16 Acid-Base Equilibria

Visualizing Concepts

16.1 *Analyze*. From the structures decide which reactant fits the description of a Brønsted-Lowry (B-L) acid, a B-L base, a Lewis acid, and a Lewis base. *Plan*. A B-L acid is an H^+ donor, and a B-L base is an H^+ acceptor. A Lewis acid is an electron pair acceptor and a Lewis base is an electron pair donor. *Solve*.

(a) H–X is a B-L acid, because it loses H^+ during reaction. NH_3 is a B-L base, because it gains H^+ during reaction.

(b) By virtue of its unshared electron pair, NH_3 is the electron pair donor and Lewis base. HX is the electron pair acceptor and Lewis acid.

16.3 *Plan*. Strong acids are completely ionized. The acid that is least ionized is weakest, and has the smallest K_a value. At equal concentrations, the weakest acid has the smallest $[H^+]$ and highest pH. *Solve*.

(a) HY is a strong acid. There are no neutral HY molecules in solution, only H^+ cations and Y^- anions.

(b) HX has the smallest K_a value. It has most neutral acid molecules and fewest ions.

(c) HX has the fewest H^+ and highest pH.

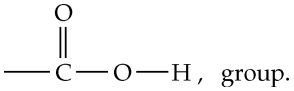
16.6 *Plan*. The stronger the acid, the greater the extent of ionization. The stronger the acid, the weaker its conjugate base. *Solve*.

(a) HY has most H^+ and is strongest; HX has the fewest H^+ and is weakest. The order of base strength is the reverse of the order of acid strength. $Y^- < Z^- < X^-$

(b) The strongest base, X^-, has the largest K_b value.

16.9 *Plan*. Evaluate the molecular structures to determine if the acids are binary acids or oxyacids. Consider the trends in acid strength for both classes of acids. *Solve*.

(a) The molecules are oxyacids; in both cases, the ionizable H atom is attached to O. The right molecule is a carboxylic acid; the ionizable H is part of a carboxyl,



group.

(b) Increasing the electronegativity of X increases the strength of both acids. As X becomes more electronegative and attracts more electron density, the O–H bond becomes weaker and more polar. This increases the likelihood of ionization and increases acid strength. An electronegative X group also stabilizes the anionic

conjugate bases by delocalizing the negative charge. This causes the ionization equilibrium to favor products, and the values of K_a to increase.

Arrhenius and Brønsted-Lowry Acids and Bases

16.13 Solutions of HCl and H_2SO_4 taste sour, turn litmus paper red (are acidic), neutralize solutions of bases, react with active metals to form $H_2(g)$ and conduct electricity. The two solutions have these properties in common because both solutes are strong acids. That is, they both ionize completely in H_2O to form $H^+(aq)$ and an anion. (The first ionization step for H_2SO_4 is complete, but the second is not.) The presence of ions enables the solutions to conduct electricity; the presence of $H^+(aq)$ in excess of 1×10^{-7} *M* accounts for all the other listed properties.

16.15 (a) According to the Arrhenius definition, an *acid* when dissolved in water increases $[H^+]$. According to the Brønsted-Lowry definition, an *acid* is capable of donating H^+, regardless of physical state. The Arrhenius definition of an acid is confined to an aqueous solution; the Brønsted-Lowry definition applies to any physical state.

(b) $HCl(g) + NH_3(g) \rightarrow NH_4^+Cl^-(s)$ HCl is the B-L (Brønsted-Lowry) acid; it donates an H^+ to NH_3 to form NH_4^+. NH_3 is the B-L base; it accepts the H^+ from HCl.

16.17 *Analyze/Plan*. Follow the logic in Sample Exercise 16.1. A conjugate base has one less H^+ than its conjugate acid. A conjugate acid has one more H^+ than its conjugate base. *Solve*.

(a) (i) IO_3^- (ii) NH_3

(b) (i) OH^- (ii) H_3PO_4

16.19 *Analyze/Plan*. Use the definitions of B-L acids and bases, and conjugate acids and bases to make the designations. Evaluate the changes going from reactant to product to inform your choices. *Solve*.

	B-L acid	+	**B-L base**	⇌	**Conjugate acid**	+	**Conjugate base**
(a)	$NH_4^+(aq)$		$CN^-(aq)$		$HCN(aq)$		$NH_3(aq)$
(b)	$H_2O(l)$		$(CH_3)_3N(aq)$		$(CH_3)_3NH^+(aq)$		$OH^-(aq)$
(c)	$HCOOH(aq)$		$PO_4^{3-}(aq)$		$HPO_4^{2-}(aq)$		$HCOO^-(aq)$

16.21 *Analyze/Plan*. Follow the logic in Sample Exercise 16.2. *Solve*.

(a) Acid: $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons C_2O_4^{2-}(aq) + H_3O^+(aq)$

B-L acid B-L base conj. base conj. acid

Base: $HC_2O_4^-(aq) + H_2O(l) \rightleftharpoons H_2C_2O_4(aq) + OH^-(aq)$

B-L base B-L acid conj. acid conj. Base

(b) $H_2C_2O_4$ is the conjugate acid of $HC_2O_4^-$.

$C_2O_4^{2-}$ is the conjugate base of $HC_2O_4^-$.

16.23 *Analyze/Plan*. Based on the chemical formula, decide whether the base is strong, weak or negligible. Is it the conjugate of a strong acid (negligible base), weak acid (weak base) or negligible acid (strong base)? Also check Figure 16.4. To write the formula of the conjugate acid, add a single H and increase the particle charge by one.

(a) CH_3COO^-, weak base; CH_3COOH, weak acid

(b) HCO_3^-, weak base; H_2CO_3, weak acid

(c) O^{2-}, strong base; OH^-, negligible acid

(d) Cl^-, negligible base; HCl, strong acid

(e) NH_3, weak base; NH_4^+, weak acid

16.25 *Analyze/Plan*. Given chemical formula, determine strength of acids and bases by checking the known strong acids (Section 16.5). Recall the paradigm "The stronger the acid, the weaker its conjugate base, and vice versa." *Solve*.

(a) HBr. It is one of the seven strong acids (Section 16.5).

(b) F^-. HCl is a stronger acid than HF, so F^- is the stronger conjugate base.

16.27 *Analyze/Plan*. Acid-base equilibria favor formation of the weaker acid and base. Compare the relative strengths of the substances acting as acids on opposite sides of the equation. (Bases can also be compared; the conclusion should be the same.) *Solve*.

	Base	+	**Acid**	⇌	**Conjugate acid**	+	**Conjugate base**
(a)	$O^{2-}(aq)$	+	$H_2O(l)$	⇌	$OH^-(aq)$	+	$OH^-(aq)$

H_2O is a stronger acid than OH^-, so the equilibrium lies to the right.

(b) $HS^-(aq) + CH_3COOH(aq) \rightleftharpoons H_2S(aq) + CH_3COO^-(aq)$

CH_3COOH is a stronger acid than H_2S, so the equilibrium lies to the right.

(c) $NO_2^-(aq) + H_2O(l) \rightleftharpoons HNO_2(aq) + OH^-(aq)$

HNO_2 is a stronger acid than H_2O, so the equilibrium lies to the left.

Autoionization of Water

16.29 (a) *Autoionization* is the ionization of a neutral molecule (in the absence of any other reactant) into an anion and a cation. The equilibrium expression for the autoionization of water is $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$.

(b) Pure water is a poor conductor of electricity because it contains very few ions. Ions, mobile charged particles, are required for the conduction of electricity in liquids.

(c) If a solution is acidic, it contains more H^+ than OH^- ($[H^+] > [OH^-]$).

16.31 *Analyze/Plan*. Follow the logic in Sample Exercise 16.5. In pure water at 25°C, $[H^+] = [OH^-] = 1 \times 10^{-7}\ M$. If $[H^+] > 1 \times 10^{-7}\ M$, the solution is acidic; if $[H^+] < 1 \times 10^{-7}\ M$, the solution is basic. *Solve*.

