17 Additional Aspects of Aqueous Equilibria

Visualizing Concepts

17.2 (a) According to Figure 16.7, methyl orange is yellow above pH 4.5 and red (really pink) below pH 3.5. The beaker on the left has a pH greater than 4.5, and the one on the right has pH less than 3.5. (By calculation, pH of left beaker = 4.7, pH of right beaker = 2.9.) The right beaker, with lower pH and greater $[H^+]$, is pure acetic acid. The left beaker contains equal amounts of the weak acid and its conjugate base, acetic acid and acetate ion. Adding the "common-ion" acetate (in the form of sodium acetate) shifts the acid ionization equilibrium to the left, decreases $[H^+]$, and raises pH.

(b) When small amounts of NaOH are added, the left beaker is better able to maintain its pH. For solutions of the same weak acid, pH depends on the **ratio** of conjugate base to conjugate acid. Small additions of base (or acid) have the least effect when this ratio is close to one. The left beaker is a buffer because it contains a weak conjugate acid-conjugate base pair and resists rapid pH change upon addition of small amounts of strong base or acid.

17.4 *Analyze/Plan.* Consider the reaction $HA + OH^- \rightarrow A^- + H_2O$. What are the major species present in solution at the listed stages of the titration? Which diagram represents these species? *Solve.*

(a) *Before addition of NaOH,* the solution is mostly HA. The only A^- is produced by the ionization equilibrium of HA and is too small to appear in the diagram. This situation is shown in diagram (iii), which contains only HA.

(b) *After addition of NaOH but before the equivalence point,* some, but not all, HA has been converted to A^-. The solution contains a mixture of HA and A^-; this is shown in diagram (i).

(c) *At the equivalence point,* all HA has been converted to A^-, with no excess HA or OH^- present. This is shown in diagram (iv).

(d) *After the equivalence point,* the same amount of A^- is present as at the equivalence point, plus some excess OH^-. This is diagram (ii).

17.5 *Analyze/Plan.* In each case, the first substance is in the buret, and the second is in the flask. If acid is in the flask, the initial pH is low; with base in the flask, the pH starts high. Strong acids have lower pH than weak acids; strong bases have higher pH than weak bases. Polyprotic acids and bases have more than one "jump" in pH.

(a) Strong base in flask, pH starts high, ends low as acid is added. Only diagram (ii) fits this description.

(b) Weak acid in flask, pH starts low, but not extremely low. Diagrams (i), (iii), and (iv) all start at low pH and get higher. Diagram (i) has very low initial pH, and likely has strong acid in the flask. Diagram (iv) has two pH jumps, so it has a polyprotic acid in the flask. Diagram (iii) best fits the profile of adding a strong base to a weak acid.

(c) Strong acid in the flask, pH starts very low, diagram (i).

(d) Polyprotic acid, more than one pH jump, diagram (iv).

17.7 *Analyze/Plan.* Common anions or cations decrease the solubility of salts. Ions that participate in acid-base or complex ion equilibria increase solubility. *Solve.*

(a) CO_2^{3-} from $BaCO_3$ reacts with H^+ from HNO_3, causing solubility of $BaCO_3$ to increase with increasing HNO_3 concentration. This behavior matches the right diagram.

(b) Extra CO_2^{3-} from Na_2CO_3 decreases the solubility of $BaCO_3$. Solubility of $BaCO_3$ decreases as $[Na_2CO_3]$ increases. This behavior matches the left diagram.

(c) $NaNO_3$ has no common ions, nor does it enter into acid-base or complex ion equilibria with Ba^{2+} or CO_3^{2-}; it does not affect the solubility of $BaCO_3$. This behavior is shown in the center diagram.

17.8 A metal hydroxide that is soluble at very low and very high pH's, that is, in strong acid or strong base, is called amphoteric.

Common-Ion Effect

17.10 (a) For a generic weak base B, $K_b = \frac{[BH^+][OH^-]}{[B]}$. If an external source of BH^+ such as BH^+Cl^- is added to a solution of B(aq), $[BH^+]$ increases, decreasing $[OH^-]$ and increasing [B], effectively suppressing the ionization (hydrolysis) of B.

(b) NH_4Cl

17.12 In general, when an acid is added to a solution pH decreases; when a base is added to a solution, pH increases.

(a) pH increases; $C_7H_5O_2^-$ decreases ionization of $HC_7H_5O_2$ and decreases $[H^+]$.

(b) pH decreases; $C_5H_5NH^+$ decreases ionization (hydrolysis) of C_5H_5N and decreases $[OH^-]$.

(c) pH increases; NH_3 reacts with HCl, decreasing $[H^+]$.

(d) pH increases; HCO_3^- decreases ionization of H_2CO_3 and decreases $[H^+]$.

(e) no change; ClO_4^- is a negligible base and Na^+ is a negligible acid.

17 Additional Aspects of Aqueous Equilibria

Solutions to Black Exercises

17.14 *Analyze/Plan.* Follow the logic in Sample Exercise 17.1. *Solve.*

(a) $HCHO_2$ is a weak acid, and $NaCHO_2$ contains the common ion CHO_2^-, the conjugate base of $HCHO_2$. Solve the common-ion equilibrium problem.

	$HCHO_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$CHO_2^-(aq)$
i	$0.260\ M$				$0.160\ M$
c	$-x$		$+x$		$+x$
e	$(0.260 - x)\ M$		$+x\ M$		$(0.160 + x)\ M$

$$K_a = 1.8 \times 10^{-4} = \frac{[H^+][CHO_2^-]}{[HCHO_2]} = \frac{(x)(0.160+x)}{(0.260-x)} \approx \frac{0.160\,x}{0.260}$$

$x = 2.93 \times 10^{-4} = 2.9 \times 10^{-4}\ M = [H^+]$, pH = 3.53

Check. Since the extent of ionization of a weak acid or base is suppressed by the presence of a conjugate salt, the 5% rule usually holds true in buffer solutions.

