Chapter 7: 31, 32, 34, 39, 47, 49, 67, 113
Chapter 8: 26, 27, 31, 103

Solutions of Acids

31. Strong acids are assumed to completely dissociate in water, e.g., $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ or $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$.

a. A 0.10 M HCl solution gives 0.10 M H^+ and 0.10 M Cl^- since HCl completely dissociates. The amount of H^+ from H_2O will be insignificant.

$pH = -\log [H^+] = -\log (0.10) = 1.00$

b. 5.0 M H^+ is produced when 5.0 M $HClO_4$ completely dissociates. The amount of H^+ from H_2O will be insignificant. $pH = -\log (5.0) = -0.70$ (Negative pH values just indicate very concentrated acid solutions.)

c. 1.0×10^{-11} M H^+ is produced when 1.0×10^{-11} M HI completely dissociates. If you take the negative log of 1.0×10^{-11} this gives pH = 11.00. This is impossible! We dissolved an acid in water and got a basic pH. What we must consider in this problem is that water by itself donates 1.0×10^{-7} M H^+. We can normally ignore the small amount of H^+ from H_2O except when we have a very dilute solution of an acid (as in the case here). Therefore, the pH is that of neutral water (pH = 7.00) since the amount of HI present is insignificant.

32. $$50.0 \text{ mL con. HCl soln} \times \frac{1.19 \text{ g}}{\text{mL}} \times \frac{38 \text{ g HCl}}{100 \text{ g con. HCl soln}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g}} = 0.62 \text{ mol HCl}$$

$$20.0 \text{ mL con. } HNO_3 \text{ soln} \times \frac{1.42 \text{ g}}{\text{mL}} \times \frac{70.\text{ g } HNO_3}{100 \text{ g soln}} \times \frac{1 \text{ mol } HNO_3}{63.0 \text{ g } HNO_3} = 0.32 \text{ mol } HNO_3$$

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$ and $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$ (Both are strong acids.)

So we will have 0.62 + 0.32 = 0.94 mol of H^+ in the final solution.

$$[H^+] = \frac{0.94 \text{ mol}}{1.00 \text{ L}} = 0.94\ M;\ pH = -\log [H^+] = -\log (0.94) = 0.027 = 0.03$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.94} = 1.1 \times 10^{-14}\ M$$

34. At pH = 2.000, $[H^+] = 10^{-2.000} = 1.00 \times 10^{-2}\ M$; At pH = 4.000, $[H^+] = 10^{-4.000} = 1.00 \times 10^{-4}\ M$

$$\text{mol } H^+ \text{ present} = 0.0100 \text{ L} \times \frac{0.0100 \text{ mol } H^+}{\text{L}} = 1.00 \times 10^{-4} \text{ mol } H^+$$

Let V = total volume of solution at pH = 4.000: $1.00 \times 10^{-4} \text{ mol/L} = \frac{1.00 \times 10^{-4} \text{ mol } H^+}{V}$, V = 1.00 L

Volume of water added = 1.00 L - 0.0100 L = 0.99 L = 990 mL

39. This is a weak acid in water. We must solve a weak acid problem. Let HBz = $C_6H_5CO_2H$.

$$0.56 \text{ g HBz} \times \frac{1 \text{ mol HBz}}{122.1 \text{ g}} = 4.6 \times 10^{-3} \text{ mol}; \quad [\text{HBz}]_o = 4.6 \times 10^{-3}\ M$$

	HBz	$\rightleftharpoons$	H^+	+	Bz^-
Initial	$4.6 \times 10^{-3}\ M$		~0		0
	x mol/L HBz dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$4.6 \times 10^{-3} - x$		x		x

$$K_a = 6.4 \times 10^{-5} = \frac{[H^+][Bz^-]}{[HBz]} = \frac{x^2}{4.6 \times 10^{-3} - x} \approx \frac{x^2}{4.6 \times 10^{-3}}$$

$x = [H^+] = 5.4 \times 10^{-4}$; Check assumptions: $\frac{x}{4.6 \times 10^{-3}} \times 100 = \frac{5.4 \times 10^{-4}}{4.6 \times 10^{-3}} \times 100 = 12\%$