(a) $$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}\ M} = 2.2 \times 10^{-11}\ M < 1 \times 10^{-7}\ M;\ \text{basic}$$

(b) $[H^+] = \frac{K_W}{[OH^-]} = \frac{1.0 \times 10^{-14}}{8.8 \times 10^{-9}\ M} = 1.1 \times 10^{-6}\ M > 1 \times 10^{-7}\ M$; acidic

(c) $[OH^-] = 100[H^+]$; $K_w = [H^+] \times 100[H^+] = 100[H^+]^2$;

$[H^+] = (K_w / 100)^{1/2} = 1.0 \times 10^{-8}\ M < 1 \times 10^{-7}\ M$; basic

16.33 *Analyze/Plan*. Follow the logic in Sample Exercise 16.4. Note that the value of the equilibrium constant (in this case, K_w) changes with temperature. *Solve*.

At 0°C, $K_w = 1.2 \times 10^{-15} = [H^+][OH^-]$.

In pure water, $[H^+] = [OH^-]$; $1.2 \times 10^{-15} = [H^+]^2$; $[H^+] = (1.2 \times 10^{-15})^{1/2}$

$[H^+] = [OH^-] = 3.5 \times 10^{-8}\ M$

The pH Scale

16.35 *Analyze/Plan*. A change of one pH unit (in either direction) is:

$\Delta pH = pH_2 - pH_1 = -(\log[H^+]_2 - \log[H^+]_1) = -\log\frac{[H^+]_2}{[H^+]_1} = \pm 1$. The antilog of +1 is 10; the antilog of –1 is 1×10^{-1}. Thus, a ΔpH of one unit represents an increase or decrease in $[H^+]$ by a factor of 10. *Solve*.

(a) ΔpH = ±2.00 is a change of $10^{2.00}$; $[H^+]$ changes by a factor of 100.

(b) ΔpH = ±0.5 is a change of $10^{0.50}$; $[H^+]$ changes by a factor of 3.2.

16.37 (a) $K_w = [H^+][OH^-]$. If NaOH is added to water, it dissociates into $Na^+(aq)$ and $OH^-(aq)$. This increases $[OH^-]$ and necessarily decreases $[H^+]$. When $[H^+]$ decreases, pH increases.

(b) 0.0006 $M = 6 \times 10^{-4}\ M$. On Figure 16.5, this is $[H^+] > 1 \times 10^{-4}$ but $< 1 \times 10^{-3}$. The pH is between 3 and 4, closer to 3. We estimate 3.3. If pH < 7, the solution is acidic.

(c) pH = 5.2 is between pH 5 and pH 6 on Figure 16.5, closer to pH = 5. At pH = 6, $[H^+] = 1 \times 10^{-6}$; at pH = 5, $[H^+] = 1 \times 10^{-5} = 10 \times 10^{-6}$. A good estimate is $7 \times 10^{-6}\ M\ H^+$.

By calculation: $[H^+] = 10^{-pH} = 10^{-5.2} = 6 \times 10^{-6}\ M$

At pH = 5, $[OH^-] = 1 \times 10^{-9}$; at pH = 6, $[OH^-] = 1 \times 10^{-8} = 10 \times 10^{-9}$.

Since pH = 5.2 is closer to pH = 5, we estimate $3 \times 10^{-9}\ M\ OH^-$.

By calculation: pOH = 14.0 – 5.2 = 8.8

$[OH^-] = 10^{-pOH} = 10^{-8.8} = 2 \times 10^{-9}\ M\ OH^-$

16.39 *Analyze/Plan*. At 25°C, $[H^+][OH^-] = 1 \times 10^{-14}$; pH = pOH = 14. Use these relationships to complete the table. If pH < 7, the solution is acidic; if pH > 7, the solution is basic. *Solve*.

$[H^+]$	$[OH^-]$	pH	pOH	acidic or basic

$7.5 \times 10^{-3}\ M$	$1.3 \times 10^{-12}\ M$	2.12	11.88	acidic
$2.8 \times 10^{-5}\ M$	$3.6 \times 10^{-10}\ M$	4.56	9.44	acidic
$5.6 \times 10^{-9}\ M$	$1.8 \times 10^{-6}\ M$	8.25	5.75	basic
$5.0 \times 10^{-9}\ M$	$2.0 \times 10^{-6}\ M$	8.30	5.70	basic

Check. pH + pOH = 14; $[H^+][OH^-] = 1 \times 10^{-14}$.

16.41 *Analyze/Plan*. Given pH and a new value of the equilibrium constant K_w, calculate equilibrium concentrations of $H^+(aq)$ and $OH^-(aq)$. The definition of pH remains $pH = -\log[H^+]$. *Solve*.

pH = 7.40; $[H^+] = 10^{-pH} = 10^{-7.40} = 4.0 \times 10^{-8}\ M$

$K_w = 2.4 \times 10^{-14} = [H^+][OH^-]$; $[OH^-] = 2.4 \times 10^{-14} / [H^+]$

$[OH^-] = 2.4 \times 10^{-14} / 4.0 \times 10^{-8} = 6.0 \times 10^{-7}\ M$, $pOH = -\log(6.0 \times 10^{-7}) = 6.22$

Alternately, $pH + pOH = pK_w$. At 37°C, $pH + pOH = -\log(2.4 \times 10^{-14})$

pH + pOH = 13.62; pOH = 13.62 – 7.40 = 6.22

$[OH^-] = 10^{-pOH} = 10^{-6.22} = 6.0 \times 10^{-7}\ M$

Strong Acids and Bases

16.43 (a) A strong acid is completely ionized in aqueous solution; a strong acid is a strong electrolyte.

(b) For a strong acid such as HCl, $[H^+]$ = initial acid concentration. $[H^+] = 0.500\ M$

(c) HCl, HBr, HI

16.45 *Analyze/Plan*. Follow the logic in Sample Exercise 16.8. Strong acids are completely ionized, so $[H^+]$ = original acid concentration, and $pH = -\log[H^+]$. For the solutions obtained by dilution, use the "dilution" formula, $M_1V_1 = M_2V_2$, to calculate molarity of the acid. *Solve*.

(a) $8.5 \times 10^{-3}\ M$ HBr = $8.5 \times 10^{-3}\ M\ H^+$; $pH = -\log(8.5 \times 10^{-3}) = 2.07$

(b) $$\frac{1.52\text{g HNO}_3}{0.575\text{L soln}} \times \frac{1\text{mol HNO}_3}{63.02\text{g HNO}_3} = 0.041947 = 0.0419\ M\ \text{HNO}_3$$

$[H^+] = 0.0419\ M$; $pH = -\log(0.041947) = 1.377$

(c) $M_c \times V_c = M_d \times V_d$; $0.250\ M \times 0.00500\ \text{L} = ?\ M \times 0.0500\ \text{L}$

$$M_d = \frac{0.250\ M \times 0.00500\ \text{L}}{0.0500\ \text{L}} = 0.0250\ M\ \text{HCl}$$

$[H^+] = 0.0250\ M$; $pH = -\log(0.0250) = 1.602$

(d) $$[H^+]_{total} = \frac{\text{mol H}^+\text{ from HBr} + \text{mol H}^+\text{ from HCl}}{\text{total L solution}}$$

$$[H^+]_{total} = \frac{(0.100\ M\ \text{HBr} \times 0.0100\ \text{L}) + (0.200\ M \times 0.0200\ \text{L})}{0.0300\ \text{L}}$$

$$[H^+]_{total} = \frac{1.00 \times 10^{-3}\ mol\ H^+ + 4.00 \times 10^{-3}\ mol\ H^+}{0.0300\ L} = 0.1667 = 0.167 M$$

pH = –log (0.1667 *M*) = 0.778

16.47 *Analyze/Plan*. Follow the logic in Sample Exercise 16.9. Strong bases dissociate completely upon dissolving. pOH = –log[OH^-]; pH = 14 – pOH.