(b) C_5H_5N is a weak base, and C_5H_5NHCl contains the common ion $C_5H_5NH^+$, which is the conjugate acid of C_5H_5N. Solve the common ion equilibrium problem.

	$C_5H_5N(aq)$ + $H_2O(l$	$\rightleftharpoons$	$C_5H_5NH^+(aq)$	+	$OH^-(aq)$
i	$0.210\ M$		$0.350\ M$		
c	$-x$		$+x$		$+x$
e	$(0.210 - x)\ M$		$(0.350 + x)\ M$		$+x\ M$

$$K_b = 1.7 \times 10^{-9} = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} = \frac{(0.350 + x)(x)}{(0.210-x)} \approx \frac{0.350\,x}{0.210}$$

$x = 1.02 \times 10^{-9} = 1.0 \times 10^{-9}\ M = [OH^-]$, pOH = 8.991, pH = 14.00 - 8.991 = 5.01

Check. In a buffer, if [conj. acid] > [conj. base], pH < pK_a of the conj. acid.
If [conj. acid] < [conj. base], pH > pK_a of the conj. acid. In this buffer, pK_a of $(CH_3)_3NH^+$ is 9.81. $[(CH_3)_3NH^+] > [(CH_3)_3N]$ and pH = 9.61, less than 9.81.

(c) mol = $M \times$ L; mol HF = $0.050\ M \times 0.125$ L = $6.25 \times 10^{-3} = 6.3 \times 10^{-3}$ mol;
mol F^- = $0.10\ M \times 0.0500$ L = 0.0050 mol

	$HF(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$F^-(aq)$
i	6.25×10^{-3} mol		0		0.0050 mol
c	$-x$		$+x$		$+x$
e	$(6.25 \times 10^{-3} - x)$ mol		x		$(0.0050 + x)$ mol

$[HF] = (6.25 \times 10^{-3} + x)/0.175$ L; $[F^-] = (0.0050 + x)\ 0.175$ L

Note that the volumes will cancel when substituted into the K_a expression.

$$K_a = 6.8 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{x(0.0050 + x)/0.175}{(6.25\,x - x)/0.175} \approx \frac{x(0.0050)}{0.00625}$$

$x = 8.50 \times 10^{-4} = 8.5 \times 10^{-4}\ M\ H^+$; pH = 3.07

Check. pK_a for HF = 3.17. $[HF] > [F^-]$, pH of buffer = 3.07, less than 3.17.

17.16

$$K_a = \frac{[H^+][Lac^-]}{[HLac]} = 1.4 \times 10^{-4}$$

	$HLac(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$Lac^-(aq)$
equil (a)	$0.085 - x\ M$		$x\ M$		$x\ M$
equil (b)	$0.085 - x\ M$		$x\ M$		$0.050 + x\ M$

(a) $K_a = 1.4 \times 10^{-4} = \frac{x^2}{0.085 - x} \approx \frac{x^2}{0.085}$; $x = [H^+] = 3.45 \times 10^{-3}\ M = 3.5 \times 10^{-3}\ M\ H^+$

$$\%\ \text{ionization} = \frac{3.5 \times 10^{-3}\ M H^+}{0.085\ M\ \text{Lac}} \times 100 = 4.1\%\ \text{ionization}$$

(b) $K_a = 1.4 \times 10^{-4} = \frac{(x)(0.050 + x)}{0.085 - x} \approx \frac{0.050\,x}{0.085}$; $x = 2.4 \times 10^{-4}\ M\ H^+$

$$\%\ \text{ionization} = \frac{2.4 \times 10^{-4}\ M H^+}{0.085\ M\ \text{Lac}} \times 100 = 0.28\%\ \text{ionization}$$

Buffers

17.18 NaOH is a strong base and will react with $HC_2H_3O_2$ to form $NaC_2H_3O_2$. As long as $HC_2H_3O_2$ is present in excess, the resulting solution will contain both the conjugate acid $HC_2H_3O_2(aq)$ and the conjugate base $C_2H_3O_2^-(aq)$, the requirements for a buffer.

mmol = $M \times$ mL; mmol $HC_2H_3O_2$ = 1.00 $M \times$ 100 mL = 10.0 mmol

mmol NaOH = 0.100 $M \times$ 50 mL = 5.0 mmol

	$HC_2H_3O_2(aq)$	+	$NaOH(aq)$	$\rightarrow$	$NaC_2H_3O_2(aq) + H_2O(l)$
initial	10.0 mmol		5.0 mmol		
after rx	5.0 mmol		0		5.0 mmol

Mixing these two solutions has created a buffer by partial neutralization of the weak acid $HC_2H_3O_2$.

17.20 Assume that % ionization is small in these buffers (Solutions 17.15 and 17.16).

(a) The conjugate acid in this buffer is HCO_3^-, so use K_{a2} for H_2CO_3, 5.6×10^{-11}

$$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]};\ [H^+] = \frac{K_a[HCO_3^-]}{[CO_3^{2-}]} = \frac{5.6 \times 10^{-11}(0.120)}{(0.105)}$$

$[H^+] = 6.40 \times 10^{-11} = 6.4 \times 10^{-11}\ M$; pH = 10.19

(b) mol = $M \times L$; total volume = 140 mL = 0.140 L

$$[H^+] = \frac{K_a\,(0.20\,M \times 0.065\,L)/0.120\,L}{(0.15\,M \times 0.075\,L)/0.120\,L} = \frac{5.6 \times 10^{-11}\,(0.20 \times 0.065)}{(0.15 \times 0.075)}$$

$[H^+] = 6.47 \times 10^{-11} = 6.5 \times 10^{-11}\,M$; pH = 10.19

17.22 NH_4^+/NH_3 is a basic buffer. Either the hydrolysis of NH_3 or the dissociation of NH_4^+ can be used to determine the pH of the buffer. Using the dissociation of NH_4^+ leads directly to $[H^+]$ and facilitates use of the Henderson-Hasselbach relationship.

