

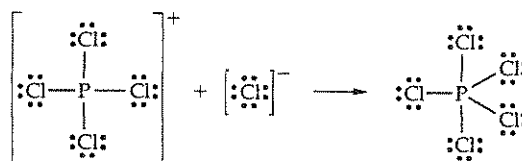
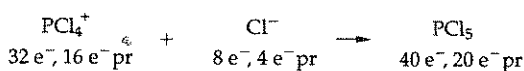
16 Acid-Base Equilibria

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.*
- $H-X$ is a B-L acid, because it loses H^+ during reaction. NH_3 is a B-L base, because it gains H^+ during reaction.
 - 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.
- 16.2 *Plan.* The stronger the acid, the greater the extent of ionization. The stronger the acid, the weaker its conjugate base. In an acid-base reaction, equilibrium will favor the side with the weaker acid and base. *Solve.*
- HY is stronger than HX . Starting with six HY molecules, four are dissociated; of six HX molecules, only two are dissociated. Because it is dissociated to a greater extent, HY is the stronger acid.
 - If HY is the stronger acid, Y^- is the weaker base and X^- is the stronger base.
 - HX and Y^- , the reactants, are the weaker acid and base. Equilibrium lies to the left, and $K_c < 1$.
- 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.*
- HY is a strong acid. There are no neutral HY molecules in solution, only H^+ cations and Y^- anions.
 - HX has the smallest K_a value. It has most neutral acid molecules and fewest ions.
 - HX has the fewest H^+ and highest pH.
- 16.4 *Analyze/Plan.* Consider how K_a and $[HA]$ influence extent of ionization (or percent ionization).
- Solve.* The greater the extent of ionization, the less valid the approximation that x is small relative to $[HA]$. The greater the value of K_a , the stronger the acid, the greater the extent of ionization. On the other hand, the smaller the $[HA]$, the greater the percent ionization. The approximation is then most valid for small K_a and large $[HA]$. Case (a) and (c) have the smaller K_a , with case (c) having the larger initial $[HA]$. The approximation is most valid for case (c).

- 16.5 (a) True. Solution A is the color of methyl orange in acidic solution.
- (b) False. Methyl orange turns yellow at a pH slightly greater than 4, so solution B could be at any pH greater than 4.
- (c) True. The basic color of any indicator occurs at higher pH than the acidic color does.
- 16.6 *Plan.* The definition of percent ionization is $\frac{[\text{H}^+]}{[\text{HA}]_{\text{initial}}} \times 100$. *Solve.*
- (a) Curve C shows the effect of concentration on percent ionization of a weak acid.
- (b) For a weak acid, the percent ionization is inversely related to acid concentration; only curve C shows a decrease in percent ionization as acid concentration increases.
- 16.7 *Analyze/Plan.* Write the formula of each molecule and compare them to the entries in Tables 16.2 and 16.4. Select the molecule that fits the definition of an acid, and the one that fits the definition of a base. *Solve.*
- (a) Molecule A is hydroxyl amine, NH_2OH . It is an entry in Table 16.4. Molecule A is an H^+ acceptor because of the nonbonded electron pair on the N atom of the amine ($-\text{NH}_2$) group, not because it contains an $-\text{OH}$ group. The presence of an $-\text{OH}$ group in an organic molecule does not mean that the molecule is a base.
- (b) Molecule B is formic acid, HCOOH . It is similar to CH_3COOH , an entry in Table 16.2. The H atom bonded to O is ionizable and HCOOH is an H^+ donor. In general, organic molecules that contain a carboxyl ($-\text{COOH}$) group are acids.
- (c) Molecule C is methanol, CH_3OH . In organic molecules, the $-\text{OH}$ functional group is an alcohol. The H atom bonded to O is not ionizable, and the $-\text{OH}$ group does not dissociate in aqueous solution. An alcohol is neither an acid nor a base.
- 16.8 Diagram C best represents an aqueous solution of NaF ; it contains mostly Na^+ and F^- , along with a few HF molecules and OH^- ions. The HF and OH^- are present because F^- is a weak Bronsted base; it accepts H^+ from a water molecule, producing HF and OH^- . The solution is basic because it contains OH^- .
- 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) If X is the same atom on both molecules, the molecule (b) is more acidic. The carboxylate anion, the conjugate base of this carboxylic acid, is stabilized by resonance, while the conjugate base of (a) is not resonance-stabilized. Stabilization of the conjugate base causes the ionization equilibrium to favor products, and (b) is the stronger acid.
- (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.

- 16.10 (a) *Plan.* Count valence electrons and draw the correct Lewis structures. Consider The definition of Lewis acids and bases. *Solve.*



PCl_4^+ accepts an electron pair from Cl^- ; PCl_4^+ is the Lewis acid and Cl^- is the Lewis base.

- (b) The hydrated cation is an oxyacid: the ionizable H is attached to O, which is bound to the central cation. As the charge on the cation increases, it attracts more electron density from the O-H bond, which becomes weaker and more polar. The degree of ionization increases and the equilibrium constant (K_a) increases.

Arrhenius and Brønsted-Lowry Acids and Bases (sections 16.1 and 16.2)

- 16.11 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 $\text{H}_2(\text{g})$ 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 $\text{H}^+(\text{aq})$ 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 $\text{H}^+(\text{aq})$ in excess of $1 \times 10^{-7} \text{ M}$ accounts for all the other listed properties.
- 16.12 When NaOH dissolves in water, it completely dissociates to form $\text{Na}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$. NH_3 is a Brønsted-Lowry base, an H^+ acceptor. When NH_3 dissolves in water, it participates in the equilibrium $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$. Thus, the properties of both solutions are dominated by the presence of $\text{OH}^-(\text{aq})$. Both solutions taste bitter, turn litmus paper blue (are basic), neutralize solutions of acids, and conduct electricity.
- 16.13 (a) According to the Arrhenius definition, an *acid* when dissolved in water increases $[\text{H}^+]$. 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) $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4^+\text{Cl}^-(\text{s})$ 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.
- 16.14 (a) According to the Arrhenius definition, a *base* when dissolved in water increases $[\text{OH}^-]$. According to the Brønsted-Lowry theory, a *base* is an H^+ acceptor regardless of physical state. A Brønsted-Lowry base is not limited to aqueous solution and need not contain OH^- or produce it in aqueous solution.

- (b) Yes, a substance can behave as an Arrhenius base even if it does not contain an OH group. One example is ammonia.

$\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$. When NH_3 dissolves in water, it accepts H^+ from H_2O . In doing so, OH^- is produced and $[\text{OH}^-]$ in the aqueous solution increases. The OH^- produced was originally part of the H_2O molecule, not part of the NH_3 molecule. Other organic amines behave in a similar manner.

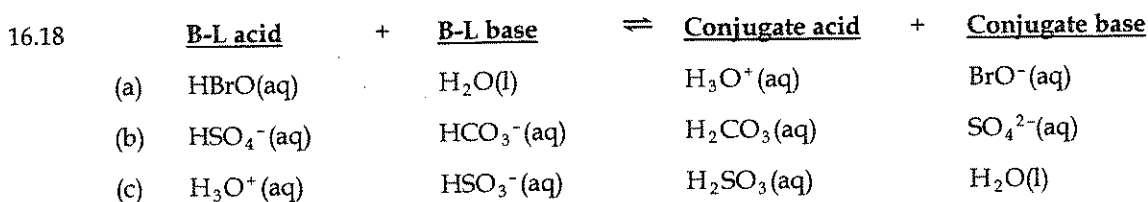
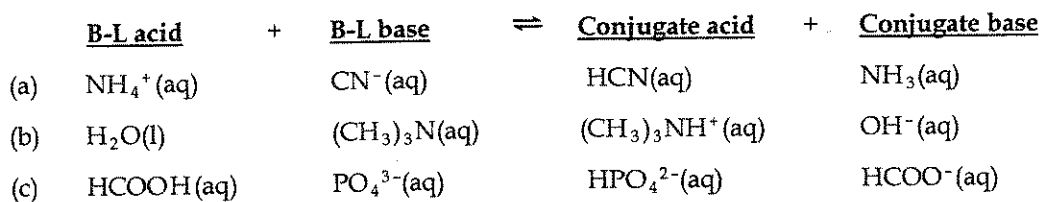
- 16.15 *Analyze/Plan.* Follow the logic in Sample Exercise 16.1. A conjugate base has one less H^+ than its conjugate acid. A conjugate acid has one more H^+ than its conjugate base. *Solve.*

- (a) (i) IO_3^- (ii) NH_3
 (b) (i) OH^- (ii) H_3PO_4

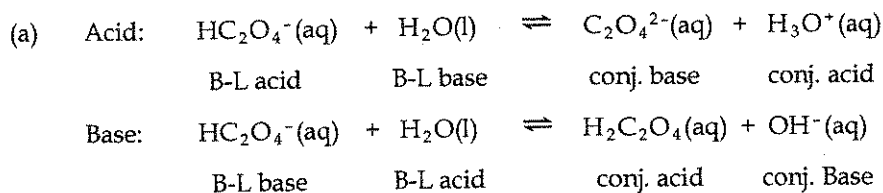
- 16.16 A conjugate base has one less H^+ than its conjugate acid. A conjugate acid has one more H^+ than its conjugate base.