(a) Pay attention to the formula of the base to get [OH^-]. *Solve*.

[OH^-] = 2[$Sr(OH)_2$] = 2(1.5 × 10^{-3} *M*) = 3.0 × 10^{-3} *M* OH^- (see Exercise 16.44(b))

pOH = –log (3.0 × 10^{-3}) = 2.52; pH = 14 – pOH = 11.48

(b) mol/LiOH = g LiOH/molar mass LiOH. [OH^-] = [LiOH]. *Solve*.

$$\frac{2.250\ g\ LiOH}{0.2500\ L\ soln} \times \frac{1\ mol\ LiOH}{23.948\ g\ LiOH} = 0.37581 = 0.3758 M\ LiOH = [OH^-]$$

pOH = –log (0.37581) = 0.4250; pH = 14 – pOH = 13.5750

(c) Use the dilution formula to get the [NaOH] = [OH^-]. *Solve*.

$M_c \times V_c = M_d \times V_d$; 0.175 *M* × 0.00100 L = ? *M* × 2.00 L

$$M_d = \frac{0.175 M \times 0.00100\ L}{2.00\ L} = 8.75 \times 10^{-5}\ M\ NaOH = [OH^-]$$

pOH = –log (8.75 × 10^{-5}) = 4.058; pH = 14 – pOH = 9.942

(d) Consider total mol OH^- from KOH and $Ca(OH)_2$, as well as total solution volume. *Solve*.

$$[OH^-]_{total} = \frac{mol\ OH^-\ from KOH + mol\ OH^-\ from Ca(OH)_2}{total\ L\ soln}$$

$$[OH^-]_{total} = \frac{(0.105 M \times 0.00500\ L) + 2(9.5 \times 10^{-2}\ M \times 0.0150\ L)}{0.0200\ L}$$

$$[OH^-]_{total} = \frac{0.525 \times 10^{-3}\ mol\ OH^- + 2.85 \times 10^{-3}\ mol\ OH^-}{0.0200\ L} = 0.16875 = 0.17 M$$

pOH = –log (0.16875) = 0.77; pH = 14 – pOH = 13.23

(9.5 × 10^{-2} *M* has 2 sig figs, so the [OH^-] has 2 sig figs and pH and pOH have 2 decimal places.)

16.49 *Analyze/Plan*. pH → pOH → [OH^-] = [NaOH]. *Solve*.

pOH = 14 – pH = 14.00 – 11.50 = 2.50

pOH = 2.50 = –log[OH^-]; [OH^-] = $10^{-2.50}$ = 3.2 × 10^{-3} *M*

[OH^-] = [NaOH] = 3.2 × 10^{-3} *M*

Weak Acids

16.51 *Analyze/Plan*. Remember that K_a = [products]/[reactants]. If $H_2O(l)$ appears in the equilibrium reaction, it will **not** appear in the K_a expression, because it is a pure liquid. *Solve*.

(a) $HBrO_2(aq) \rightleftharpoons H^+(aq) + BrO_2^-(aq); \; K_a = \dfrac{[H^+][BrO_2^-]}{[HBrO_2]}$

$HBrO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + BrO_2^-(aq); \; K_a = \dfrac{[H_3O^+][BrO_2^-]}{[HBrO_2]}$

(b) $C_2H_5COOH(aq) \rightleftharpoons H^+(aq) + C_2H_5COO^-(aq); \; K_a = \dfrac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$

$C_2H_5COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_5COO^-(aq);$

$$K_a = \frac{[H_3O^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

16.53 *Analyze/Plan*. Follow the logic in Sample Exercise 16.10. *Solve*.

$CH_3CH(OH)COOH$

$$\rightleftharpoons H^+(aq) + CH_3CH(OH)COO^-(aq); \; K_a = \frac{[H^+][CH_3CH(OH)COO^-]}{[CH_3CH(OH)COOH]}$$

$[H^+] = [CH_3CH(OH)COO^-] = 10^{-2.44} = 3.63 \times 10^{-3} = 3.6 \times 10^{-3}\ M$

$[CH_3CH(OH)COOH] = 0.10 - 3.63 \times 10^{-3} = 0.0964 = 0.096\ M$

$$K_a = \frac{(3.63 \times 10^{-3})^2}{(0.096)} = 1.4 \times 10^{-4}$$

16.55 *Analyze/Plan*. Write the equilibrium reaction and the K_a expression. Use % ionization to get equilibrium concentration of $[H^+]$, and by stoichiometry, $[X^-]$ and [HX]. Calculate K_a *Solve*.

$[H^+] = 0.110 \times [CH_2ClCOOH]_{initial} = 0.0110\ M$

	$CH_2ClCOOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$CH_2ClCOO^-(aq)$
initial	0.100 *M*		0		0
equil.	0.089 *M*		0.0110 *M*		0.0110 *M*

$$K_a = \frac{[H^+][CH_2ClCOO^-]}{[CH_2ClCOOH]} = \frac{(0.0110)^2}{0.089} = 1.4 \times 10^{-3}$$

16.57 *Analyze/Plan*. Write the equilibrium reaction and the K_a expression.

$[H^+] = 10^{-pH} = [CH_3COO^-]; \quad [CH_3COOH] = x - [H^+]$.

Substitute into the K_a expression and solve for x. *Solve*.

$[H^+] = 10^{-pH} = 10^{-2.90} = 1.26 \times 10^{-3} = 1.3 \times 10^{-3}\ M$

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(1.26 \times 10^{-3})^2}{(x - 1.26 \times 10^{-3})}$$

$1.8 \times 10^{-5}\,(x - 1.26 \times 10^{-3}) = (1.26 \times 10^{-3})^2$;

$1.8 \times 10^{-5}\,x = 1.585 \times 10^{-6} + 2.268 \times 10^{-8} = 1.608 \times 10^{-6}$;

$x = 0.08932 = 0.089\ M\ CH_3COOH$

16.59 *Analyze/Plan*. Follow the logic in Sample Exercise 16.12. Write K_a, construct the equilibrium table, solve for $x = [H^+]$, then get equilibrium $[C_6H_5COO^-]$ and $[C_6H_5COOH]$ by substituting $[H^+]$ for x. *Solve*.

	$C_6H_5COOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_6H_5COO^-(aq)$
initial	0.050 *M*		0		0
equil.	(0.050 – x) *M*		x *M*		x *M*

$$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{x^2}{(0.050 - x)} \approx \frac{x^2}{0.050} = 6.3 \times 10^{-5}$$

$x^2 = 0.050\,(6.3 \times 10^{-5})$; $x = 1.8 \times 10^{-3}\ M = [H^+] = [H_3O^+] = [C_6H_5COO^-]$

$[C_6H_5COOH] = 0.050 - 0.0018 = 0.048\ M$

$$\textit{Check:}\ \frac{1.8 \times 10^{-3}\ M\ H^+}{0.050 M\ C_6H_5COOH} \times 100 = 3.6\%\ \text{ionization; the approximation is valid}$$

16.61 *Analyze/Plan*. Follow the logic in Sample Exercise 16.12.

(a) *Solve*.