(a) $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}$$

$$[NH_3] = \frac{5.0\,g\,NH_3}{2.50\,L\,soln} \times \frac{1\,mol\,NH_3}{17.0\,g\,NH_3} = 0.118 = 0.12\,M\,NH_3$$

$$[NH_4^+] = \frac{20.0\,g\,NH_4Cl}{2.50\,L} \times \frac{1\,mol\,NH_4Cl}{53.50\,g\,NH_4Cl} = 0.1495 = 0.15\,M\,NH_4^+$$

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]};\ [H^+] = \frac{K_a[NH_4^+]}{[NH_3]} = \frac{5.56 \times 10^{-10}\,(0.1495 - x)}{(0.118 + x)} \approx \frac{5.56 \times 10^{-10}\,(0.1495)}{(0.118)}$$

$[H^+] = 7.044 \times 10^{-10} = 7.0 \times 10^{-10}\,M$, pH = 9.15

(b) $NH_3(aq) + H^+(aq) + NO_3^-(aq) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

(c) $NH_4^+(aq) + Cl^-(aq) + K^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l) + Cl^-(aq) + K^+(aq)$

17.24 $HC_3H_5O_3(aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$

$$[H^+] = \frac{K_a[HC_3H_5O_3]}{[C_3H_5O_3^-]};\ [H^+] = 10^{-4.00} = 1.0 \times 10^{-4}$$

$[HC_3H_5O_3] = 0.150\,M$; calculate $[C_3H_5O_3^-]$

$$[C_3H_5O_3^-] = \frac{K_a[HC_3H_5O_3]}{[H^+]} = \frac{1.4 \times 10^{-4}\,(0.150)}{1.0 \times 10^{-4}} = 0.2100 = 0.21\,M$$

$$\frac{0.210\,mol\,NaC_3H_5O_3}{1.00\,L} \times \frac{112.1\,g\,NaC_3H_5O_3}{1\,mol\,NaC_3H_5O_3} = 23.54 = 24\,g\,NaC_3H_5O_3$$

17.26 (a) $$K_a = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]};\ [H^+] = \frac{K_a[HC_3H_5O_2]}{[C_3H_5O_2^-]}$$

Since this expression contains a ratio of concentrations, we can ignore total volume and work directly with moles.

$$[H^+] = \frac{1.3 \times 10^{-5}\,(0.12 - x)}{(0.10 + x)} \approx \frac{1.3 \times 10^{-5}\,(0.12)}{0.10} = 1.56 \times 10^{-5} = 1.6 \times 10^{-5}\,M,\ pH = 4.81$$

(b)

$HC_3H_5O_2(aq)$	+	$OH^-(aq)$	→	$C_2H_3O_2^-(aq) + H_2O(l)$
0.12 mol		0.01 mol		0.10 mol
-0.01 mol		-0.01 mol		+0.01 mol
0.11 mol		0 mol		0.11 mol

$$[H^+] \approx \frac{1.3 \times 10^{-5}\,(0.11)}{(0.11)} = 1.3 \times 10^{-5}\ M;\ pH = 4.89$$

(c)

$C_3H_5O_2^-(aq)$	+	$HI(aq)$	→	$HC_3H_5O_2(aq) + I^-(aq)$
0.10 mol		0.01 mol		0.12 mol
-0.01 mol		-0.01 mol		+0.01 mol
0.09 mol		0 mol		0.13 mol

$$[H^+] \approx \frac{1.3 \times 10^{-5}\,(0.13)}{(0.09)} = 1.88 \times 10^{-3} = 2 \times 10^{-3}\ M;\ pH = 4.73 = 4.7$$

17.28 $$\frac{6.5\ g\ NaH_2PO_4}{0.355\ L\ soln} \times \frac{1\ mol\ NaH_2PO_4}{120\ g\ NaH_2PO_4} = 0.153 = 0.15\ M$$

$$\frac{8.0\ g\ Na_2HPO_4}{0.355\ L\ soln} \times \frac{1\ mol\ Na_2HPO_4}{142\ g\ Na_2HPO_4} = 0.159 = 0.16\ M$$

Use Equation [17.9] to find the pH of the buffer. K_a for $H_2PO_4^-$ is K_{a2} for H_3PO_4, 6.2×10^{-8}

$$pH = -\log(6.2 \times 10^{-8}) + \log\frac{0.159}{0.153} = 7.2076 + 0.0167 = 7.22$$

17.30 The solutes listed contain three possible conjugate acid/conjugate base (CA/CB) pairs. These are:

$HCHO_2/NaCHO_2$, $pK_a = 3.74$

$HC_3H_5O_2/NaC_3H_5O_2$, $pK_a = 4.80$

H_3PO_4/NaH_2PO_4, $pK_a = 2.12$

For maximum buffer capacity, pK_a should be within 1 pH unit of the buffer. The propionic acid/propionate pair are most appropriate for a buffer with pH 4.80.

$$pH = pK_a + \log\frac{[CB]}{CA};\ 4.80 = 4.886 + \log\frac{[NaC_3H_5O_2]}{[HC_3H_5O_2]}$$

$$\log\frac{[NaC_3H_5O_2]}{[HC_3H_5O_2]} = -0.0861;\ \frac{[NaC_3H_5O_2]}{[HC_3H_5O_2]} = 0.8202 = 0.82$$

Since we are making a total of 1 L of buffer, let y = vol $NaC_3H_5O_2$ and (1 - y) = vol $HC_3H_5O_2$.

$$0.8202 = \frac{[NaC_3H_5O_2]}{[HC_3H_5O_2]} = \frac{(0.1\ M \times y)/1.0\ L}{[0.10\ M \times (1-y)]/1.0\ L} = \frac{0.10\ y}{0.10 - 0.10\ y}$$

$0.8202(0.10 - 0.10\ y) = 0.10\ y;\ 0.08202 = 0.18202\ y;\ y = 0.4506 = 0.45\ L$

450 mL of 0.10 *M* $NaC_3H_5O_2$, 550 mL $HC_3H_5O_2$

Check. pH (buffer) < pK_a (CA) and the calculated amount of CA in the buffer is greater than the amount of CB.