- (a) (i) HCOO^- (ii) PO_4^{3-}
 (b) (i) HSO_4^- (ii) CH_3NH_3^+

- 16.17 *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.*

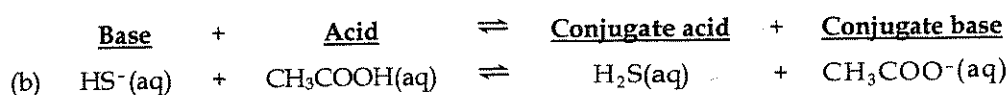


- 16.19 *Analyze/Plan.* Follow the logic in Sample Exercise 16.2. *Solve.*



- (b) $\text{H}_2\text{C}_2\text{O}_4$ is the conjugate acid of HC_2O_4^- .
 $\text{C}_2\text{O}_4^{2-}$ is the conjugate base of HC_2O_4^- .

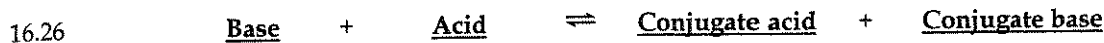
- 16.20 (a) $\text{H}_2\text{C}_6\text{H}_7\text{O}_5^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{C}_6\text{H}_7\text{O}_5(\text{aq}) + \text{OH}^-(\text{aq})$
 (b) $\text{H}_2\text{C}_6\text{H}_7\text{O}_5^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_6\text{H}_7\text{O}_5^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
 (c) $\text{H}_3\text{C}_6\text{H}_7\text{O}_5$ is the conjugate acid of $\text{H}_2\text{C}_6\text{H}_7\text{O}_5^-$
 $\text{HC}_6\text{H}_7\text{O}_5^{2-}$ is the conjugate base of $\text{H}_2\text{C}_6\text{H}_7\text{O}_5^-$
- 16.21 *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 16.3. 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
- 16.22 Based on the chemical formula, decide whether the acid is strong, weak, or negligible. Is it one of the known seven strong acids (Section 16.5)? Also check Figure 16.3. Remove a single H and decrease the particle charge by one to write the formula of the conjugate base. *Solve.*
- (a) HCOOH , weak acid; HCOO^- , weak base
 (b) H_2 , negligible acid; H^- , strong base
 (c) CH_4 , negligible acid; CH_3^- , strong base
 (d) HF , weak acid; F^- , weak base
 (e) NH_4^+ , weak acid; NH_3 , weak base
- 16.23 *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.
- 16.24 (a) HClO_3 . It is one of the seven strong acids (Section 16.5). Also, in a series of oxyacids with the same central atom (Cl), the acid with more O atoms is stronger (Section 16.10).
 (b) HS^- . H_2SO_4 is a stronger acid than H_2S , so HS^- is the stronger conjugate base. In fact, since H_2SO_4 is one of the seven strong acids, HSO_4^- is a negligible base.
- 16.25 *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.*
- | <u>Base</u> | + | <u>Acid</u> | \rightleftharpoons | <u>Conjugate acid</u> | + | <u>Conjugate base</u> |
|--------------------------------|---|--------------------------------|----------------------|--------------------------|---|--------------------------|
| (a) $\text{O}^{2-}(\text{aq})$ | + | $\text{H}_2\text{O}(\text{l})$ | \rightleftharpoons | $\text{OH}^-(\text{aq})$ | + | $\text{OH}^-(\text{aq})$ |
- H_2O is a stronger acid than OH^- , so the equilibrium lies to the right.



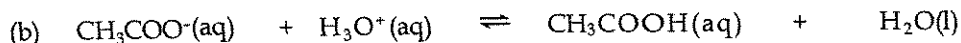
CH_3COOH is a stronger acid than H_2S , so the equilibrium lies to the right.



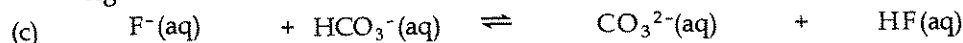
HNO_2 is a stronger acid than H_2O , so the equilibrium lies to the left.



OH^- is a stronger base than NH_3 (Figure 16.3), so the equilibrium lies to the right.



H_3O^+ is a stronger acid than $\text{HC}_2\text{H}_3\text{O}_2$ (Figure 16.3), so the equilibrium lies to the right.

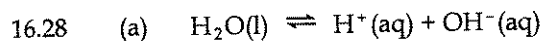


CO_3^{2-} is a stronger base than F^- , so the equilibrium lies to the left.

Autoionization of Water (section 16.3)

16.27 No. In pure water, the only source of H^+ is the autoionization reaction, which produces equal concentrations of H^+ and OH^- . As the temperature of water changes, the value of K_w changes, and the pH at which $[\text{H}^+] = [\text{OH}^-]$ changes. At 50°C , if $\text{pH} = 6.63$,

$$[\text{H}^+] = [\text{OH}^-] = 10^{-6.63} = 2.34 \times 10^{-7}; K_w = (2.34 \times 10^{-7})(2.34 \times 10^{-7}) = 5.5 \times 10^{-14}$$



(b) $K_w = [\text{H}^+][\text{OH}^-]$. The $[\text{H}_2\text{O}(\text{l})]$ is omitted because water is a pure liquid. The molarity (mol/L) of pure solids or liquids does not change as equilibrium is established, so it is usually omitted from equilibrium expressions.

(c) If a solution is basic, it contains more OH^- than H^+ ($[\text{OH}^-] > [\text{H}^+]$).

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

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

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

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

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

16.30 In pure water at 25°C , $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$. If $[\text{OH}^-] > 1 \times 10^{-7} \text{ M}$, the solution is basic; if $[\text{OH}^-] < 1 \times 10^{-7} \text{ M}$, the solution is acidic.

(a)
$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{0.0505 \text{ M}} = 1.98 \times 10^{-13} \text{ M} < 1 \times 10^{-7} \text{ M}; \text{ acidic}$$

$$(b) \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-10} \text{ M}} = 4.0 \times 10^{-5} \text{ M} > 1 \times 10^{-7} \text{ M}; \text{ basic}$$

$$(c) \quad [\text{H}^+] = 1000[\text{OH}^-]; K_w = 1000[\text{OH}^-][\text{OH}^-] = 1000[\text{OH}^-]^2$$

$$[\text{OH}^-] = (K_w/1000)^{1/2} = 3.2 \times 10^{-9} \text{ M} < 1 \times 10^{-7} \text{ M}; \text{ acidic}$$

16.31 *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.*

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

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

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

16.32 $K_w = [\text{D}^+][\text{OD}^-]$; for pure D_2O , $[\text{D}^+] = [\text{OD}^-]$; $8.9 \times 10^{-16} = [\text{D}^+]^2$;

$$[\text{D}^+] = [\text{OD}^-] = 3.0 \times 10^{-8} \text{ M}$$

The pH Scale (section 16.4)

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

$$\Delta\text{pH} = \text{pH}_2 - \text{pH}_1 = -(\log[\text{H}^+]_2 - \log[\text{H}^+]_1) = -\log \frac{[\text{H}^+]_2}{[\text{H}^+]_1} = \pm 1. \text{ The antilog of } +1 \text{ is } 10;$$

the antilog of -1 is 1×10^{-1} . Thus, a ΔpH of one unit represents an increase or decrease in $[\text{H}^+]$ by a factor of 10. *Solve.*

(a) $\Delta\text{pH} = \pm 2.00$ is a change of $10^{2.00}$; $[\text{H}^+]$ changes by a factor of 100.