Assumption is not good (x is 12% of 4.6×10^{-3}). When assumption(s) fail, we must solve exactly using the quadratic formula or the method of successive approximations (see Appendix 1.4 of text). Using successive approximations:

$$\frac{x^2}{(4.6 \times 10^{-4} - 5.4 \times 10^{-4})} = 6.4 \times 10^{-5}, \ x = 5.1 \times 10^{-4}$$

$$\frac{x^2}{(4.6 \times 10^{-3} - 5.1 \times 10^{-4})} = 6.4 \times 10^{-5}, \ x = 5.1 \times 10^{-4}\ M \text{ (consistent answer)}$$

So: $x = [H^+] = [Bz^-] = [C_6H_5CO_2^-] = 5.1 \times 10^{-4}\ M$

$[HBz] = [C_6H_5CO_2H] = 4.6 \times 10^{-3} - x = 4.1 \times 10^{-3}\ M$

pH = $-\log(5.1 \times 10^{-4}) = 3.29$; pOH = 14.00 - pH = 10.71; $[OH^-] = 10^{-10.71} = 1.9 \times 10^{-11}\ M$

47. In all parts of this problem, acetic acid ($HC_2H_3O_2$) is the best weak acid present. We must solve a weak acid problem.

a.

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	+	$C_2H_3O_2^-$
Initial	$0.50\ M$		~0		0
	x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.50 - x$		x		x

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50}$$

$x = [H^+] = [C_2H_3O_2^-] = 3.0 \times 10^{-3}\ M$ Assumptions good.

$$\text{Percent dissociation} = \frac{[H^+]}{[HC_2H_3O_2]_o} \times 100 = \frac{3.0 \times 10^{-3}}{0.50} \times 100 = 0.60\%$$

b. The set-up for solutions b and c are similar to solution a except the final equation is slightly different, reflecting the new concentration of $HC_2H_3O_2$.

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$x = [H^+] = [C_2H_3O_2^-] = 9.5 \times 10^{-4}\ M$ Assumptions good.

$$\%\ \text{dissociation} = \frac{9.5 \times 10^{-4}}{0.050} \times 100 = 1.9\%$$

c. $K_a = 1.8 \times 10^{-5} = \dfrac{x^2}{0.0050 - x} \approx \dfrac{x^2}{0.0050}$

$x = [H^+] = [C_2H_3O_2^-] = 3.0 \times 10^{-4}\ M$; Check assumptions.

Assumption that x is negligible is borderline (6.0% error). We should solve exactly. Using the method of successive approximations (see Appendix 1.4 of text):

$$1.8 \times 10^{-5} = \frac{x^2}{0.0050 - 3.0 \times 10^{-4}} = \frac{x^2}{0.0047},\ x = 2.9 \times 10^{-4}$$

Next trial also gives $x = 2.9 \times 10^{-4}$.

$$\%\ \text{dissociation} = \frac{2.9 \times 10^{-4}}{5.0 \times 10^{-3}} \times 100 = 5.8\%$$

d. As we dilute a solution, all concentrations are decreased. Dilution will shift the equilibrium to the side with the greater number of particles. For example, suppose we double the volume of an equilibrium mixture of a weak acid by adding water, then:

$$Q = \frac{\left(\frac{[H^+]_{eq}}{2}\right)\left(\frac{[X^-]_{eq}}{2}\right)}{\left(\frac{[HX]_{eq}}{2}\right)} = \frac{1}{2}K_a$$

$Q < K_a$, so the equilibrium shifts to the right or towards a greater percent dissociation.

e. $[H^+]$ depends on the initial concentration of weak acid and on how much weak acid dissociates. For solutions a-c the initial concentration of acid decreases more rapidly than the percent dissociation increases. Thus, $[H^+]$ decreases.