Acid-Base Titrations

17.32 (a) The quantity of base required to reach the equivalence point is the same in the two titrations.

(b) The pH is higher initially in the titration of a weak acid.

(c) The pH is higher at the equivalence point in the titration of a weak acid.

(d) The pH in excess base is essentially the same for the two cases.

(e) In titrating a weak acid, one needs an indicator that changes at a higher pH than for the strong acid titration. The choice is more critical because the change in pH close to the equivalence point is smaller for the weak acid titration.

17.34 (a) $HCHO_2(aq) + NaOH(aq) \rightarrow NaCHO_2(aq) + H_2O(l)$

At the equivalence point, the major species are Na^+ and CHO_2^-. Na^+ is negligible and CHO_2^- is the CB of $HCHO_2$. The solution is basic, above pH 7.

(b) $Ca(OH)_2(aq) + 2HClO_4(aq) \rightarrow Ca(ClO_4)_2(aq) + 2H_2O(l)$

At the equivalence point, the major species are Ca^{2+} and ClO_4^-; both are negligible. The solution is at pH 7.

(c) $C_5H_5N(aq) + HNO_3(aq) \rightarrow C_5H_5NH^+NO_3^-(aq)$

At the equivalence point, the major species are $C_5H_5NH^+$ and NO_3^-. NO_3^- is negligible and $C_5H_5NH^+$ is the CA of C_5H_5N. The solution is acidic, below pH 7.

17.36 (a) At the equivalence point, moles HX added = moles B initially present = 0.10 *M* × 0.0300 L = 0.0030 moles HX added.

(b) $BH^+(aq)$

(c) Both K_a for BH^+ and concentration BH^+ determine pH at the equivalence point.

(d) Because the pH at the equivalence point will be less than 7, methyl red would be more appropriate.

17.38 (a)
$$55.0 \text{ mL NaOH} \times \frac{0.0950 \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}} = 49.8 \text{ mL HCl soln}$$

(b)
$$22.5 \text{ mL } NH_3 \times \frac{0.118 \text{ mol } NH_3}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol } NH_3} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}} = 25.3 \text{ mL HCl soln}$$

(c)
$$125.0 \text{ mL} \times \frac{1.35 \text{ g NaOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}} = 40.2 \text{ mL HCl soln}$$

17 Additional Aspects of Aqueous Equilibria

Solutions to Black Exercises

17.40 moles $OH^- = M_{KOH} \times L_{KOH} = 0.150\ M \times 0.0300\ L = 4.50 \times 10^{-3}$ mol

moles $H^+ = M_{HClO_4} \times L_{HClO_4} = 0.125\ M \times L_{HClO_4}$

	mL_{KOH}	**mL_{HClO_4}**	Total Volume	**Moles OH^-**	**Moles H^+**	**Molarity Excess Ion**	**pH**
(a)	30.0	30.0	60.0	4.50×10^{-3}	3.75×10^{-3}	$0.0125(OH^-)$	12.10
(b)	30.0	35.0	65.0	4.50×10^{-3}	4.38×10^{-3}	$1.9 \times 10^{-3}(OH^-)$	11.28
(c)	30.0	36.0	66.0	4.50×10^{-3}	4.50×10^{-3}	$1.0 \times 10^{-7}(OH^-)$	7.00
(d)	30.0	37.0	67.0	4.50×10^{-3}	4.63×10^{-3}	$1.9 \times 10^{-3}(H^+)$	2.73
(e)	30.0	40.0	70.0	4.50×10^{-3}	5.00×10^{-3}	$7.1 \times 10^{-3}(H^+)$	2.15

$$\text{molarity of excess ion} = \frac{\text{moles ion}}{\text{total vol in L}}$$

(a) $$\frac{4.50 \times 10^{-3}\ \text{mol OH}^- - 3.75 \times 10^{-3}\ \text{mol H}^+}{0.0600\ \text{L}} = 0.0125 = 0.013\ M\ \text{OH}^-$$

(b) $$\frac{4.50 \times 10^{-3}\ \text{mol OH}^- - 4.38 \times 10^{-3}\ \text{mol H}^+}{0.0650\ \text{L}} = 1.92 \times 10^{-3} = 1.9 \times 10^{-3}\ M\ \text{OH}^-$$

(c) equivalence point, mol H^+ = mol OH^- M

$KClO_4$ does not hydrolyze, so $[H^+] = [OH^-] = 1 \times 10^{-7}$

(d) $$\frac{4.50 \times 10^{-3}\ \text{mol OH}^- - 4.63 \times 10^{-3}\ \text{mol H}^+}{0.0670\ \text{L}} = 1.87 \times 10^{-3} = 1.9 \times 10^{-3}\ M\ \text{H}^+$$

(e) $$\frac{4.50 \times 10^{-3}\ \text{mol OH}^- - 5.00 \times 10^{-3}\ \text{mol H}^+}{0.0700\ \text{L}} = 7.14 \times 10^{-3} = 7.1 \times 10^{-3}\ M\ \text{H}^+$$

17.42 (a) Weak base problem: $K_b = 1.8 \times 10^{-5} = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

At equilibrium, $[OH^-] = x$, $[NH_3] = (0.030 - x)$; $[NH_4^+] = x$

$$1.8 \times 10^{-5} = \frac{x^2}{(0.030 - x)} \approx \frac{x^2}{0.030};\ x = [OH^-] = 7.348 \times 10^{-4} = 7.3 \times 10^{-4}\ M$$

pH = 14.00 - 3.13 = 10.87

(b–f) Calculate mol NH_3 and mol NH_4^+ after the acid-base reaction takes place. 0.030 M $NH_3 \times 0.0300\ L = 9.0 \times 10^{-4}$ mol NH_3 present initially.