	$C_2H_5COOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_2H_5COO^-(aq)$
initial	0.095 *M*		0		0
equil	(0.095 – x) *M*		x *M*		x *M*

$$K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]} = \frac{x^2}{(0.095 - x)} \approx \frac{x^2}{0.095} = 1.3 \times 10^{-5}$$

$x^2 = 0.095(1.3 \times 10^{-5})$; $x = 1.111 \times 10^{-3} = 1.1 \times 10^{-3}\ M\ H^+$; pH = 2.95

$$\textit{Check:}\ \frac{1.1 \times 10^{-3}\ M\ H^+}{0.095 M\ C_2H_5COOH} \times 100 = 1.2\%\ \text{ionization; the approximation is valid}$$

(b) *Solve*.

$$K_a = \frac{[H^+][CrO_4^{2-}]}{[HCrO_4^-]} = \frac{x^2}{(0.100 - x)} \approx \frac{x^2}{0.100} = 3.0 \times 10^{-7}$$

$x^2 = 0.100(3.0 \times 10^{-7})$; $x = 1.732 \times 10^{-4} = 1.7 \times 10^{-4}\ M\ H^+$

$pH = -\log(1.732 \times 10^{-4}) = 3.7614 = 3.76$

$$\text{Check: } \frac{1.7 \times 10^{-4}\ M\ H^+}{0.100 M\ HCrO_4^-} \times 100 = 0.17\%\ \text{ionization; the approximation is valid}$$

(c) Follow the logic in Sample Exercise 16.15. pOH = –log[OH^-]. pH = 14 – pOH

Solve.

	$C_5H_5N(aq) + H_2O(l)$	$\rightleftharpoons$	$C_5H_5NH^+(aq)$	+	$OH^-(aq)$
initial	0.120 *M*		0		0
equil	(0.120 – x) *M*		x *M*		x *M*

$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]} = \frac{x^2}{(0.120 - x)} \approx \frac{x^2}{0.120} = 1.7 \times 10^{-9}$$

$x^2 = 0.120(1.7 \times 10^{-9})$; $x = 1.428 \times 10^{-5} = 1.4 \times 10^{-5}\ M\ OH^-$; pH = 9.15

$$\text{Check } \frac{1.4 \times 10^{-5}\ M\ OH^-}{0.120 M\ C_5H_5N} \times 100 = 0.012\%\ \text{ionization; the approximation is valid}$$

16.63 *Analyze/Plan*. $K_a = 10^{-pK_a}$. Follow the logic in Sample Exercise 16.13. *Solve*.

Let $[H^+] = [NC_7H_4SO_3^-] = z$. K_a = antilog (–2.32) = $4.79 \times 10^{-3} = 4.8 \times 10^{-3}$

$$\frac{z^2}{0.10 - z} = 4.79 \times 10^{-3}. \quad \text{Since } K_a \text{ is relatively large, solve the quadratic.}$$

$z^2 = 4.79 \times 10^{-3} z - 4.79 \times 10^{-4} = 0$

$$z = \frac{-4.79 \times 10^{-3} \pm \sqrt{(4.79 \times 10^{-3})^2 - 4(1)(-4.79 \times 10^{-4})}}{2(1)} = \frac{-4.79 \times 10^{-3} \pm \sqrt{1.937 \times 10^{-3}}}{2}$$

$z = 1.96 \times 10^{-2} = 2.0 \times 10^{-2}\ M\ H^+$; pH = –log ($1.96 \times 10^{-2}$) = 1.71

16.65 *Analyze/Plan*. Follow the logic in Sample Exercise 16.13. *Solve*.

(a)

	$HN_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$N_3^-(aq)$
initial	0.400 *M*		0		0
equil	(0.400 – x) *M*		x *M*		x *M*

$$K_a = \frac{[H^+][N_3^-]}{[HN_3]} = 1.9 \times 10^{-5}; \frac{x^2}{(0.400 - x)} \approx \frac{x^2}{0.400} = 1.9 \times 10^{-5}$$

$$x = 0.00276 \approx 2.8 \times 10^{-3}\ M = [H^+]; \%\ \text{ionization} = \frac{2.76 \times 10^{-3}}{0.400} \times 100 = 0.69\%$$

(b) $1.9 \times 10^{-5} \approx \frac{x^2}{0.100}$; $x = 0.00138 \approx 1.4 \times 10^{-3}\ M\ H^+$

$$\%\ \text{ionization} = \frac{1.38 \times 10^{-3}\ M\ H^+}{0.100 M\ HN_3} \times 100 = 1.4\%$$

(c) $1.9 \times 10^{-5} \approx \frac{x^2}{0.0400}$; $x = 8.72 \times 10^{-4} = 8.7 \times 10^{-4}\ M\ H^+$

$$\%\text{ ionization} = \frac{8.72 \times 10^{-4}\ M\ H^+}{0.0400 M\ HN_3} \times 100 = 2.2\%$$

Check. Notice that a tenfold dilution [part (a) versus part (c)] leads to a slightly more than threefold increase in percent ionization.

16.67 *Analyze/Plan*. Let the weak acid be HX. HX(aq) $\rightleftharpoons$ $H^+(aq) + X^-(aq)$. Solve the K_a expression symbolically for $[H^+]$ in terms of [HX]. Substitute into the formula for % ionization, $([H^+]/[HX]) \times 100$. *Solve*.

$$K_a = \frac{[H^+][X^-]}{[HX]};\ [H^+] = [X^-] = y;\ K_a = \frac{y^2}{[HX] - y};\ \text{assume that \% ionization is small}$$

$$K_a = \frac{y^2}{[HX]};\ y = K_a^{1/2}[HX]^{1/2}$$

$$\%\text{ ionization} = \frac{y}{[HX]} \times 100 = \frac{K_a^{1/2}[HX]^{1/2}}{[HX]} \times 100 = \frac{K_a^{1/2}}{[HX]^{1/2}} \times 100$$

That is, percent ionization varies inversely as the square root of concentration HX.

16.69 *Analyze/Plan*. Follow the logic in Sample Exercise 16.14. Citric acid is a triprotic acid with three K_a values that do not differ by more than 10^3. We must consider all three steps. Also, $C_6H_5O_7^{3-}$ is only produced in step 3. *Solve*.

$$H_3C_6H_5O_7(aq) \rightleftharpoons H^+(aq) + H_2C_6H_5O_7^-(aq) \qquad K_{a1} = 7.4 \times 10^{-4}$$

$$H_2C_6H_5O_7^-(aq) \rightleftharpoons H^+(aq) + HC_6H_5O_7^{2-}(aq) \qquad K_{a2} = 1.7 \times 10^{-5}$$

$$HC_6H_5O_7^{2-}(aq) \rightleftharpoons H^+(aq) + C_6H_5O_7^{3-}(aq) \qquad K_{a3} = 4.0 \times 10^{-7}$$

To calculate the pH of a 0.050 *M* solution, assume initially that only the first ionization is important:

	$H_3C_6H_5O_7(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$H_2C_6H_5O_7^-(aq)$
initial	0.050 *M*		0		0
equil.	(0.050 – x) *M*		x *M*		x *M*

$$K_{a_1} = \frac{[H^+][H_2C_6H_5O_7^-]}{[H_3C_6H_5O_7]} = \frac{x^2}{(0.050 - x)} = 7.4 \times 10^{-4}$$

$x^2 = (0.050 - x)(7.4 \times 10^{-4})$; $x^2 \approx (0.050)(7.4 \times 10^{-4})$; $x = 0.00608 = 6.1 \times 10^{-3}\ M$

Since this value for x is rather large in relation to 0.050, a better approximation for x can be obtained by substituting this first estimate into the expression for x^2, then solving again for x:

$$x^2 = (0.050 - x)\ (7.4 \times 10^{-4}) = (0.050 - 6.08 \times 10^{-3})\ (7.4 \times 10^{-4})$$

$$x^2 = 3.2 \times 10^{-5};\ x = 5.7 \times 10^{-3}\ M$$

(This is the same result obtained from the quadratic formula.)

The correction to the value of x, though not large, is significant. Does the second ionization produce a significant additional concentration of H^+?