49. pH = 2.77, $[H^+] = 10^{-2.77} = 1.7 \times 10^{-3}\ M$

	$HOCN$	$\rightleftharpoons$	H^+	+	OCN^-
Initial	0.0100		~0		0
Equil.	0.0100 - x		x		x

$x = [H^+] = [OCN^-] = 1.7 \times 10^{-3}\ M$; $[HOCN] = 0.0100 - x = 0.0100 - 0.0017 = 0.0083\ M$

$$K_a = \frac{[H^+][OCN^-]}{[HOCN]} = \frac{(1.7 \times 10^{-3})^2}{8.3 \times 10^{-3}} = 3.5 \times 10^{-4}$$

Solutions of Bases

67. $\frac{5.0\times10^{-3}\text{ g}}{0.0100\text{ L}}\times\frac{1\text{ mol}}{299.4\text{ g}} = 1.7\times10^{-3}\ M = [\text{codeine}]_o$; Let cod = codeine, $C_{18}H_{21}NO_3$

Solving the weak base equilibrium problem:

	cod + H_2O	$\rightleftharpoons$	$codH^+$	+	OH^-	$K_b = 10^{-6.05} = 8.9\times10^{-7}$
Initial	$1.7\times10^{-3}\ M$		0		~0	
	x mol/L codeine reacts with H_2O to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$1.7\times10^{-3} - x$		x		x	

$K_b = 8.9\times10^{-7} = \frac{x^2}{1.7\times10^{-3}-x} \approx \frac{x^2}{1.7\times10^{-3}}$, $x = 3.9\times10^{-5}$ Assumptions good.

$[OH^-] = 3.9\times10^{-5}\ M$; $[H^+] = K_w/[OH^-] = 2.6\times10^{-10}\ M$; pH = $-\log[H^+] = 9.59$

Challenge Problems

113.

	HA	$\rightleftharpoons$	H^+	+	A^-	$K_a = 1.00\times10^{-6}$
Initial	C		~0		0	C = $[HA]_o$ for pH = 4.000 solution
Equil.	C - 1.00×10^{-4}		1.00×10^{-4}		1.00×10^{-4}	$x = [H^+] = 1.00\times10^{-4}\ M$

$K_a = \frac{(1.00\times10^{-4})^2}{C-1.00\times10^{-4}} = 1.00\times10^{-6}$; Solving: C = 0.0101 M

The solution initially contains 50.0×10^{-3} L × 0.0101 mol/L = 5.05×10^{-4} mol HA. We then dilute to a total volume V in liters. The resulting pH = 5.000, so $[H^+] = 1.00\times10^{-5}$. In the typical weak acid problem, $x = [H^+]$, so:

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial	5.05×10^{-4} mol/V		~0		0
Equil.	$5.05\times10^{-4}/V - 1.00\times10^{-5}$		1.00×10^{-5}		1.00×10^{-5}

$K_a = \frac{(1.00\times10^{-5})^2}{5.05\times10^{-4}/V - 1.00\times10^{-5}} = 1.00\times10^{-6}$, $1.00\times10^{-4} = 5.05\times10^{-4}/V - 1.00\times10^{-5}$

V = 4.59 L; 50.0 mL are present initially, so we need to add 4540 mL of water.

Chapter 8: 26, 27, 31, 103

Buffers

26. a. $HNO_2 \rightleftharpoons H^+ + NO_2^-$ $K_a = 4.0 \times 10^{-4}$, $pK_a = -\log(4.0 \times 10^{-4}) = 3.40$

This is a buffer solution. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]} = 3.40 + \log\frac{(0.15)}{(0.10)} = 3.40 + 0.18 = 3.58$$

b. $25.0\text{ g } HC_2H_3O_2 \times \frac{1\text{ mol}}{60.05\text{ g}} = 0.416\text{ mol } HC_2H_3O_2$; $[HC_2H_3O_2] = \frac{0.416\text{ mol}}{0.500\text{ L}} = 0.832\ M$

$40.0\text{ g } NaC_2H_3O_2 \times \frac{1\text{ mol}}{82.03\text{ g}} = 0.488\text{ mol } NaC_2H_3O_2$; $[C_2H_3O_2^-] = \frac{0.488\text{ mol}}{0.500\text{ L}} = 0.976\ M$

$pH = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$; $K_a = 1.8 \times 10^{-5}$; $pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

$$pH = 4.74 + \log\frac{(0.976)}{(0.832)} = 4.74 + 0.0693 = 4.81$$

c. Let's work with mmol in this problem. This requires the use of mmol/mL for molarity units instead of mol/L (the 10^3 conversion factors cancel).