		$NH_3(aq)$	+	$HCl(aq)$	→	$NH_4^+(aq) + Cl^-(aq)$
				$(0.025\ M \times 0.0100\ L) =$		
(b)	before rx	9.0×10^{-4} mol		2.5×10^{-4} mol		0 mol
	after rx	**6.5×10^{-4} mol**		**0 mol**		**2.5×10^{-4} mol**

		$NH_3(aq)$	+	$HCl(aq)$	→	$NH_4^+(aq) + Cl^-(aq)$
				$(0.025\ M \times 0.0200\ L) =$		
(c)	before rx	9.0×10^{-4} mol		5.0×10^{-4} mol		0 mol
	after rx	**4.0×10^{-4} mol**		**0 mol**		**5.0×10^{-4} mol**
				$(0.025\ M \times 0.0350\ L) =$		
(d)	before rx	9.0×10^{-4} mol		8.75×10^{-4} mol		0 mol
	after rx	**0.25×10^{-4} mol**		**0 mol**		**8.75×10^{-4} mol**
				$(0.025\ M \times 0.0360\ L) =$		
(e)	before rx	9.0×10^{-4} mol		9.0×10^{-4} mol		0 mol
	after rx	**0 mol**		**0 mol**		**9.0×10^{-4} mol**
				$(0.025\ M \times 0.0370\ L) =$		
(f)	before rx	9.0×10^{-4} mol		9.25×10^{-4} mol		0 mol
	after rx	**0 mol**		**0.25×10^{-4} mol**		**9.0×10^{-4} mol**

(b) Using the acid dissociation equilibrium for NH_4^+ (so that we calculate $[H^+]$ directly), $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$

$$K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{K_w}{K_b \text{ for } NH_3} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}$$

$$[NH_3] = \frac{6.5 \times 10^{-4}\ \text{mol}}{0.0400\ \text{L}} = 0.01625\ M; [NH_4^+] = \frac{2.50 \times 10^{-4}\ \text{mol}}{0.0400\ \text{L}} = 6.25 \times 10^{-3}\ M$$

$$[H^+] = \frac{5.56 \times 10^{-10}\ [NH_4^+]}{[NH_3]} \approx \frac{5.56 \times 10^{-10}\ (6.25 \times 10^{-3})}{(0.01625)} = 2.14 \times 10^{-10}; \text{pH} = 9.67$$

(We will assume $[H^+]$ is small compared to $[NH_3]$ and $[NH_4^+]$.)

(c) $$[NH_3] = \frac{4.0 \times 10^{-4}\ \text{mol}}{0.0500\ \text{L}} = 0.0080\ M; [NH_4^+] = \frac{5.0 \times 10^{-4}\ \text{mol}}{0.0500\ \text{L}} = 0.010M$$

$$[H^+] = \frac{5.56 \times 10^{-10}\ (0.010)}{(0.0080)} = 6.94 \times 10^{-10} = 6.9 \times 10^{-10}\ M; \text{pH} = 9.16$$

(d) $$[NH_3] = \frac{0.25 \times 10^{-4}\ \text{mol}}{0.0650\ \text{L}} = 3.846 \times 10^{-4} = 4 \times 10^{-4}\ M; [NH_4^+] = \frac{8.75 \times 10^{-4}\ \text{mol}}{0.0650\ \text{L}}$$

$$= 0.01346 = 0.013\ M$$

$$[H^+] = \frac{5.56 \times 10^{-10}\ (0.01346)}{3.846 \times 10^{-4}} = 1.946 \times 10^{-8} = 2 \times 10^{-8}\ M; \text{pH} = 7.7$$

(e) At the equivalence point, $[H^+] = [NH_3] = x$

$$[NH_4^+] = \frac{9.0 \times 10^{-4}\ M}{0.0660\ L} = 0.01364 = 0.014\ M$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.01364};\ x = [H^+] = 2.754 \times 10^{-6} = 2.8 \times 10^{-6};\ pH = 5.56$$

(f) Past the equivalence point, $[H^+]$ from the excess HCl determines the pH.

$$[H^+] = \frac{0.25 \times 10^{-4}\ mol}{0.0670\ L} = 3.731 \times 10^{-4} = 4 \times 10^{-4}\ M;\ pH = 3.4$$

17.44 The volume of NaOH solution required in all cases is

$$V_{base} = \frac{V_{acid} \times M_{acid}}{M_{base}} = \frac{(0.100)\ V_{acid}}{(0.080)} = 1.25\ V_{acid}$$

The total volume at the equivalence point is $V_{base} + V_{acid} = 2.25\ V_{acid}$.