	$H_2C_6H_5O_7^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HC_6H_5O_7^{2-}(aq)$
initial	$5.7 \times 10^{-3}\ M$		$5.7 \times 10^{-3}\ M$		0
equil.	$(5.7 \times 10^{-3} - y)$		$(5.7 \times 10^{-3} + y)$		y

$$K_{a_2} = \frac{[H^+][HC_6H_5O_7^{2-}]}{[H_2C_6H_5O_7^-]} = 1.7 \times 10^{-5};\ \frac{(5.7 \times 10^{-3} + y)(y)}{(5.7 \times 10^{-3} - y)} = 1.7 \times 10^{-5}$$

Assume that y is small relative to 5.7×10^{-3}; that is, that additional ionization of $H_2C_6H_5O_7^-$ is small, then

$$\frac{(5.7 \times 10^{-3})y}{(5.7 \times 10^{-3})} = 1.7 \times 10^{-5}\ M;\ y = 1.7 \times 10^{-5}\ M$$

This value is indeed small compared to $5.7 \times 10^{-3}\ M$; $[H^+]$ and pH are determined by the first ionization step. If we were only interested in pH, we could stop here. However, to calculate $[C_6H_5O_7^{3-}]$, we must consider the third ionization, with adjusted $[H^+] = 5.7 \times 10^{-3} + 1.7 \times 10^{-5} = 5.72 \times 10^{-3}\ M$ $(= 5.7 \times 10^{-3})$

	$HC_6H_5O_7^{2-}$	$\rightleftharpoons$	H^+ (aq)	+	$C_6H_5O_7^{3-}$ (aq)
initial	$1.7 \times 10^{-5}\ M$		$5.72 \times 10^{-3}\ M$		0
equil.	$1.7 \times 10^{-5} - z$		$5.72 \times 10^{-3} + z$		z

$$K_{a_3} = \frac{[H^+][C_6H_5O_7^{3-}]}{[HC_6H_5O_7^{2-}]} = \frac{(5.72 \times 10^{-3} + z)(z)}{(1.7 \times 10^{-5} - z)} = 4.0 \times 10^{-7}$$

Assume z is small relative to 5.72×10^{-3}, but not relative to 1.7×10^{-5}.

$(4.0 \times 10^{-7})(1.7 \times 10^{-5} - z) = 5.72 \times 10^{-3}\ z$; $6.8 \times 10^{-12} - 4.0 \times 10^{-7}\ z = 5.72 \times 10^{-3}\ z$;

$6.8 \times 10^{-12} = 5.72 \times 10^{-3}\ z + 4.0 \times 10^{-7}\ z = 5.72 \times 10^{-3}\ z$; $z = 1.19 \times 10^{-9} = 1.2 \times 10^{-9}\ M$

$[C_6H_5O_7^{3-}] = 1.2 \times 10^{-9}\ M$; $[H^+] = 5.72 \times 10^{-3}\ M + 1.2 \times 10^{-9}\ M = 5.72 \times 10^{-3}\ M$

$pH = -\log(5.72 \times 10^{-3}) = 2.24$

Note that neither the second nor third ionizations contributed significantly to $[H^+]$ and pH.

Weak Bases

16.71 All Brønsted-Lowry bases contain at least one unshared (lone) pair of electrons to attract H^+.

16.73 *Analyze/Plan*. Remember that K_b = [products]/[reactants]. If $H_2O(l)$ appears in the equilibrium reaction, it will not appear in the K_b expression, because it is a pure liquid. *Solve*.

(a) $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq); K_b = \dfrac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$

(b) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq); K_b = \dfrac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$

(c) $HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq); K_b = \dfrac{[HCOOH][OH^-]}{[HCOO^-]}$

16.75 *Analyze/Plan*. Follow the logic in Sample Exercise 16.15. *Solve*.

	$C_2H_5NH_2(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$C_2H_5NH_3^+(aq)$ +	$OH^-(aq)$
initial	0.075 *M*	0	0
equil.	(0.075 – x) *M*	x *M*	x *M*

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(x)(x)}{(0.075-x)} = \frac{x^2}{0.075} = 6.4 \times 10^{-4}$$

$x^2 = 0.075\ (6.4 \times 10^{-4})$; $x = [OH^-] = 6.9 \times 10^{-3}\ M$; pH = 11.84

$$\textit{Check}\ \frac{6.9 \times 10^{-3}\ M\ OH^-}{0.075 M\ C_2H_5NH_2} \times 100 = 9.2\%\ \text{ionization; the assumption is not valid}$$

To obtain a more precise result, the K_b expression is rewritten in standard quadratic form and solved via the quadratic formula.

$$\frac{x^2}{0.075-x} = 6.4 \times 10^{-4}; x^2 + 6.4 \times 10^{-4}x - 4.8 \times 10^{-5} = 0$$

$$x = \frac{b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-6.4 \times 10^{-4} \pm \sqrt{(6.4 \times 10^{-4})^2 - 4(1)(-4.8 \times 10^{-5})}}{2}$$

$x = 6.61 \times 10^{-3} = 6.6 \times 10^{-3}\ M\ OH^-$; pOH = 2.18, pH = 14.00 – pOH = 11.82

Note that the pH values obtained using the two algebraic techniques are very similar.

16.77 *Analyze/Plan*. Given pH and initial concentration of base, calculate all equilibrium concentrations. pH → pOH → $[OH^-]$ at equilibrium. Construct the equilibrium table and calculate other equilibrium concentrations. Substitute into the K_b expression and calculate K_b. *Solve*.

(a) $[OH^-] = 10^{-pOH}$; pOH = 14 – pH = 14.00 – 11.33 = 2.67

$[OH^-] = 10^{-2.67} = 2.138 \times 10^{-3} = 2.1 \times 10^{-3}\ M$

	$C_{10}H_{15}ON(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$C_{10}H_{15}ONH^+(aq)$ +	$OH^-(aq)$
initial	0.035 *M*	0	0
equil.	0.033 *M*	$2.1 \times 10^{-3}\ M$	$2.1 \times 10^{-3}\ M$

(b) $$K_b = \frac{[C_{10}H_{15}ONH^+][OH^-]}{[C_{10}H_{15}ON]} = \frac{(2.138 \times 10^{-3})^2}{(0.0328)6} = 1.4 \times 10^{-4}$$

The $K_a - K_b$ Relationship; Acid-Base Properties of Salts

16.79 (a) For a conjugate acid/conjugate base pair such as $C_6H_5OH/C_6H_5O^-$, K_b for the conjugate base is always K_w/K_a for the conjugate acid. K_b for the conjugate base can always be calculated from K_a for the conjugate acid, so a separate list of K_b values is not necessary.

(b) $K_b = K_w/K_a = 1.0 \times 10^{-14} \,/\, 1.3 \times 10^{-10} = 7.7 \times 10^{-5}$

(c) K_b for phenolate (7.7×10^{-5}) > K_b for ammonia (1.8×10^{-5}).

Phenolate is a stronger base than NH_3.

16.81 *Analyze/Plan*. Given K_a, determine relative strengths of the acids and their conjugate bases. The greater the magnitude of K_a, the stronger the acid and the weaker the conjugate base. K_b (conjugate base) = K_w/K_a. *Solve*.

(a) Acetic acid is stronger, because it has the larger K_a value.

(b) Hypochlorite ion is the stronger base because the weaker acid, hypochlorous acid, has the stronger conjugate base.

(c) K_b for $CH_3COO^- = K_w/K_a$ for $CH_3COOH = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

K_b for $ClO^- = K_w/K_a$ for $HClO = 1 \times 10^{-14}/3.0 \times 10^{-8} = 3.3 \times 10^{-7}$

Note that K_b for ClO^- is greater than K_b for CH_3COO^-.

16.83 *Analyze*. When the solute in an aqueous solution is a salt, evaluate the acid/base properties of the component ions.