(b) $\Delta\text{pH} = \pm 0.5$ is a change of $10^{0.50}$; $[\text{H}^+]$ changes by a factor of 3.2.

16.34 $[\text{H}^+]_A = 250 [\text{H}^+]_B$ From Solution 16.33, $\Delta\text{pH} = -\log \frac{[\text{H}^+]_B}{[\text{H}^+]_A}$

$$\Delta\text{pH} = -\log \frac{[\text{H}^+]_B}{250 [\text{H}^+]_B} = -\log \left(\frac{1}{250} \right) = 2.40$$

The pH of solution A is 2.40 pH units lower than the pH of solution B, because $[\text{H}^+]_A$ is 250 times greater than $[\text{H}^+]_B$. The greater $[\text{H}^+]$, the lower the pH of the solution.

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

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

$$\text{By calculation: } \text{pH} = -\log[\text{H}^+] = -\log(6 \times 10^{-4} \text{ M}) = 3.2$$

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

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

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

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

By calculation: $\text{pOH} = 14.0 - 5.2 = 8.8$

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

- 16.36 (a) $K_w = [\text{H}^+][\text{OH}^-]$. If HNO_3 is added to water, it ionizes to form H^+ (aq) and NO_3^- (aq). This increases $[\text{H}^+]$ and necessarily decreases $[\text{OH}^-]$. When $[\text{H}^+]$ increases, pH decreases.
- (b) On Figure 16.5, $1.4 \times 10^{-2} \text{ M OH}^-$ is between $\text{pH} = 12$ ($1 \times 10^{-2} \text{ M OH}^-$) and $\text{pH} = 13$ ($1 \times 10^{-1} \text{ M OH}^-$), slightly higher than $\text{pH} = 12$, so we estimate $\text{pH} = 12.1$. If $\text{pH} > 7$, the solution is basic.
- (c) $\text{pH} = 6.6$ is midway between $\text{pH} = 6$ and $\text{pH} = 7$ on Figure 16.5.
 At $\text{pH} = 7$, $[\text{H}^+] = 1 \times 10^{-7}$; at $\text{pH} = 6$, $[\text{H}^+] = 1 \times 10^{-6} = 10 \times 10^{-7}$.
 A reasonable estimate is $5 \times 10^{-7} \text{ M H}^+$. By calculation:
 $\text{pH} = 6.6$, $[\text{H}^+] = 10^{-\text{pH}} = 10^{-6.6} = 3 \times 10^{-7}$
 At $\text{pH} = 6$, $[\text{OH}^-] = 1 \times 10^{-8}$; at $\text{pH} = 7$, $[\text{OH}^-] = 1 \times 10^{-7} = 10 \times 10^{-8}$.
 A reasonable estimate is $5 \times 10^{-8} \text{ M OH}^-$. By calculation:
 $\text{pOH} = 14.0 - 6.6 = 7.4$; $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-7.4} = 4 \times 10^{-8} \text{ M OH}^-$.

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

$[\text{H}^+]$	$[\text{OH}^-]$	pH	pOH	acidic or basic
$7.5 \times 10^{-3} \text{ M}$	$1.3 \times 10^{-12} \text{ M}$	2.12	11.88	acidic
$2.8 \times 10^{-5} \text{ M}$	$3.6 \times 10^{-10} \text{ M}$	4.56	9.44	acidic
$5.6 \times 10^{-9} \text{ M}$	$1.8 \times 10^{-6} \text{ M}$	8.25	5.75	basic
$5.0 \times 10^{-9} \text{ M}$	$2.0 \times 10^{-6} \text{ M}$	8.30	5.70	basic

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

16.38

pH	pOH	$[\text{H}^+]$	$[\text{OH}^-]$	acidic or basic
5.25	8.75	$5.6 \times 10^{-6} \text{ M}$	$1.8 \times 10^{-9} \text{ M}$	acidic
11.98	2.02	$1.1 \times 10^{-12} \text{ M}$	$9.6 \times 10^{-3} \text{ M}$	basic
9.36	4.64	$4.4 \times 10^{-10} \text{ M}$	$2.3 \times 10^{-5} \text{ M}$	basic
12.93	1.07	$1.2 \times 10^{-13} \text{ M}$	$8.5 \times 10^{-2} \text{ M}$	basic

- 16.39 *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 $37^\circ C$, $pH + pOH = -\log(2.4 \times 10^{-14})$
- $pH + pOH = 13.62$; $pOH = 13.62 - 7.40 = 6.22$
- $[OH^-] = 10^{-pOH} = 10^{-6.22} = 6.0 \times 10^{-7} M$
- 16.40 The pH ranges from 5.2–5.6; pOH ranges from $(14.0-5.2 =) 8.8$ to $(14.0-5.6 =) 8.4$.
- $[H^+] = 10^{-pH}$, $[OH^-] = 10^{-pOH}$
- $[H^+] = 10^{-5.2} = 6.31 \times 10^{-6} = 6 \times 10^{-6} M$; $[H^+] = 10^{-5.6} = 2.51 \times 10^{-6} = 3 \times 10^{-6} M$
- The range of $[H^+]$ is $6 \times 10^{-6} M$ to $3 \times 10^{-6} M$.
- $[OH^-] = 10^{-8.8} = 1.58 \times 10^{-9} = 2 \times 10^{-9} M$; $[OH^-] = 10^{-8.4} = 3.98 \times 10^{-9} = 4 \times 10^{-9} M$.
- The range of $[OH^-]$ is $2 \times 10^{-9} M$ to $4 \times 10^{-9} M$.
- (The pH has one decimal place, so concentrations are reported to one sig fig.)

Strong Acids and Bases (section 16.5)

- 16.41 (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
- 16.42 (a) A strong base is completely dissociated in aqueous solution; a strong base is a strong electrolyte.
- (b) $Sr(OH)_2$ is a soluble strong base.
- $Sr(OH)_2(aq) \rightarrow Sr^{2+}(aq) + 2OH^-(aq)$
- $0.035 M Sr(OH)_2(aq) = 0.070 M OH^-$
- (c) False. Base strength should not be confused with solubility. Base strength describes the tendency of a dissolved molecule (formula unit for ionic compounds such as $Mg(OH)_2$) to dissociate into cations and hydroxide ions. $Mg(OH)_2$ is a strong base because each $Mg(OH)_2$ unit that dissolves also dissociates into $Mg^{2+}(aq)$ and $OH^-(aq)$. $Mg(OH)_2$ is not very soluble, so relatively few $Mg(OH)_2$ units dissolve when the solid compound is added to water.
- 16.43 *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) $8.5 \times 10^{-3} \text{ M HBr} = 8.5 \times 10^{-3} \text{ M H}^+$; $\text{pH} = -\log(8.5 \times 10^{-3}) = 2.07$

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

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

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

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

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

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

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

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

$$\text{pH} = -\log(0.1667 \text{ M}) = 0.778$$

16.44 For a strong acid, which is completely ionized, $[\text{H}^+] =$ the initial acid concentration.

(a) $0.0167 \text{ M HNO}_3 = 0.0167 \text{ M H}^+$; $\text{pH} = -\log(0.0167) = 1.777$

(b) $\frac{0.225 \text{ g HClO}_3}{2.00 \text{ L soln}} \times \frac{1 \text{ mol HClO}_3}{84.46 \text{ g HClO}_3} = 1.332 \times 10^{-3} = 1.33 \times 10^{-3} \text{ M HClO}_3$

$$[\text{H}^+] = 1.33 \times 10^{-3} \text{ M}; \text{pH} = -\log(1.332 \times 10^{-3}) = 2.875$$

(c) $M_c \times V_c = M_d \times V_d$; $0.500 \text{ L} = 500 \text{ mL}$

$$1.00 \text{ M HCl} \times 15.00 \text{ mL HCl} = M_d \text{ HCl} \times 500 \text{ mL HCl}$$

$$M_d \text{ HCl} = \frac{1.00 \text{ M} \times 15.00 \text{ mL}}{500 \text{ mL}} = 3.00 \times 10^{-2} \text{ M HCl} = 3.00 \times 10^{-2} \text{ M H}^+$$

$$\text{pH} = -\log(3.00 \times 10^{-2}) = 1.523$$

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

$$[\text{H}^+]_{\text{total}} = \frac{(0.020 \text{ M HCl} \times 0.0500 \text{ L}) + (0.010 \text{ M HI} \times 0.125 \text{ L})}{0.175 \text{ L}}$$

$$[\text{H}^+]_{\text{total}} = \frac{1.0 \times 10^{-3} \text{ mol H}^+ + 1.25 \times 10^{-3} \text{ mol H}^+}{0.175 \text{ L}} = 0.01286 = 0.013 \text{ M}$$

$$\text{pH} = -\log(0.01286) = 1.89$$

16.45 *Analyze/Plan.* Follow the logic in Sample Exercise 16.9. Strong bases dissociate completely upon dissolving. $\text{pOH} = -\log[\text{OH}^-]$; $\text{pH} = 14 - \text{pOH}$.