The concentration of the salt at the equivalence point is $\frac{M_{acid}\ V_{acid}}{2.25\ V_{acid}} = \frac{0.100}{2.25} = 0.0444\ M$

(a) 0.0444 M NaBr, pH = 7.00

(b) 0.0444 M Na^+ $C_3H_5O_3^-$; $C_3H_5O_3^-(aq) + H_2O(l) \rightleftharpoons HC_3H_5O_3(aq) + OH^-(aq)$

$$K_b = \frac{[HC_3H_5O_3][OH^-]}{[C_3H_5O_3^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.14 \times 10^{-11} = 7.1 \times 10^{-11}$$

$[HC_3H_5O_3] = [OH^-]$; $[C_3H_5O_3^-] \approx 0.0444$

$[OH^-]^2 \approx 0.0444(7.14 \times 10^{-11})$; $[OH^-] = 1.78 \times 10^{-6} = 1.8 \times 10^{-6}\ M$, pOH = 5.75;

pH = 8.25

(c) $CrO_4^{2-}(aq) + H_2O(l) \rightleftharpoons HCrO_4^-(aq) + OH^-(aq)$

$$K_b = \frac{[HCrO_4^-][OH^-]}{[CrO_4^{2-}]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-7}} = 3.33 \times 10^{-8} = 3.3 \times 10^{-8}$$

$[OH^-]^2 \approx 0.0444(3.33 \times 10^{-8})$; $[OH^-] = 3.849 \times 10^{-5} = 3.8 \times 10^{-5}$, pH = 9.59

Solubility Equilibria and Factors Affecting Solubility

17.46 (a) Solubility is the amount (grams, moles) of solute that will dissolve in a certain volume of solution. Solubility-product constant is an equilibrium constant, the product of the molar concentrations of all the dissolved ions in solution.

(b) $K_{sp} = [Mn^{2+}][CO_3^{2-}]$; $K_{sp} = [Hg^{2+}][OH^-]^2$; $K_{sp} = [Cu^{2+}]^3[PO_4^{3-}]^2$

17.48 (a) $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$

$K_{sp} = [Pb^{2+}][Br^-]^2$; $[Pb^{2+}] = 1.0 \times 10^{-2}\ M$, $[Br^-] = 2.0 \times 10^{-2}\ M$

$K_{sp} = (1.0 \times 10^{-2}\ M)(2.0 \times 10^{-2}\ M)^2 = 4.0 \times 10^{-6}$

(b) $AgIO_3(s) \rightleftharpoons Ag^+(aq) + IO_3^-(aq);\quad K_{sp} = [Ag^+][IO_3^-]$

$$[Ag^+] = [IO_3^-] = \frac{0.0490\text{ g }AgIO_3}{1.00\text{ L soln}} \times \frac{1\text{ mol }AgIO_3}{282.8\text{ g }AgIO_3} = 1.733 \times 10^{-4} = 1.73 \times 10^{-4}\ M$$

$K_{sp} = (1.733 \times 10^{-4}\ M)\ (1.733 \times 10^{-4}\ M) = 3.00 \times 10^{-8}$

(c) $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq);\quad K_{sp} = [Cu^{2+}][OH^-]^2$

$[Cu^{2+}] = x,\ [OH^-] = 2x;\ K_{sp} = 4.8 \times 10^{-20} = (x)(2x)^2$

$4.8 \times 10^{-20} = 4x^3;\ x = [Cu^{2+}] = 2.290 \times 10^{-7} = 2.3 \times 10^{-7}\ M$

$$\frac{2.290 \times 10^{-7}\text{ mol }Cu(OH)_2}{1\text{ L}} \times \frac{97.56\text{ g }Cu(OH)_2}{1\text{ mol }Cu(OH)_2} = 2.2 \times 10^{-5}\text{ g }Cu(OH)_2$$

However, $[OH^-]$ from $Cu(OH)_2 = 4.58 \times 10^{-7}$ M; this is similar to $[OH^-]$ from the autoionization of water.

$K_w = [H^+][OH^-];\ [H^+] = y,\ [OH^-] = (4.58 \times 10^{-7} + y)$

$1.0 \times 10^{-14} = y(4.58 \times 10^{-7} + y);\ y^2 + 4.58 \times 10^{-7}\,y - 1.0 \times 10^{-14}$

$$y = \frac{-4.58 \times 10^{-7} \pm \sqrt{(4.58 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2};\ y = 2.09 \times 10^{-8}$$

$[OH^-]_{total} = 4.58 \times 10^{-7}\ M + 0.209 \times 10^{-7}\ M = 4.79 \times 10^{-7}\ M$

Recalculating $[Cu^{2+}]$ and thus molar solubility of $Cu(OH)_2(s)$:

$4.8 \times 10^{-20} = x(4.79 \times 10^{-7})^2;\ x = 2.09 \times 10^{-7}\ M\ Cu^{2+}$

$$\frac{2.09 \times 10^{-7}\text{ mol }Cu(OH)_2(s)}{1\text{ L}} \times \frac{97.56\text{ g }Cu(OH)_2}{1\text{ mol }Cu(OH)_2} = 2.0 \times 10^{-5}\text{ g }Cu(OH)_2$$

Note that the presence of OH^- as a common ion decreases the water solubility of $Cu(OH)_2$.

17.50 $PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq);\quad K_{sp} = [Pb^{2+}][I^-]^2$

$$[Pb^{2+}] = \frac{0.54\text{ g }PbI_2}{1.00\text{ L soln}} \times \frac{1\text{ mol }PbI_2}{461.0\text{ g }PbI_2} = 1.17 \times 10^{-3} = 1.2 \times 10^{-3}\ M$$

$[I^-] = 2[Pb^{2+}];\ K_{sp} = [Pb^{2+}](2[Pb^{2+}])^2 = 4[Pb^{2+}]^3 = 4(1.17 \times 10^{-3})^3 = 6.4 \times 10^{-9}$

17.52 $LaF_3(s) \rightleftharpoons La^{3+}(aq) + 3F^-(aq);\quad K_{sp} = [La^{3+}][F^-]^3$

(a) molar solubility $= x = [La^{3+}];\ [F^-] = 3x$

$K_{sp} = 2 \times 10^{-19}\ (x)(3x)3;\ 2 \times 10^{-19} = 27\,x^4;\ x = (7.41 \times 10^{-21})^{1/4},\ x = 9.28 \times 10^{-6}$

$= 9 \times 10^{-6}\text{ M }La^{3+}$

$$\frac{9.28 \times 10^{-6}\text{ mol }LaF_3}{1\text{ L}} \times \frac{195.9\text{ g }LaF_3}{1\text{ mol}} = 1.82 \times 10^{-3} = 2 \times 10^{-3}\text{ g }LaF_3/L$$

(b) molar solubility = x = $[La^{3+}]$

There are two sources of F^-: KF(0.010 *M*) and LaF_3 (3x *M*)

$K_{sp} = (x)(0.010 + 3x)^3$; assume x is small compared to 0.010 M.