(a) *Plan*. NaCN is a soluble salt and thus a strong electrolyte. When it is dissolved in H_2O, it dissociates completely into Na^+ and CN^-. [NaCN] = [Na^+] = [CN^-] = 0.10 M. Na^+ is the conjugate acid of the strong base NaOH and thus does not influence the pH of the solution. CN^-, on the other hand, is the conjugate base of the weak acid HCN and **does** influence the pH of the solution. Like any other weak base, it hydrolyzes water to produce OH^-(aq). Solve the equilibrium problem to determine [OH^-]. *Solve*.

	$CN^-(aq)$	+ $H_2O(l)$	⇌	HCN(aq)	+	$OH^-(aq)$
initial	0.10 *M*			0		0
equil.	(0.10 – x) *M*			x *M*		x *M*

$$K_b \text{ for } CN^- = \frac{[HCN][OH^-]}{[CN^-]} = \frac{K_w}{K_a \text{ for HCN}} = \frac{1 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5} = 2.0 \times 10^{-5}$$

$$2.04 \times 10^{-5} = \frac{(x)(x)}{(0.10 - x)}; \text{ assume the percent of } CN^- \text{ that hydrolyzes is small}$$

$x^2 = 0.10\ (2.04 \times 10^{-5})$; $x = [OH^-] = 0.00143 = 1.4 \times 10^{-3}\ M$

pOH = 2.85; pH = 14 – 2.85 = 11.15

(b) *Plan*. $Na_2CO_3(aq) \rightarrow 2Na^+(aq) + CO_3^{2-}(aq)$

CO_3^{2-} is the conjugate base of HCO_3^- and its hydrolysis reaction will determine the $[OH^-]$ and pH of the solution (see similar explanation for NaCN in part (a)). We will assume the process $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-$ will not add significantly to the $[OH^-]$ in solution because $[HCO_3^-(aq)]$ is so small. Solve the equilibrium problem for $[OH^-]$. *Solve*.

	$CO_3^{2-}(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$HCO_3^-(aq)$	+ $OH^-(aq)$
initial	0.080 *M*	0	0
equil.	(0.080 – x) *M*	x	x

$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]} = \frac{K_w}{K_a \text{ for } HCO_3^-} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.79 \times 10^{-4} = 1.8 \times 10^{-4}$$

$$1.8 \times 10^{-4} = \frac{x^2}{(0.080 - x)}; x^2 = 0.080(1.79 \times 10^{-4}); x = 0.00378 = 3.8 \times 10^{-3}\ M\ OH^-$$

(Assume x is small compared to 0.080); pOH = 2.42; pH = 14 – 2.42 = 11.58

$$\textit{Check}\ \frac{3.8 \times 10^{-3}\ M\ OH^-}{0.080 M\ CO_3^{2-}} \times 100 = 4.75\%\ \text{hydrolysis; the approximation is valid}$$

(c) *Plan*. For the two salts present, Na^+ and Ca^{2+} are negligible acids. NO_2^- is the conjugate base of HNO_2 and will determine the pH of the solution. *Solve*.

Calculate total $[NO_2^-]$ present initially.

$[NO_2^-]_{total}$ = $[NO_2^-]$ from $NaNO_2$ + $[NO_2^-]$ from $Ca(NO_2)_2$

$[NO_2^-]_{total} = 0.10\ M + 2(0.20\ M) = 0.50\ M$

The hydrolysis equilibrium is:

	$NO_2^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$	HNO_2	+ $OH^-(aq)$
initial	0.50 *M*	0	0
equil.	(0.50 – x) *M*	x *M*	x *M*

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = \frac{K_w}{K_a \text{ for } HNO_2} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.22 \times 10^{-11} = 2.2 \times 10^{-11}$$

$$2.2 \times 10^{-11} = \frac{x^2}{(0.50 - x)} \approx \frac{x^2}{0.50}; x^2 = 0.50\,(2.22 \times 10^{-11})$$

$x = 3.33 \times 10^{-6} = 3.3 \times 10^{-6}\ M\ OH^-$; pOH = 5.48; pH = 14 – 5.48 = 8.52

16.85 *Analyze/Plan*. Given the formula of a salt, predict whether an aqueous solution will be acidic, basic, or neutral. Evaluate the acid-base properties of both ions and determine the overall effect on solution pH. *Solve*.

(a) acidic; NH_4^+ is a weak acid, Br^- is negligible.

(b) acidic; Fe^{3+} is a highly charged metal cation and a Lewis acid; Cl^- is negligible.

(c) basic; CO_3^{2-} is the conjugate base of HCO_3^-; Na^+ is negligible.

(d) neutral; both K^+ and ClO_4^- are negligible.

(e) acidic; $HC_2O_4^-$ is amphoteric, but K_a for the acid dissociation (6.4×10^{-5}) is much greater than K_b for the base hydrolysis ($1.0 \times 10^{-14} / 5.9 \times 10^{-2} = 1.7 \times 10^{-13}$).

16.87 *Plan*. Estimate pH using relative base strength and then calculate to confirm prediction. NaCl is a neutral salt, so it is not the unknown. The unknown is a relatively weak base, because a pH of 8.08 is not very basic. Since F^- is a weaker base than OCl^-, the unknown is probably NaF. Calculate K_b for the unknown from the data provided. *Solve*.

$[OH^-] = 10^{-pOH}$; pOH = 14.00 – pH = 14.00 – 8.08 = 5.92

$[OH^-] = 10^{-5.92} = 1.202 \times 10^{-6} = 1.2 \times 10^{-6}\ M = [HX]$

[NaX] = $[X^-]$ = 0.050 mol salt / 0.500 L = 0.10 *M*

$$K_b = \frac{[OH^-][HX]}{[X^-]} = \frac{(1.202 \times 10^{-6})^2}{(0.10 - 1.2 \times 10^{-6})} = \frac{(1.202 \times 10^{-6})^2}{0.10} = 1.4 \times 10^{-11}$$

K_b for $F^- = K_w / K_a$ for HF = $1.0 \times 10^{-14} / 6.8 \times 10^{-4} = 1.5 \times 10^{-11}$

The unknown is NaF.

16.89 *Analyze/Plan*. The solution will be basic because of the hydrolysis of the sorbate anion, $C_5H_7COO^-$. Calculate the initial molarity of $C_5H_7COO^-$. Calculate K_b from K_w/K_a. Solve the K_b expression for $[OH^-]$. *Solve*.

$$\frac{11.25\text{ g } C_5H_7COOK}{1.75\text{ L}} \times \frac{1\text{ mol } C_5H_7COOK}{150.2\text{ g } KC_6H_7O_2} = 0.04289 = 0.0428\ M\ C_5H_7COOK$$

$[C_5H_7COO^-] = [C_5H_7COOK] = 0.0428\ M$

	$C_5H_7COO^-(aq) + H_2O(l)$	$\rightleftharpoons$	$C_5H_7COOH(aq)$	+	$OH^-(aq)$
initial	0.0428 *M*		0		0
equil.	(0.0428 – x) *M*		x *M*		x *M*

$$K_b = \frac{[C_5H_7COOH][OH^-]}{[C_5H_7COO^-]} = \frac{K_w}{K_a \text{ for } C_5H_7COOK} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10} = 5.9 \times 10^{-10}$$

$$5.88 \times 10^{-10} = \frac{x^2}{0.0428 - x} \approx \frac{x^2}{0.0428};\ x^2 = 0.0428(5.88 \times 10^{-10})$$

$x = [OH^-] = 5.018 \times 10^{-6} = 5.0 \times 10^{-6}\ M$; pOH = 5.30; pH = 14 – pOH = 8.70

Acid-Base Character and Chemical Structure

16.91 (a) As the electronegativity of the central atom (X) increases, more electron density is withdrawn from the X–O and O–H bonds, respectively. In water, the O–H bond is ionized to a greater extent and the strength of the oxyacid increases.

(b) As the number of nonprotonated oxygen atoms in the molecule increases, they withdraw electron density from the other bonds in the molecule and the strength of the oxyacid increases.

16.93 (a) HNO_3 is a stronger acid than HNO_2 because it has one more nonprotonated oxygen atom, and thus a higher oxidation number on N.