$50.0\text{ mL} \times \frac{1.0\text{ mmol}}{\text{mL}} = 50.\text{ mmol HOCl}$; $30.0\text{ mL} \times \frac{0.80\text{ mmol NaOH}}{\text{mL}} = 24\text{ mmol } OH^-$

The strong base reacts with the best acid available, HOCl. The reaction goes to completion. Whenever strong base or strong acid reacts, the reaction is always assumed to go to completion.

	$HOCl$	+	OH^-	$\rightarrow$	OCl^-	+	H_2O	
Before	50. mmol		24 mmol		0			
	24 mmol OH^- reacts completely.							
Change	-24		-24	$\rightarrow$	+24			Reacts completely
After	26 mmol		0		24 mmol			

After reaction, the solution contains 26 mmol HOCl and 24 mmol OCl^- in 250 mL of solution. This is a buffer solution. Using the Henderson-Hasselbalch equation:

$pH = pK_a + \log\frac{[\text{Base}]}{[\text{Acid}]}$; $K_a = 3.5 \times 10^{-8}$; $pK_a = 7.46$

$$pH = 7.46 + \log\frac{\frac{24\text{ mmol } OCl^-}{250\text{ mL}}}{\frac{26\text{ mmol HOCl}}{250\text{ mL}}} = 7.46 + (-0.035) = 7.43$$

d. $26.4\ \text{g NaC}_2\text{H}_3\text{O}_2 \times \dfrac{1\ \text{mol}}{82.03\ \text{g}} = 0.322\ \text{mol NaC}_2\text{H}_3\text{O}_2$

$$50.0\ \text{mL HCl} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{6.00\ \text{mol HCl}}{\text{L}} = 0.300\ \text{mol HCl}$$

H^+ reacts completely with best base present, $C_2H_3O_2^-$. (Strong acids are always assumed to react to completion.)

	H^+	+	$C_2H_3O_2^-$	$\rightarrow$	$HC_2H_3O_2$	
Before	0.300 mol		0.322 mol		0	
Change	-0.300		-0.300	$\rightarrow$	+0.300	Reacts completely
After	0		0.022 mol		0.300 mol	

After reaction, a buffer solution results. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 4.74 + \log\frac{(0.022\ \text{mol}/0.500\ \text{L})}{(0.300\ \text{mol}/0.500\ \text{L})},\ \text{pH} = 4.74 - 1.13 = 3.61$$

27. $C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N \quad K_a = \dfrac{K_w}{K_b} = \dfrac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6};\ \text{pK}_a = -\log(5.9 \times 10^{-6}) = 5.23$

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. $4.50 = 5.23 + \log\dfrac{[C_5H_5N]}{[C_5H_5NH^+]}$

$$\log\frac{[C_5H_5N]}{[C_5H_5NH^+]} = -0.73$$

$$\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{-0.73} = 0.19$$

b. $5.00 = 5.23 + \log\dfrac{[C_5H_5N]}{[C_5H_5NH^+]}$

$$\log\frac{[C_5H_5N]}{[C_5H_5NH^+]} = -0.23$$

$$\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{-0.23} = 0.59$$

c. $5.23 = 5.23 + \log\dfrac{[C_5H_5N]}{[C_5H_5NH^+]}$

$$\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{0.0} = 1.0$$

d. $5.50 = 5.23 + \log\dfrac{[C_5H_5N]}{[C_5H_5NH^+]}$

$$\frac{[C_5H_5N]}{[C_5H_5NH^+]} = 10^{0.27} = 1.9$$

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

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

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

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

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

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

Additional Exercises

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

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

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). See Figure 8.8 of the text.