(a) Pay attention to the formula of the base to get $[\text{OH}^-]$. *Solve.*

$$[\text{OH}^-] = 2[\text{Sr}(\text{OH})_2] = 2(1.5 \times 10^{-3} \text{ M}) = 3.0 \times 10^{-3} \text{ M OH}^- \text{ (see Exercise 16.42(b))}$$

$$\text{pOH} = -\log(3.0 \times 10^{-3}) = 2.52; \text{pH} = 14 - \text{pOH} = 11.48$$

- (b) mol/LiOH = g LiOH/molar mass LiOH. $[\text{OH}^-] = [\text{LiOH}]$. *Solve.*

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

$$\text{pOH} = -\log(0.37581) = 0.4250; \text{pH} = 14 - \text{pOH} = 13.5750$$

- (c) Use the dilution formula to get the $[\text{NaOH}] = [\text{OH}^-]$. *Solve.*

$$M_c \times V_c = M_d \times V_d; 0.175 \text{ M} \times 0.00100 \text{ L} = ? \text{ M} \times 2.00 \text{ L}$$

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

$$\text{pOH} = -\log(8.75 \times 10^{-5}) = 4.058; \text{pH} = 14 - \text{pOH} = 9.942$$

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

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

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

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

$$\text{pOH} = -\log(0.16875) = 0.77; \text{pH} = 14 - \text{pOH} = 13.23$$

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

- 16.46 For a strong base, which is completely dissociated, $[\text{OH}^-]$ = the initial base concentration. Then, $\text{pOH} = -\log [\text{OH}^-]$ and $\text{pH} = 14 - \text{pOH}$.

- (a) $0.182 \text{ M KOH} = 0.182 \text{ M OH}^-$; $\text{pOH} = -\log(0.182) = 0.740$; $\text{pH} = 14 - 0.740 = 13.260$

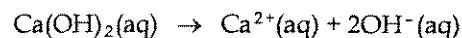
- (b) $\frac{3.165 \text{ g KOH}}{0.5000 \text{ L}} \times \frac{1 \text{ mol KOH}}{56.106 \text{ g KOH}} = 0.112822 = 0.1128 \text{ M} = [\text{OH}^-]$

$$\text{pOH} = -\log(0.112822) = 0.9476; \text{pH} = 14 - \text{pOH} = 13.0524$$

- (c) $M_c \times V_c = M_d \times V_d$

$$0.0105 \text{ M Ca}(\text{OH})_2 \times 10.0 \text{ mL} = M_d \text{ Ca}(\text{OH})_2 \times 500 \text{ mL}$$

$$M_d \text{ Ca}(\text{OH})_2 = \frac{0.0105 \text{ M Ca}(\text{OH})_2 \times 10.0 \text{ mL}}{500.0 \text{ mL}} = 2.10 \times 10^{-4} \text{ M Ca}(\text{OH})_2$$



$$[\text{OH}^-] = 2[\text{Ca}(\text{OH})_2] = 2(2.10 \times 10^{-4} \text{ M}) = 4.20 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log(4.20 \times 10^{-4}) = 3.377; \text{pH} = 14 - \text{pOH} = 10.623$$

$$(d) \quad [\text{OH}^-]_{\text{total}} = \frac{\text{mol OH}^- \text{ from NaOH} + \text{mol OH}^- \text{ from Ba(OH)}_2}{\text{total L solution}}$$

$$\frac{(8.2 \times 10^{-3} \text{ M} \times 0.0400 \text{ L}) + 2(0.015 \text{ M} \times 0.0200 \text{ L})}{0.0600 \text{ L}}$$

$$[\text{OH}^-]_{\text{total}} = \frac{3.28 \times 10^{-4} \text{ mol OH}^- + 6.0 \times 10^{-4} \text{ mol OH}^-}{0.0600 \text{ L}} = 0.01547 = 0.015 \text{ M OH}^-$$

$$\text{pOH} = -\log(0.01547) = 1.81; \text{pH} = 14 - 1.81 = 12.19$$

16.47 *Analyze/Plan.* pH \rightarrow pOH \rightarrow $[\text{OH}^-] = [\text{NaOH}]$. *Solve.*

$$\text{pOH} = 14 - \text{pH} = 14.00 - 11.50 = 2.50$$

$$\text{pOH} = 2.50 = -\log[\text{OH}^-]; [\text{OH}^-] = 10^{-2.50} = 3.2 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = [\text{NaOH}] = 3.2 \times 10^{-3} \text{ M}$$

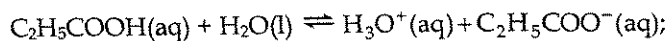
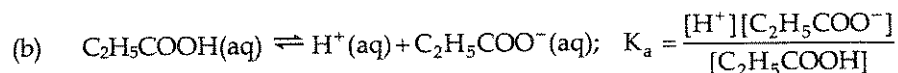
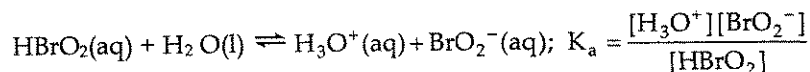
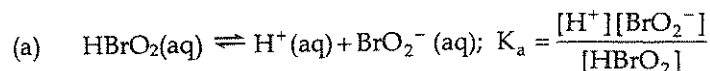
16.48 $\text{pOH} = 14 - \text{pH} = 14.00 - 10.05 = 3.95$

$$\text{pOH} = 3.95 = -\log[\text{OH}^-]; [\text{OH}^-] = 10^{-3.95} = 1.122 \times 10^{-4} \text{ M} = 1.1 \times 10^{-4} \text{ M}$$

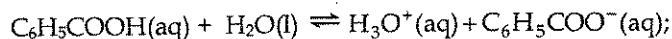
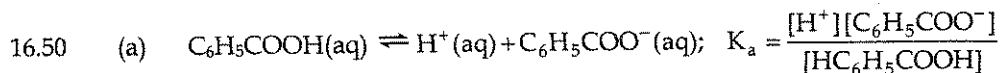
$$[\text{OH}^-] = 2[\text{Ca(OH)}_2]; [\text{Ca(OH)}_2] = [\text{OH}^-] / 2 = 1.122 \times 10^{-4} \text{ M} / 2 = 5.6 \times 10^{-5} \text{ M}$$

Weak Acids (section 16.6)

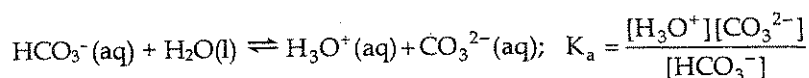
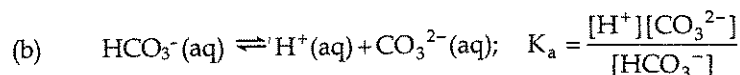
16.49 *Analyze/Plan.* Remember that $K_a = [\text{products}]/[\text{reactants}]$. If $\text{H}_2\text{O}(\text{l})$ appears in the equilibrium reaction, it will **not** appear in the K_a expression, because it is a pure liquid. *Solve.*