(b) For binary hydrides, acid strength increases going down a family, so H_2S is a stronger acid than H_2O.

(c) H_2SO_4 is a stronger acid because H^+ is much more tightly held by the anion HSO_4^-.

(d) For oxyacids, the greater the electronegativity of the central atom, the stronger the acid, so H_2SO_4 is a stronger acid than H_2SeO_4.

(e) CCl_3COOH is stronger because the electronegative Cl atoms withdraw electron density from other parts of the molecule, which weakens the O–H bond and makes H^+ easier to remove. Also, the electronegative Cl delocalizes negative charge on the carboxylate anion. This stabilizes the conjugate base, favoring products in the ionization equilibrium and increasing K_a.

16.95 (a) BrO^- (HClO is the stronger acid due to a more electronegative central atom, so BrO^- is the stronger base.)

(b) BrO^- ($HBrO_2$ has more nonprotonated O atoms and is the stronger acid, so BrO^- is the stronger base.)

(c) HPO_4^{2-} (larger negative charge, greater attraction for H^+)

16.97 (a) True.

(b) False. In a series of acids that have the same central atom, acid strength increases with the number of nonprotonated oxygen atoms bonded to the central atom.

(c) False. H_2Te is a stronger acid than H_2S because the H–Te bond is longer, weaker, and more easily dissociated than the H–S bond.

Lewis Acids and Bases

16.99 Yes. If a substance is an Arrhenius base, it must also be a Brønsted base and a Lewis base. The Arrhenius definition (hydroxide ion) is the most restrictive, the Brønsted (H^+ acceptor) more general and the Lewis (electron pair donor) most general. Since a hydroxide ion is both an H^+ acceptor and an electron pair donor, any substance that fits the narrow Arrhenius definition will fit the broader Brønsted and Lewis definitions.

16.101 *Analyze/Plan*. Identify each reactant as an electron pair donor (Lewis base) or electron pair acceptor (Lewis acid). Remember that a Brønsted acid is necessarily a Lewis acid, and a Brønsted base is necessarily a Lewis base (Solution 16.100). *Solve*.

	Lewis Acid	Lewis Base
(a)	$Fe(ClO_4)_3$ or Fe^{3+}	H_2O
(b)	H_2O	CN^-
(c)	BF_3	$(CH_3)_3N$
(d)	HIO	NH_2^-

16.103 (a) Cu^{2+}, higher cation charge

(b) Fe^{3+}, higher cation charge

(c) Al^{3+}, smaller cation radius, same charge

Additional Exercises

16.105 (a) K_w is the equilibrium constant for the reaction of two water molecules to form hydronium ion and hydroxide ion.

(b) K_a is the equilibrium constant for the reaction of any acid, neutral or ionic, with water to form hydronium ion and the conjugate base of the acid.

(c) pOH is the negative log of hydroxide ion concentration; pOH decreases as hydroxide ion concentration increases.

(d) pK_b is the negative log of K_b; pK_b increases as base strength decreases. The stronger the base, the smaller its pK_b.

16.108 $H_3C_6H_5O_7 + CH_3NH_2 \rightarrow CH_3NH_3^+ + H_2C_6H_5O_7^-$

citric acid methylamine odorless salt

$$H_3C_6H_5O_7 \rightleftharpoons H^+ + H_2C_6H_5O_7^- \qquad K_{a_1} = 7.4 \times 10^{-4}$$

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^- \qquad K_b = 4.4 \times 10^{-4}$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad 1/K_w = 1/1.0 \times 10^{-14}$$

$$H_3C_6H_5O_7 + CH_3NH_2 + H_2O + H^+ + OH^- \rightleftharpoons H_2C_6H_5O_7^- + CH_3NH_3^+ + H^+ + OH^- + H_2O$$

$$H_3C_6H_5O_7 + CH_3NH_2 \rightleftharpoons H_2C_6H_5O_7^- + CH_3NH_3^+$$

$$K = \frac{K_{a_1} \times K_b}{K_w} = \frac{(7.4 \times 10^{-4})(4.4 \times 10^{-4})}{1.0 \times 10^{-14}} = 3.256 \times 10^{7} = 3.3 \times 10^{7}$$

16.111 The solution with the higher pH has the lower $[H^+]$.

(a) For solutions with equal concentrations, the weaker acid will have a lower $[H^+]$ and higher pH.

(b) The acid with $K_a = 8 \times 10^{-6}$ is the weaker acid, so it has the higher pH.

(c) The base with $pK_b = 4.5$ is the stronger base, has greater $[OH^-]$ and smaller $[H^+]$, so higher pH.

16.113 $K_a = \dfrac{[H^+][C_5H_{11}COO^-]}{[C_5H_{11}COOH]}$; $[H^+] = [C_5H_{11}COO^-] = 10^{-pH} = 10^{-2.94} = 0.00114$

$= 1.1 \times 10^{-3}\ M$

$$[C_5H_{11}COOH] = \frac{11\text{ g } C_5H_{11}COOH}{\text{L}} \times \frac{1\text{ mol } C_5H_{11}COOH}{116\text{ g } C_5H_{11}COOH} = 0.0947 - 0.095 M$$

$$K_a = \frac{[H^+][C_5H_{11}COO^-]}{[C_5H_{11}COOH]} = \frac{(0.00114)^2}{(0.0947 - 0.00114)} = 1.4092 \times 10^{-5} = 1.41 \times 10^{-5}$$

16.117 Considering the stepwise dissociation of H_3PO_4:

	$H_3PO_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$H_2PO_4^-(aq)$
initial	0.025		0		0
equil.	$(0.025 - x)\ M$		x		x

$$K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{(0.025 - x)} = 7.5 \times 10^{-3};\ x^2 + 7.5 \times 10^{-3}\,x - 1.875 \times 10^{-4} = 0$$

$$x = \frac{-7.5 \times 10^{-3} \pm \sqrt{(7.5 \times 10^{-3})^2 - 4(1)(-1.875 \times 10^{-4})}}{2(1)} = \frac{-7.5 \times 10^{-3} \pm \sqrt{8.06 \times 10^{-4}}}{2}$$

x = 0.01045 = 0.010 *M* H^+, 0.010 *M* $H_2PO_4^-$ available for further ionization

	$H_2PO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HPO_4^{2-}(aq)$
initial	0.010 *M*		0.010 *M*		0 *M*
equil.	$(0.010 - y)\ M$		$(0.010 + y)\ M$		y *M*

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(y)(0.010 + y)}{(0.010 - y)} = 6.2 \times 10^{-8}$$

Since K_{a2} is very small, assume y is small compared to 0.010 *M*.

$$6.2 \times 10^{-8} = \frac{0.010\,y}{0.010};\ y = [HPO_4^{2-}] = 6.2 \times 10^{-8}\ M$$

$[H_2PO_4^-] = (0.010\ M + 6.2 \times 10^{-8}\ M) = 0.010\ M$

$[H^+] = (0.010\ M - 6.2 \times 10^{-8}\ M) = 0.010\ M$

$[HPO_4^{2-}]$ available for further ionization $= 6.2 \times 10^{-8}\ M$

	HPO_4^{2-}	$\rightleftharpoons$	$H^+(aq)$	+	$PO_4^{3-}(aq)$
initial	$6.2 \times 10^{-8}\ M$		0.010 *M*		0 *M*
equil.	$(6.2 \times 10^{-8} - z)\ M$		$(0.010 + z)\ M$		z *M*

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.010 + z)(z)}{(6.2 \times 10^{-8} - z)} = 4.2 \times 10^{-13}$$

Assuming z is small compared to 6.2×10^{-8} (and 0.010),

$$\frac{(0.010)(z)}{(6.2 \times 10^{-8})} = 4.2 \times 10^{-13}; z = 2.6 \times 10^{-18}\ M\ PO_4^{3-}$$

The contribution of z to $[HPO_4^{2-}]$ and $[H^+]$ is negligible. In summary, after all dissociation steps have reached equilibrium:

$[H^+] = 0.010\ M$, $[H_2PO_4^-] = 0.010\ M$, $[HPO_4^{2-}] = 6.2 \times 10^{-8}\ M$, $[PO_4^{3-}] = 2.6 \times 10^{-18}\ M$

Note that the first ionization step is the major source of H^+ and the others are important as sources of HPO_4^{2-} and PO_4^{3-}. The $[PO_4^{3-}]$ is very small at equilibrium.