$2 \times 10^{-19} = (0.010)^3\ x$; $x = 2 \times 10^{-19}/1.0 \times 10^{-6} = 2 \times 10^{-13}\ M\ La^{3+}$

$$\frac{2 \times 10^{-13}\ \text{mol } LaF_3}{1\ \text{L}} \times \frac{195.9\ \text{g } LaF_3}{1\ \text{mol}} = 3.92 \times 10^{-11} = 4 \times 10^{-11}\ \text{g } LaF_3/\text{L}$$

(c) molar solubility = x, $[F^-] = 3x$, $[La^{3+}] = 0.050\ M + x$

$K_{sp} = (0.050 + x)(3x)^3$; assume x is small compared to 0.050 *M*.

$2 \times 10^{-19} = (0.050)(27\ x^3) = 1.35\ x^3$; $x = (1.48 \times 10^{-19})^{1/3} = 5.29 \times 10^{-7} = 5 \times 10^{-7}\ M$

$$\frac{5.29 \times 10^{-7}\ \text{mol } LaF_3}{1\ \text{L}} \times \frac{195.9\ \text{g } LaF_3}{1\ \text{mol}} = 1.04 \times 10^{-4} = 1 \times 10^{-4}\ \text{g } LaF_3/\text{L}$$

17.54 $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$; $K_{sp} = 8.0 \times 10^{-16}$

Since the $[OH^-]$ is set by the pH of the solution, the solubility of $Fe(OH)_2$ is just $[Fe^{2+}]$.

(a) pH = 7.0, pOH = 14 - pH = 7.0, $[OH^-] = 10^{-pOH} = 1.0 \times 10^{-7} = 1 \times 10^{-7}\ M$

$$K_{sp} = 7.9 \times 10^{-16} = [Fe^{2+}](1.0 \times 10^{-7})^2; [Fe^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-14}} = 7.9 \times 10^{-2} = 8 \times 10^{-2}\ M$$

Check. In pure water, $[OH^-]$ from $Fe(OH)_2$ is similar to (OH^-) from the autoionization of water, resulting in a cubic equation for $[Fe^{2+}]$. The solubility of $Fe(OH)_2$ at a buffered pH = 7.0 is actually greater than the solubility in pure water.

(b) pH = 10.0, pOH = 4.0, $[OH^-] = 1.0 \times 10^{-4} = 1 \times 10^{-4}\ M$

$$K_{sp} = 7.9 \times 10^{-16} = [Fe^{2+}][1.0 \times 10^{-4}]^2; [Fe^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 8^{-10}} = 7.9 \times 10^{-8} = 8 \times 10^{-8}\ M$$

(c) pH = 12.0, pOH = 2.0, $[OH^-] = 1.0 \times 10^{-2} = 1 \times 10^{-2}\ M$

$$K_{sp} = 7.9 \times 10^{-16} = [Fe^{2+}][1.0 \times 10^{-2}]^2; [Fe^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-4}} = 7.9 \times 10^{-12} = 8 \times 10^{-12}\ M$$

17.56 If the anion in the slightly soluble salt is the conjugate base of a strong acid, there will be no reaction.

(a) $MnS(s) + 2H^+(aq) \rightarrow H_2S(aq) + Mn^{2+}(aq)$

(b) $PbF_2(s) + 2H^+(aq) \rightarrow 2HF(aq) + Pb^{2+}(aq)$

(c) $AuCl_3(s) + H^+(aq) \rightarrow$ no reaction

(d) $Hg_2C_2O_4(s) + 2H^+(aq) \rightarrow H_2C_2O_4(aq) + Hg_2{}^{2+}(aq)$

(e) $CuBr(s) + H^+(aq) \rightarrow$ no reaction

17.58 $NiC_2O_4(s) \rightleftharpoons Ni^{2+}(aq) + C_2O_4^{2-}(aq); \quad K_{sp} = [Ni^{2+}][C_2O_4^{2-}] = 4 \times 10^{-10}$

When the salt has just dissolved, $[C_2O_4^{2-}]$ will be 0.020 *M*. Thus $[Ni^{2+}]$ must be less than 4×10^{-10} / 0.020 = 2×10^{-8} *M*. To achieve this low $[Ni^{2+}]$ we must complex the Ni^{2+} ion with NH_3: Ni^{2+} (aq) + $6NH_3$ (aq) *f* $Ni(NH_3)_6^{2+}$ (aq). Essentially all Ni(II) is in the form of the complex, so $[Ni(NH_3)_6^{2+}]$ = 0.020. Find K_f for $Ni(NH_3)_6^{2+}$ in Table 17.1.

$$K_f = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = \frac{(0.020)}{(2 \times 10^{-8})[NH_3]^6} = 1.2 \times 10^9; [NH_3]^6 = 8.33 \times 10^{-4};$$

$$[NH_3] = 0.307 = 0.3\ M$$

17.60

$$Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq) \qquad K_{sp}$$

$$S^{2-}(aq) + 2H^+(aq) \rightleftharpoons H_2S(aq) \qquad 1/(K_{a1} \times K_{a2})$$

$$2[Ag]^+(aq) + 2Cl^-(aq) \rightleftharpoons AgCl_2^-(aq) \qquad K_f^2$$

$$Ag_2S(s) + 2H^+(aq) + 4Cl^-(aq) \rightleftharpoons 2AgCl_2^-(aq) + H_2S(aq)$$

$$K = \frac{K_{sp} \times K_f^2}{K_{a1} \times K_{a2}} = \frac{(6 \times 10^{-51})(1.1 \times 10^5)^2}{(9.5 \times 10^{-8})(1 \times 10^{-19})} = 7.64 \times 10^{-15} = 8 \times 10^{-15}$$