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$



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



$$[\text{H}^+] = [\text{CH}_3\text{CH}(\text{OH})\text{COO}^-] = 10^{-2.44} = 3.63 \times 10^{-3} = 3.6 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{CH}(\text{OH})\text{COOH}] = 0.10 - 3.63 \times 10^{-3} = 0.0964 = 0.096 \text{ M}$$

$$K_a = \frac{(3.63 \times 10^{-3})^2}{(0.0964)} = 1.4 \times 10^{-4}$$

16.52 $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_6\text{H}_5\text{CH}_2\text{COO}^-(\text{aq}); K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{CH}_2\text{COO}^-]}{[\text{C}_6\text{H}_5\text{CH}_2\text{COOH}]}$

$$[\text{H}^+] = [\text{C}_6\text{H}_5\text{CH}_2\text{COO}^-] = 10^{-2.68} = 2.09 \times 10^{-3} = 2.1 \times 10^{-3} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{CH}_2\text{COOH}] = 0.085 - 2.09 \times 10^{-3} = 0.0829 = 0.083 \text{ M}$$

$$K_a = \frac{(2.09 \times 10^{-3})^2}{0.0829} = 5.3 \times 10^{-5}$$

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

$$[\text{H}^+] = 0.110 \times [\text{CH}_2\text{ClCOOH}]_{\text{initial}} = 0.0110 \text{ M}$$

	$\text{CH}_2\text{ClCOOH}(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{CH}_2\text{ClCOO}^-(\text{aq})$
initial	0.100 M		0		0
equil.	0.089 M		0.0110 M		0.0110 M

$$K_a = \frac{[\text{H}^+][\text{CH}_2\text{ClCOO}^-]}{[\text{CH}_2\text{ClCOOH}]} = \frac{(0.0110)^2}{0.089} = 1.4 \times 10^{-3}$$

16.54 $[\text{H}^+] = 0.132 \times [\text{BrCH}_2\text{COOH}]_{\text{initial}} = 0.0132 \text{ M}$

	$\text{BrCH}_2\text{COOH}(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{BrCH}_2\text{COO}^-(\text{aq})$
initial	0.100 M		0		0
equil.	0.087		0.0132 M		0.0132 M

$$K_a = \frac{[\text{H}^+][\text{BrCH}_2\text{COO}^-]}{[\text{BrCH}_2\text{COOH}]} = \frac{(0.0132)^2}{0.087} = 2.0 \times 10^{-3}$$

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

$$[\text{H}^+] = 10^{-\text{pH}} = [\text{CH}_3\text{COO}^-]; [\text{CH}_3\text{COOH}] = x - [\text{H}^+].$$

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

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

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(1.26 \times 10^{-3})^2}{(x - 1.26 \times 10^{-3})}$$

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

$$1.8 \times 10^{-5} x = 1.585 \times 10^{-6} + 2.266 \times 10^{-8} = 1.608 \times 10^{-6};$$

$$x = 0.08931 = 0.089 \text{ M CH}_3\text{COOH}$$

16.56 $[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.65} = 2.239 \times 10^{-4} = 2.2 \times 10^{-4} \text{ M}$

$$K_a = 6.8 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(2.239 \times 10^{-4})^2}{x - 2.239 \times 10^{-4}}$$

$$6.8 \times 10^{-4} (x - 2.239 \times 10^{-4}) = (2.239 \times 10^{-4})^2;$$

$$6.8 \times 10^{-4} x = 1.522 \times 10^{-7} + 0.501 \times 10^{-7} = 2.024 \times 10^{-7}$$

$$x = 2.976 \times 10^{-4} = 3.0 \times 10^{-4} \text{ M HF}$$

16.57 *Analyze/Plan.* Follow the logic in Sample Exercise 16.12. Write K_a , construct the equilibrium table, solve for $x = [\text{H}^+]$, then get equilibrium $[\text{C}_6\text{H}_5\text{COO}^-]$ and $[\text{C}_6\text{H}_5\text{COOH}]$ by substituting $[\text{H}^+]$ for x . *Solve.*

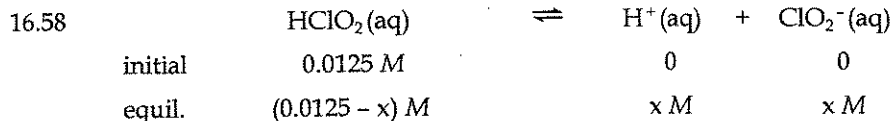


$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{x^2}{(0.050 - x)} \approx \frac{x^2}{0.050} = 6.3 \times 10^{-5}$$

$$x^2 = 0.050 (6.3 \times 10^{-5}); x = 1.8 \times 10^{-3} \text{ M} = [\text{H}^+] = [\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\text{COO}^-]$$

$$[\text{C}_6\text{H}_5\text{COOH}] = 0.050 - 0.0018 = 0.048 \text{ M}$$

Check. $\frac{1.8 \times 10^{-3} \text{ M H}^+}{0.050 \text{ M C}_6\text{H}_5\text{COOH}} \times 100 = 3.6\% \text{ ionization; the approximation is valid}$



$$K_a = \frac{[\text{H}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} = \frac{x^2}{(0.0125 - x)} \approx \frac{x^2}{0.0125} = 1.1 \times 10^{-2}$$

Assuming x is small relative to 0.0125, $x^2 = 0.0125(0.011)$; $x = 1.2 \times 10^{-2} \text{ M}$.

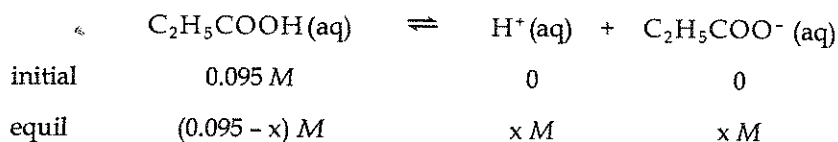
Clearly x is not small relative to 0.0125, so we must solve the quadratic formula for $[\text{H}^+]$.

$$x^2 = 0.011 (0.0125 - x); x^2 + 0.011x - 1.38 \times 10^{-4} = 0$$

$$x = \frac{-0.011 \pm \sqrt{(0.011)^2 - 4(1)(-1.38 \times 10^{-4})}}{2(1)} = 0.007452 = 0.0075 \text{ M};$$

$$[\text{H}^+] = [\text{H}_3\text{O}^+] = [\text{ClO}_2^-] = 0.0075 \text{ M}; [\text{HClO}_2] = 0.0125 - 0.0075 = 0.005045 = 5.0 \times 10^{-3} \text{ M}$$

Check. $K_a = \frac{(7.5 \times 10^{-3})^2}{5.0 \times 10^{-3}} = 0.011$; our results agree.

16.59 *Analyze/Plan.* Follow the logic in Sample Exercise 16.12.(a) *Solve.*

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} = \frac{x^2}{(0.095 - x)} \approx \frac{x^2}{0.095} = 1.3 \times 10^{-5}$$

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

$$\text{Check. } \frac{1.1 \times 10^{-3} \text{ M H}^+}{0.095 \text{ M C}_2\text{H}_5\text{COOH}} \times 100 = 1.2\% \text{ ionization; the approximation is valid}$$

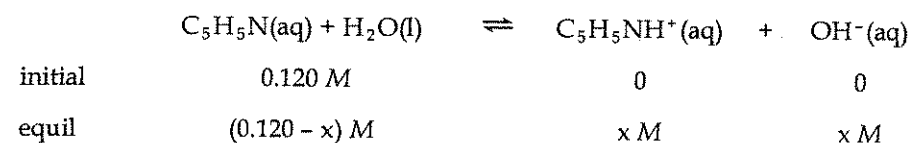
(b) *Solve.*

$$K_a = \frac{[\text{H}^+][\text{CrO}_4^{2-}]}{[\text{HCrO}_4^-]} = \frac{x^2}{(0.100 - x)} \approx \frac{x^2}{0.100} = 3.0 \times 10^{-7}$$

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

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

$$\text{Check. } \frac{1.7 \times 10^{-4} \text{ M H}^+}{0.100 \text{ M HCrO}_4^-} \times 100 = 0.17\% \text{ ionization; the approximation is valid}$$

(c) Follow the logic in Sample Exercise 16.15. $\text{pOH} = -\log[\text{OH}^-]$. $\text{pH} = 14 - \text{pOH}$ *Solve.*

$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = \frac{x^2}{(0.120 - x)} \approx \frac{x^2}{0.120} = 1.7 \times 10^{-9}$$

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

$$\text{Check. } \frac{1.4 \times 10^{-5} \text{ M OH}^-}{0.120 \text{ M C}_5\text{H}_5\text{N}} \times 100 = 0.012\% \text{ ionization; the approximation is valid}$$

16.60 (a)

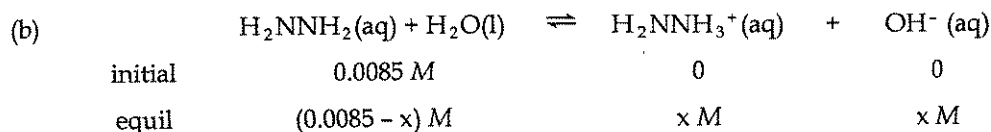


$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{x^2}{(0.095 - x)} \approx \frac{x^2}{0.095} = 3.0 \times 10^{-8}$$

$$x^2 = 0.095(3.0 \times 10^{-8}); x = [\text{H}^+] = 5.3 \times 10^{-5} \text{ M, pH} = 4.27$$

Check. $\frac{5.3 \times 10^{-5} M H^+}{0.095 M HOCl} \times 100 = 0.056\%$ ionization; the approximation is nearly valid.