Integrative Exercises

16.121 At 25°C, $[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$

$$\frac{1.0 \times 10^{-7}\ \text{mol}\ H^+}{1\ \text{L}\ H_2O} \times 0.0010\ \text{L} \times \frac{6.022 \times 10^{23}\ H^+\ \text{ions}}{\text{mol}\ H^+} = 6.0 \times 10^{13}\ H^+\ \text{ions}$$

16.124 *Analyze*. If pH were directly related to CO_2 concentration, this exercise would be simple. Unfortunately, we must solve the equilibrium problem for the diprotic acid H_2CO_3 to calculate $[H^+]$ and pH. We are given ppm CO_2 in the atmosphere at two different times, and the pH that corresponds to one of these CO_2 levels. We are asked to find pH at the other atmospheric CO_2 level.

Plan. Assume all dissolved CO_2 is present as H_2CO_3 (aq) (Sample Exercise 16.14).

pH $\rightarrow$ $[H^+]$ $\rightarrow$ $[H_2CO_3]$. While H_2CO_3 is a diprotic acid, the two K_a values differ by more than 10^3, so we can ignore the second ionization when calculating $[H_2CO_3]$. Change 380 ppm CO_2 to pressure and calculate the Henry's law constant for CO_2. Calculate the dissolved $[CO_2] = [H_2CO_3]$ at 315 ppm, then solve the K_{a1} expression for $[H^+]$ and pH.

(a) *Solve*. $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$$K_{a1} = 4.3 \times 10^{-7} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}; [H^+] = 10^{-5.4} = 3.98 \times 10^{-6} = 4 \times 10^{-6}\ M$$

$[H^+] = [HCO_3^-]$; $[H_2CO_3] = x - 4 \times 10^{-6}$

$$4.3 \times 10^{-7} = \frac{(3.98 \times 10^{-6})^2}{(x - 3.98 \times 10^{-6})}; 4.3 \times 10^{-7}\,x = 1.585 \times 10^{-11} + 1.712 \times 10^{-12}$$

$x = 1.756 \times 10^{-11} / 4.3 \times 10^{-7} = 4.084 \times 10^{-5} = 4 \times 10^{-5}\ M\ H_2CO_3$

380 ppm = 380 mol CO_2 / 1×10^6 mol air = 0.000380 mol % CO_2

Because of the properties of gases, mol % = pressure %. $P_{CO_2} = 0.000380$ atm.
According to Equation [13.4], $S_{CO_2} = kP_{CO_2}$;

4.084×10^{-5} mol/L $= k(3.80 \times 10^{-4}$ atm) $k = 0.1075 = 0.1$ mol/L-atm.

$$\text{Forty years ago, } S_{CO_2} = 0.1075\frac{\text{mol}}{\text{L-atm}} \times 3.15 \times 10^{-4}\ \text{atm} = 3.385 \times 10^{-5}$$

$$= 3 \times 10^{-5}\ M$$

Now solve K_{a1} for $[H^+]$ at this $[H_2CO_3]$. $[H^+] = x$

We cannot assume x is small, because $[H_2CO_3]$ is so low.

$4.3 \times 10^{-7} = x^2/(3.385 \times 10^{-5} - x)$; $x^2 + 4.3 \times 10^{-7}\,x - 1.456 \times 10^{-11} = 0$

$$x = \frac{-4.3 \times 10^{-7} \pm \sqrt{(4.3 \times 10^{-7})^2 - 4(-1.456 \times 10^{-11})}}{2} = \frac{-4.3 \times 10^{-7} + 7.644 \times 10^{-6}}{2}$$

$$= 3.607 \times 10^{-6} = 4 \times 10^{-6}\ M\ H^+$$

$[H^+] = 4 \times 10^{-6}\ M$, pH = 5.443 = 5.4

(Note that, to the precision that the pH data is reported, the change in atmospheric CO_2 leads to no change in pH.)

(b) From part (a), $[H_2CO_3]$ today = $4.084 \times 10^{-5}\ M$

$$\frac{4.084 \times 10^{-5}\ \text{mol}\ H_2CO_3}{1\ \text{L}} \times 200\ \text{L} = 8.168 \times 10^{-4} = 8 \times 10^{-4}\ \text{mol}\ CO_2$$

$$V = \frac{nRT}{P} = 8.168 \times 10^{-4}\ \text{mol} \times \frac{298\ \text{K}}{1.0\ \text{atm}} \times \frac{0.08206\ \text{L-atm}}{\text{mol-K}} = 0.01997 \approx 0.02\ \text{L} = 20\ \text{mL}$$

16.127 Calculate M of the solution from osmotic pressure, and K_b using the equilibrium expression for the hydrolysis of cocaine. Let Coc = cocaine and $CocH^+$ be the conjugate acid of cocaine.

$$\Pi = MRT;\ M = \Pi/RT = \frac{527\ \text{torr}}{288\ \text{K}} \times \frac{1\ \text{atm}}{760\ \text{torr}} \times \frac{\text{mol-K}}{0.08206\ \text{L-atm}}$$

$$= 0.002934 = 2.93 \times 10^{-3}\ M\ \text{Coc}$$

pH = 8.53; pOH = 14 − pH = 5.47; $[OH^-] = 10^{-5.47} = 3.39 \times 10^{-6} = 3.4 \times 10^{-6}\ M$

	$Coc(aq) + H_2O(l)$	$\rightleftharpoons$	$CocH^+(aq)$	+	$OH^-(aq)$
initial	$2.93 \times 10^{-3}\ M$		0		0
equil.	$(2.93 \times 10^{-3} - 3.4 \times 10^{-6})\ M$		$3.4 \times 10^{-6}\ M$		$3.4 \times 10^{-6}\ M$

$$K_b = \frac{[CocH^+][OH^-]}{[Coc]} = \frac{(3.39 \times 10^{-6})^2}{(2.934 \times 10^{-3} - 3.39 \times 10^{-6})} = 3.9 \times 10^{-9}$$

Note that % hydrolysis is small in this solution, so "x," $3.4 \times 10^{-6}\ M$, is small compared to $2.93 \times 10^{-3}\ M$ and could be ignored in the denominator of the calculation.

16.129 (a) (i) $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ $\quad K_1 = K_{a2}\ \text{for}\ H_2CO_3 = 5.6 \times 10^{-11}$

$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$ $\quad K_2 = 1/K_w = 1 \times 10^{14}$

$HCO_3^-(aq) + OH^-(aq) \rightleftharpoons CO_3^{2-}(aq) + H_2O(l)$ $K = K_1 \times K_2 = 5.6 \times 10^3$

(ii) $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$ $K_1 = K_a \text{ for } NH_4^+ = 5.6 \times 10^{-10}$

$CO_3^{2-}(aq) + H^+(aq) \rightleftharpoons HCO_3^-(aq)$ $K_2 = 1/K_{a2} \text{ for } H_2CO_3 = 1.8 \times 10^{10}$

$NH_4^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + NH_3(aq)$ $K = K_1 \times K_2 = 10$

(b) Both (i) and (ii) have K > 1, although K = 10 is not **much** greater than 1. Both could be written with a single arrow. (This is true in general when a strong acid or strong base, $H^+(aq)$ or $OH^-(aq)$, is a reactant.)