = 6.5\times10^{-8}\text{ M}$$

c) pH = 10.0

This pH is not within 2 units of either pK_a, but it is between the two, so $[HS^{1-}] = 0.10$ M.

$$[H_2S] = \frac{[HS^{1-}][H_3O^{1+}]}{K_1} = \frac{(0.10)(1.0\times10^{-10})}{1.0\times10^{-7}} = 1.0\times10^{-4}\text{ M} \;\;\&\;\; [S^{2-}] = \frac{K_2[HS^{1-}]}{[H_3O^{1+}]} = \frac{(1.3\times10^{-13})(0.10)}{1.0\times10^{-10}} = 1.3\times10^{-4}\text{ M}$$

d) pH = 13.0

The pH is within 2 units of pK_2, so both S^{2-} and HS^{1-} are important, so $[HS^{1-}] = 0.10 - [S^{2-}]$

$$\frac{0.10 - [HS^{1-}]}{[HS^{1-}]} = \frac{K_2}{[H_3O^{1+}]} = 1.3 \;\Rightarrow\; [HS^{1-}] = \frac{0.10}{2.3} = 0.043\text{ M} \;\;\&\;\; [S^{2-}] = 0.10 - 0.043 = 0.057\text{ M}$$

$$[H_2S] = \frac{[HS^{1-}][H_3O^{1+}]}{K_1} = \frac{(0.057)(1.0\times10^{-13})}{1.0\times10^{-7}} = 5.7\times10^{-8}\text{ M}$$

47. To what pH must a 0.100 M H_2S solution be adjusted to obtain the following sulfide ion concentrations?

a) $[S^{2-}] = 0.085$ M

Sulfide can only be present in appreciable amounts with HS^{1-}, so $[HS^{1-}] = 0.100 – 0.085 = 0.015$ M. Use the Henderson-Hasselbalch equation to determine the pH of this buffer system.

$$pH = pK_2 + \log\left(\frac{[S^{2-}]}{[HS^{1-}]}\right) = 7.00 + \log\left(\frac{0.085}{0.015}\right) = 7.75$$

b) $[S^{2-}] = 1.0\text{x}10^{-14}$ M

Assume only neglibible reaction by H_2S because the sulfide concentration is so low and use the K_{12} expression.

$$K_{12} = 1.3\times10^{-20} = \frac{[S^{2-}][H_3O^{1+}]^2}{[H_2S]} \;\Rightarrow\; [H_3O^{1+}] = \sqrt{\frac{1.3\times10^{-20}[H_2S]}{[S^{2-}]}} = \sqrt{\frac{1.3\times10^{-20}(0.10)}{1.0\times10^{-14}}} = 1.1\times10^{-7} \;\Rightarrow\; pH = 6.96$$

c) $[HS^{1-}] = 0.10$ M

A solution of an amphiprotic substance, so $pH = ½(pK_1 + pK_2) = ½(7.00+12.89) = 9.95$

49. HCl is added to a 0.140 M phosphate ion solution until the dihydrogen phosphate ion concentration is 0.075 M but the hydrogen phosphate ion concentration is negligible. What is the pH?

$[H_2PO_4^{1-}] = 0.075$ M, so another ion must be $0.140 – 0.075 = 0.065$ M. $H_2PO_4^{1-}$ can be appreciable with only HPO_4^{2-} or H_3PO_4, but the problem states that it is not HPO_4^{2-}, $[H_3PO_4] = 0.065$ M. Use the Henderson-Hasselbalch equation to determine the pH of this buffer system.

$$pH = pK_1 + \log\left(\frac{[H_2PO_4^{1-}]}{[H_3PO_4]}\right) = 2.12 + \log\left(\frac{0.075}{0.065}\right) = 2.18$$

Mixtures of Acids and Bases

51. In molecular biology, PO_4^{3-} buffers are normally utilized to maintain a physiological pH of 6.8 to 7.4. However for RNA isolation more acidic conditions (pH around 5.8) are often required for optimal enzymatic function.

a) Explain why an acetate buffer is preferred over a phosphate buffer for RNA isolation.

Examine each buffer's pK_a value(s).

$H_3PO_4/H_2PO_4^{1-}$	$pK_{a1} = 2.12$
$H_2PO_4^{1-}/HPO_4^{2-}$	$pK_{a2} = 7.21$
CH_3COOH/CH_3COO^{1-}	$pK_a = 4.74$

Phosphate buffers work well near pH = 2 and pH = 7 while the acetate buffer works best near pH = 5 making it the better choice.

b) How many grams of CH_3COONa should be dissolved in 500 mL of 0.112 M CH_3COOH to make a pH = 5.8 buffer?

Use Eqn. 7.1 to calculate the ratio of concentrations of acetate to acetic acid:

$$\frac{n_a}{n_b} = \frac{[H_3O^{1+}]}{K_a} = \frac{10^{-5.8}}{10^{-4.74}} = \frac{0.087\text{ mol acetic acid}}{\text{mol acetate ion}}$$

$$\text{moles of acetic acid} = 0.500\text{ L} \times \frac{0.112\text{ mol acetic acid}}{\text{L}} = 0.0560\text{ mol acetic acid}$$

$$0.056\text{ mol acetic acid} \times \frac{1\text{ mol acetate ion}}{0.087\text{ mol acetic acid}} = 0.64\text{ mol acetate ion}$$

Determine the mass of sodium acetate: $0.64\text{ mol } CH_3COONa \times \frac{82.0\text{g } CH_3COONa}{1\text{mol } CH_3COONa} = 52.\text{ g } CH_3COONa$