To 2 sig figs, the quadratic formula gives the same $M H^+$.



$$K_b = \frac{[H_2NNH_3^+][OH^-]}{[H_2NNH_2]} = \frac{x^2}{(0.0085 - x)} \approx \frac{x^2}{0.0085} = 1.3 \times 10^{-6}$$

$$x^2 = 0.0085 (1.3 \times 10^{-6}); x = [OH^-] = 1.051 \times 10^{-4} = 1.1 \times 10^{-4} M$$

Clearly $1.1 \times 10^{-4} M OH^-$ is not small compared to $8.5 \times 10^{-3} M H_2NNH_2$, and we must solve the quadratic.

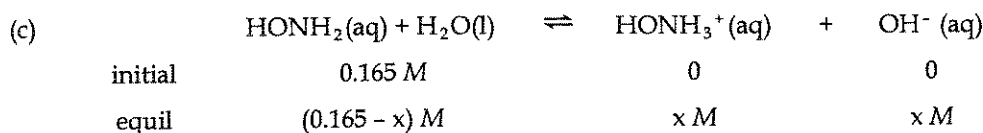
$$x^2 = 1.3 \times 10^{-6} (0.0085 - x); x^2 + 1.3 \times 10^{-6} x - 1.105 \times 10^{-8} = 0$$

$$x = \frac{-1.3 \times 10^{-6} \pm \sqrt{(1.3 \times 10^{-6})^2 - 4(1)(-1.105 \times 10^{-8})}}{2(1)} = 1.0447 \times 10^{-4}$$

$$= 1.0 \times 10^{-4} M OH^-$$

$$pOH = 3.981 = 3.98; pH = 14 - pOH = 14 - 3.981 = 10.019 = 10.02$$

Check. Although this solution has more than 12% ionization, the difference in $[OH^-]$ between the estimate and the quadratic is not great.



$$K_b = \frac{[HONH_3^+][OH^-]}{[HONH_2]} = \frac{x^2}{(0.165 - x)} \approx \frac{x^2}{0.165} = 1.1 \times 10^{-8}$$

$$x^2 = 0.165 (1.1 \times 10^{-8}); x = [OH^-] = 4.3 \times 10^{-5} M, pH = 9.63$$

Check. $\frac{4.3 \times 10^{-5} M OH^-}{0.165 M HONH_2} \times 100 = 0.026\%$ ionization; the approximation is valid

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

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

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

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

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

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

16.62 Calculate the initial concentration of $\text{HC}_9\text{H}_7\text{O}_4$.

$$2 \text{ tablets} \times \frac{500 \text{ mg}}{\text{tablet}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol HC}_9\text{H}_7\text{O}_4}{180.2 \text{ g HC}_9\text{H}_7\text{O}_4} = 0.005549 = 0.00555 \text{ mol HC}_9\text{H}_7\text{O}_4$$

$$\frac{0.005549 \text{ mol HC}_9\text{H}_7\text{O}_4}{0.250 \text{ L}} = 0.02220 = 0.0222 \text{ M HC}_9\text{H}_7\text{O}_4$$

	$\text{HC}_9\text{H}_7\text{O}_4 \text{ (aq)}$	\rightleftharpoons	$\text{C}_9\text{H}_7\text{O}_4^- +$	$\text{H}^+ \text{ (aq)}$
Initial	0.0222 M		0 M	0 M
equil	(0.0222 - x)		x M	x M

$$K_a = 3.3 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]} = \frac{x^2}{(0.0222 - x)}$$

Assuming x is small compared to 0.0222,

$$x^2 = 0.0222 (3.3 \times 10^{-4}); x = [\text{H}^+] = 2.7 \times 10^{-3} \text{ M}$$

$$\frac{2.7 \times 10^{-3} \text{ M H}^+}{0.0222 \text{ M HC}_9\text{H}_7\text{O}_4} \times 100 = 12\% \text{ ionization; the approximation is not valid}$$

Using the quadratic formula, $x^2 + 3.3 \times 10^{-4} x - 7.325 \times 10^{-6} = 0$

$$x = \frac{-3.3 \times 10^{-4} \pm \sqrt{(3.3 \times 10^{-4})^2 - 4(1)(-7.325 \times 10^{-6})}}{2(1)} = \frac{-3.3 \times 10^{-4} \pm \sqrt{2.941 \times 10^{-5}}}{2}$$

$$x = 2.547 \times 10^{-3} = 2.5 \times 10^{-3} \text{ M H}^+; \text{pH} = -\log(2.547 \times 10^{-3}) = 2.594 = 2.59$$

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

(a)	$\text{HN}_3 \text{ (aq)}$	\rightleftharpoons	$\text{H}^+ \text{ (aq)}$	+	$\text{N}_3^- \text{ (aq)}$
initial	0.400 M		0		0
equil	(0.400 - x) M		x M		x M

$$K_a = \frac{[\text{H}^+][\text{N}_3^-]}{[\text{HN}_3]} = 1.9 \times 10^{-5}; \frac{x^2}{(0.400 - x)} \approx \frac{x^2}{0.400} = 1.9 \times 10^{-5}$$

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

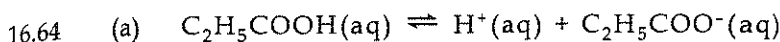
(b) $1.9 \times 10^{-5} \approx \frac{x^2}{0.100}; x = 0.00138 = 1.4 \times 10^{-3} \text{ M H}^+$

$$\% \text{ ionization} = \frac{1.38 \times 10^{-3} \text{ M H}^+}{0.100 \text{ M HN}_3} \times 100 = 1.4\%$$

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

$$\% \text{ ionization} = \frac{8.72 \times 10^{-4} \text{ M H}^+}{0.0400 \text{ M HN}_3} \times 100 = 2.2\%$$

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



$$K_a = 1.3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_5\text{COO}^-]}{[\text{C}_2\text{H}_5\text{COOH}]} = \frac{x^2}{0.250 - x}$$

$$x^2 \approx 0.250 (1.3 \times 10^{-5}); x = 1.803 \times 10^{-3} = 1.8 \times 10^{-3} \text{ M H}^+$$

$$\% \text{ ionization} = \frac{1.803 \times 10^{-3} \text{ M H}^+}{0.250 \text{ M C}_2\text{H}_5\text{COOH}} \times 100 = 0.721\%$$

(b) $\frac{x^2}{0.0800} \approx 1.3 \times 10^{-5}; x = 1.020 \times 10^{-3} = 1.0 \times 10^{-3} \text{ M H}^+$

$$\% \text{ ionization} = \frac{1.020 \times 10^{-3} \text{ M H}^+}{0.0800 \text{ M C}_2\text{H}_5\text{COOH}} \times 100 = 1.27\%$$

(c) $\frac{x^2}{0.0200} \approx 1.3 \times 10^{-5}; x = 5.099 \times 10^{-4} = 5.1 \times 10^{-4} \text{ M H}^+$

$$\% \text{ ionization} = \frac{5.099 \times 10^{-4} \text{ M H}^+}{0.0200 \text{ M C}_2\text{H}_5\text{COOH}} \times 100 = 2.55\%$$