Precipitation; Qualitative Analysis

17.62 (a) $Co(OH)_2(s) \rightleftharpoons Co^{2+}(aq) + 2OH^-(aq); \; K_{sp} = [Co^{2+}][OH^-]^2 = 1.3 \times 10^{-15}$

pH = 8.5; pOH = 14 - 8.5 = 5.5; $[OH^-] = 10^{-5.5} = 3.16 \times 10^{-6} = 3 \times 10^{-6}$ *M*

$Q = (0.020)(3.16 \times 10^{-6})^2 = 2 \times 10^{-13}$; $Q > K_{sp}$, $Co(OH)_2$ will precipitate

(b) $AgIO_3(s) \rightleftharpoons Ag+(aq) + IO_3^-(aq); \; K_{sp} = [Ag+][IO_3^-] = 3.1 \times 10^{-8}$

$$[Ag^+] = \frac{0.010\,M\ Ag^+ \times 0.100\ L}{0.110\ L} = 9.09 \times 10^{-3} = 9.1 \times 10^{-3}\ M$$

$$[IO_3^-] = \frac{0.015\,M\ IO_3^- \times 0.010\ L}{0.110\ L} = 1.36 \times 10^{-3} = 1.4 \times 10^{-3}\ M$$

$Q = (9.09 \times 10^{-3})(1.36 \times 10^{-3}) = 1.2 \times 10^{-5}$; $Q > K_{sp}$, $AgIO_3$ will precipitate

17.64 $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq); \; K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

$$[Ag^+] = \frac{0.10\,M \times 0.2\ mL}{10\ mL} = 2 \times 10^{-3}\,M; \quad [Cl^-] = \frac{1.8 \times 10^{-10}}{2 \times 10^{-3}\,M} = 9 \times 10^{-8}\,M$$

$$\frac{9 \times 10^{-8}\ mol\ Cl^-}{1\ L} \times \frac{35.45\ g\ Cl^-}{1\ mol\ Cl^-} \times 0.010\ L = 3.19 \times 10^{-8}\ g\ Cl^- = 3 \times 10^{-8}\ g\ Cl^-$$

17.66 (a) Precipitation will begin when $Q = K_{sp}$.

$BaSO_4$: $K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10}$

$1.1 \times 10^{-10} = (0.010)[SO_4^{2-}]$; $[SO_4^{2-}] = 1.1 \times 10^{-8}$ *M*

$SrSO_4$: $K_{sp} = [Sr^{2+}][SO_4^{2-}] = 3.2 \times 10^{-7}$

$3.2 \times 10^{-7} = (0.010)[SO_4^{2-}]$; $[SO_4^{2-}] = 3.2 \times 10^{-5}$ *M*

The $[SO_4^{2-}]$ necessary to begin precipitation is the smaller of the two values, 1.1×10^{-8} *M* SO_4^{2-}.

(b) Ba^{2+} precipitates first, because it requires the smaller $[SO_4^{2-}]$.

(c) Sr^{2+} will begin to precipitate when $[SO_4^{2-}]$ in solution (not bound in $BaSO_4$) reaches 3.2×10^{-5} *M*.

17.68 Initial solubility in water rules out CdS and HgO. Formation of a precipitate on addition of HCl indicates the presence of $Pb(NO_3)_2$ (formation of $PbCl_2$). Formation of a precipitate on addition of H_2S at pH 1 probably indicates $Cd(NO_3)_2$ (formation of CdS). (This test can be misleading because enough Pb^{2+} can remain in solution after filtering $PbCl_2$ to lead to visible precipitation of PbS.) Absence of a precipitate on addition of H_2S at pH 8 indicates that $ZnSO_4$ is not present. The yellow flame test indicates presence of Na^+. In summary, $Pb(NO_3)_2$ and Na_2SO_4 are definitely present, $Cd(NO_3)_2$ is probably present, and CdS, HgO and $ZnSO_4$ are definitely absent.

17.70 (a) Make the solution slightly basic and saturate with H_2S; CdS will precipitate, Na^+ remains in solution.

(b) Make the solution acidic, saturate with H_2S; CuS will precipitate, Mg^{2+} remains in solution.

(c) Add HCl, $PbCl_2$ precipitates. (It is best to carry out the reaction in an ice-water bath to reduce the solubility of $PbCl_2$.)

(d) Add dilute HCl; AgCl precipitates, Hg^{2+} remains in solution.

17.72 The addition of $(NH_4)_2HPO_4$ could result in precipitation of salts from metal ions of the other groups. The $(NH_4)_2HPO_4$ will render the solution basic, so metal hydroxides could form as well as insoluble phosphates. It is essential to separate the metal ions of a group from other metal ions before carrying out the specific tests for that group.

Additional Exercises

17.74 $K_a = \dfrac{[H^+][In^-]}{[HIn]}$; at pH = 4.68, $[HIn] = [In^-]$; $[H^+] = K_a$; $pH = pK_a = 4.68$

17.75 (a) $HA(aq) + B(aq) \rightleftharpoons HB^+(aq) + A^-(aq) \quad K_{eq} = \dfrac{[HB^+][A^-]}{[HA][B]}$

(b) Note that the solution is slightly basic because B is a stronger base than HA is an acid. (Or, equivalently, that A^- is a stronger base than HB^+ is an acid.) Thus, a little of the A^- is used up in reaction: $A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$. Since pH is not very far from neutral, it is reasonable to assume that the reaction in part (a) has gone far to the right, and that $[A^-] \approx [HB^+]$ and $[HA] \approx [B]$. Then