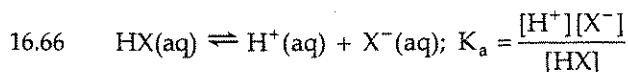
16.65 *Analyze/Plan.* Let the weak acid be HX. $\text{HX}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{X}^-(\text{aq})$. Solve the K_a expression symbolically for $[\text{H}^+]$ in terms of $[\text{HX}]$. Substitute into the formula for % ionization, $([\text{H}^+]/[\text{HX}]) \times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

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

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

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

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



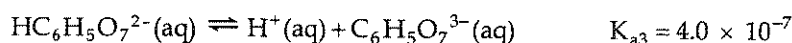
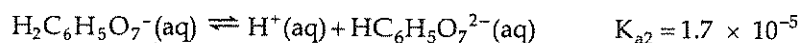
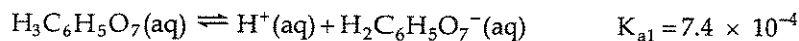
$$[\text{H}^+] = [\text{X}^-]; \text{assume the \% ionization is small}; K_a = \frac{[\text{H}^+]^2}{[\text{HX}]}; [\text{H}^+] = K_a^{1/2} [\text{HX}]^{1/2}$$

$$\text{pH} = -\log K_a^{1/2} [\text{HX}]^{1/2} = -\log K_a^{1/2} - \log [\text{HX}]^{1/2}; \text{pH} = -1/2 \log K_a - 1/2 \log [\text{HX}]$$

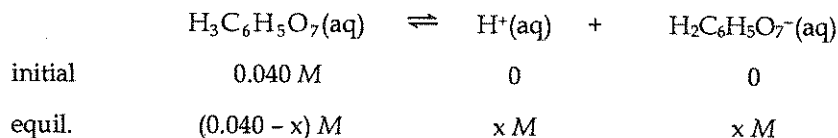
This is the equation of a straight line, where the intercept is $-1/2 \log K_a$, the slope is $-1/2$, and the independent variable is $\log [\text{HX}]$.

16.67 *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, $\text{C}_6\text{H}_5\text{O}_7^{3-}$ is only produced in step 3.

Solve. Assumptions are explained as they are used in the solution.



To calculate the pH of a 0.040 M solution, assume initially that only the first ionization is important:



$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]}{[\text{H}_3\text{C}_6\text{H}_5\text{O}_7]} = \frac{x^2}{(0.040 - x)} = 7.4 \times 10^{-4}$$

$$x^2 = (0.040 - x)(7.4 \times 10^{-4}); \quad x^2 \approx (0.040)(7.4 \times 10^{-4}); \quad x = 0.00544 = 5.4 \times 10^{-3} \text{ M}$$

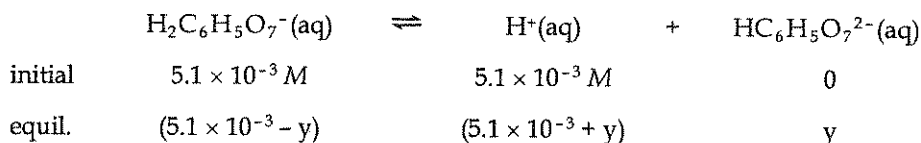
Since this value for x is rather large in relation to 0.050, a better approximation for x can be obtained by substituting this first estimate into the expression for x^2 , then solving again for x :

$$x^2 = (0.040 - x)(7.4 \times 10^{-4}) = (0.040 - 5.44 \times 10^{-3})(7.4 \times 10^{-4})$$

$$x^2 = 2.557 \times 10^{-5}; \quad x = 5.057 \times 10^{-3} = 5.1 \times 10^{-3} \text{ M}$$

(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^+ ?



$$K_{a2} = \frac{[\text{H}^+][\text{HC}_6\text{H}_5\text{O}_7^{2-}]}{[\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-]} = 1.7 \times 10^{-5}; \quad \frac{(5.1 \times 10^{-3} + y)y}{(5.1 \times 10^{-3} - y)} = 1.7 \times 10^{-5}$$

Assume that y is small relative to 5.1×10^{-3} ; that is, that additional ionization of $\text{H}_2\text{C}_6\text{H}_5\text{O}_7^-$ is small, then

$$\frac{(5.1 \times 10^{-3})y}{(5.1 \times 10^{-3})} = 1.7 \times 10^{-5} \text{ M}; \quad y = 1.7 \times 10^{-5} \text{ M}$$

This value is indeed small compared to $5.1 \times 10^{-3} \text{ M}$; $[\text{H}^+]$ and pH are determined by the first ionization step. If we were only interested in pH, we could stop here. However, to calculate $[\text{C}_6\text{H}_5\text{O}_7^{3-}]$, we must consider the third ionization, with adjusted $[\text{H}^+] = 5.1 \times 10^{-3} + 1.7 \times 10^{-5} = 5.12 \times 10^{-3} \text{ M} (= 5.1 \times 10^{-3})$

	$\text{HC}_6\text{H}_5\text{O}_7^{2-}$	\rightleftharpoons	H^+ (aq)	+	$\text{C}_6\text{H}_5\text{O}_7^{3-}$ (aq)
initial	$1.7 \times 10^{-5} \text{ M}$		$5.12 \times 10^{-3} \text{ M}$		0
equil.	$1.7 \times 10^{-5} - z$		$5.12 \times 10^{-3} + z$		z

$$K_{a3} = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{O}_7^{3-}]}{[\text{HC}_6\text{H}_5\text{O}_7^{2-}]} = \frac{(5.12 \times 10^{-3} + z)(z)}{(1.7 \times 10^{-5} - z)} = 4.0 \times 10^{-7}$$

Assume z is small relative to 5.12×10^{-3} , but not relative to 1.7×10^{-5} .

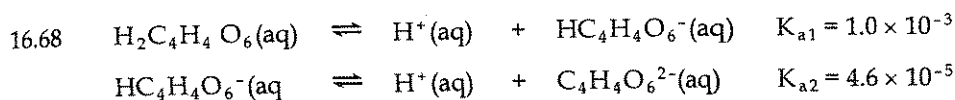
$$(4.0 \times 10^{-7})(1.7 \times 10^{-5} - z) = 5.12 \times 10^{-3} z; 6.8 \times 10^{-12} - 4.0 \times 10^{-7} z = 5.12 \times 10^{-3} z;$$

$$6.8 \times 10^{-12} = 5.12 \times 10^{-3} z + 4.0 \times 10^{-7} z = 5.12 \times 10^{-3} z; z = 1.33 \times 10^{-9} = 1.3 \times 10^{-9} \text{ M}$$

$$[\text{C}_6\text{H}_5\text{O}_7^{3-}] = 1.3 \times 10^{-9} \text{ M}; [\text{H}^+] = 5.12 \times 10^{-3} \text{ M} + 1.3 \times 10^{-9} \text{ M} = 5.1 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(5.12 \times 10^{-3}) = 2.29$$

The concentration of citrate ion, $[\text{C}_6\text{H}_5\text{O}_7^{3-}]$, is much less than $[\text{H}^+]$. Note that neither the second nor third ionizations contributed significantly to $[\text{H}^+]$ and pH.



Begin by calculating the $[\text{H}^+]$ from the first ionization. The equilibrium concentrations are $[\text{H}^+] = [\text{HC}_4\text{H}_4\text{O}_6^-] = x$, $[\text{H}_2\text{C}_4\text{H}_4\text{O}_6] = 0.25 - x$.

$$K_{a1} = \frac{[\text{H}^+][\text{HC}_4\text{H}_4\text{O}_6^-]}{[\text{H}_2\text{C}_4\text{H}_4\text{O}_6]} = \frac{x^2}{0.25 - x}; x^2 + 1.0 \times 10^{-3} x - 2.5 \times 10^{-4} = 0$$

Using the quadratic formula, $x = 1.532 \times 10^{-2} = 0.015 \text{ M H}^+$ from the first ionization. Next calculate the H^+ contribution from the second ionization.

	$\text{HC}_4\text{H}_4\text{O}_6^-(\text{aq})$	\rightleftharpoons	H^+ (aq)	+	$\text{C}_4\text{H}_4\text{O}_6^{2-}(\text{aq})$
initial	0.015		0.015		0
equil.	$(0.015 - y)$		$(0.015 + y)$		y

$$K_{a2} = \frac{(0.015 + y)(y)}{(0.015 - y)} = 4.6 \times 10^{-5}; \text{ assuming } y \text{ is small compared to } 0.015,$$

$$y = 4.6 \times 10^{-5} \text{ M C}_4\text{H}_4\text{O}_6^{2-}(\text{aq})$$

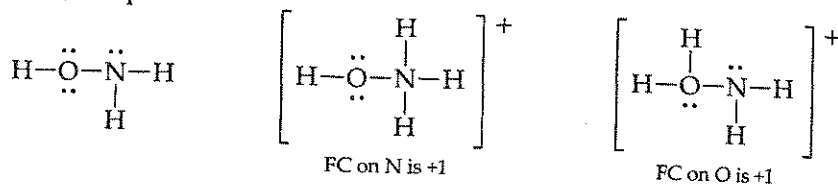
This approximation is reasonable, since 4.6×10^{-5} is only 0.3% of 0.015. $[\text{H}^+] = 0.015 \text{ M}$ (first ionization) + 4.6×10^{-5} (second ionization). Since 4.6×10^{-5} is 0.3% of 0.015 M, it can be safely ignored when calculating total $[\text{H}^+]$. Thus, $\text{pH} = -\log(0.01532) = 1.18148 = 1.181$.

Assumptions:

- 1) The ionization can be treated as a series of steps (valid by Hess' law).
- 2) The extent of ionization in the second step (y) is small relative to that from the first step (valid for this acid and initial concentration). This assumption was used twice, to calculate the value of y from K_{a2} and to calculate total $[\text{H}^+]$ and pH.

Weak Bases (section 16.7)

- 16.69 (a) HONH_3^+
 (b) When hydroxylamine acts as a base, the nitrogen atom accepts a proton.
 (c) $14 e^-, 7 e^-$ pairs



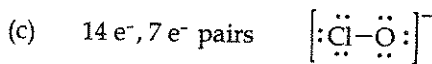
In neutral hydroxylamine, both O and N have zero formal charges. Nitrogen is less electronegative than oxygen, and more likely to share a lone pair of electrons with an incoming (and electron deficient) H^+ . The resulting cation with the +1 formal charge on N is more stable than the one with the +1 formal charge on O.

- 16.70 (a) *Analyze/Plan.* To determine relative strength, compare the K_b values of the two bases. *Solve.*

$$K_b \text{ for } \text{OCI}^- = \frac{K_w}{K_a \text{ for } \text{HClO}} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.3 \times 10^{-7}$$

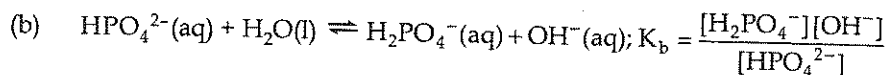
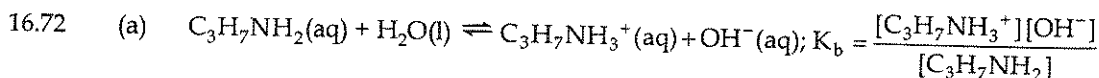
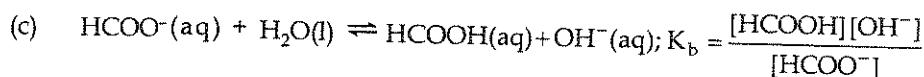
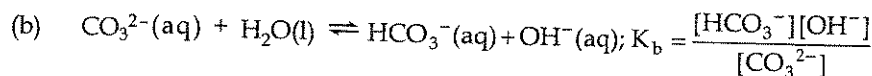
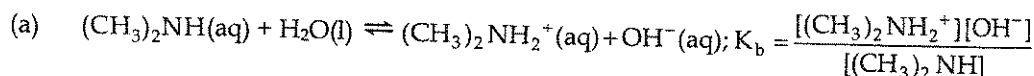
K_b for hydroxylamine is 1.1×10^{-8} . OCI^- is a stronger base than hydroxylamine.

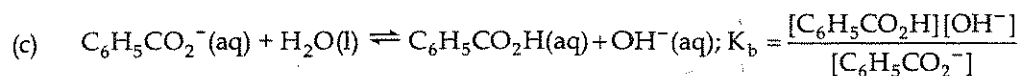
- (b) When OCI^- acts as a base, the O atom is the proton acceptor.



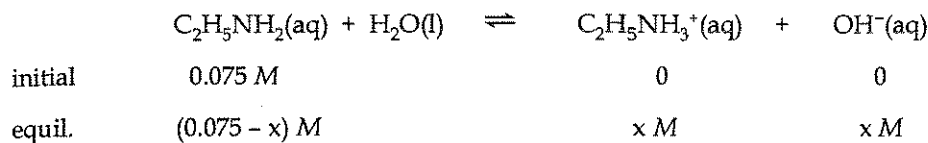
In OCI^- the -1 formal charge is on O. H^+ attaches to the atom with the negative formal charge.

- 16.71 *Analyze/Plan.* Remember that $K_b = [\text{products}]/[\text{reactants}]$. If $\text{H}_2\text{O}(\text{l})$ appears in the equilibrium reaction, it will not appear in the K_b expression, because it is a pure liquid. *Solve.*





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



$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} = \frac{(x)(x)}{(0.075 - x)} = \frac{x^2}{0.075} = 6.4 \times 10^{-4}$$

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

$$\text{Check. } \frac{6.9 \times 10^{-3} \text{ M OH}^-}{0.075 \text{ M C}_2\text{H}_5\text{NH}_2} \times 100 = 9.2\% \text{ ionization; the assumption is not valid}$$

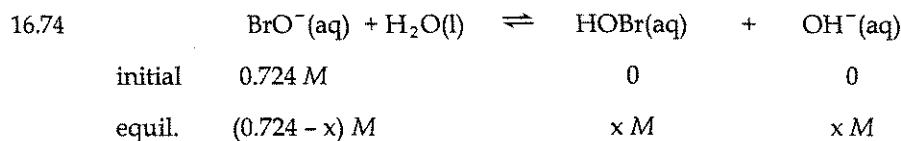
To obtain a more precise result, the K_b expression is rewritten in standard quadratic form and solved via the quadratic formula.

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

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

$$x = 6.62 \times 10^{-3} = 6.6 \times 10^{-3} \text{ M OH}^-; \text{pOH} = 2.18, \text{pH} = 14.00 - \text{pOH} = 11.82$$

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



$$K_b = \frac{[\text{HOBr}][\text{OH}^-]}{[\text{BrO}^-]} = \frac{x^2}{0.724 - x} \approx \frac{x^2}{0.724} = 4.0 \times 10^{-6}$$

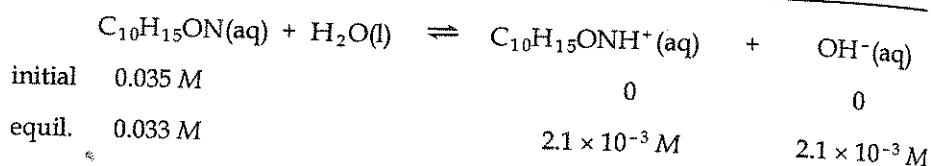
$$x^2 = 0.724 (4.0 \times 10^{-6}); x = [\text{OH}^-] = 1.70 \times 10^{-3} = 1.7 \times 10^{-3} \text{ M}; \text{pH} = 11.23$$

$$\text{Check. } \frac{1.7 \times 10^{-3} \text{ M OH}^-}{0.724 \text{ M BrO}^-} \times 100 = 0.24\% \text{ hydrolysis; the approximation is valid}$$

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

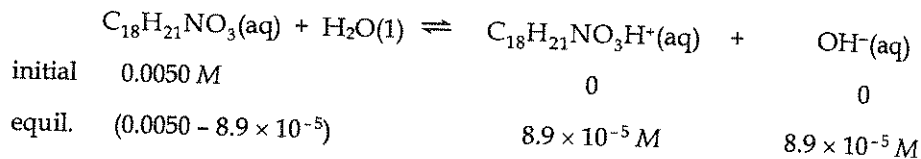
$$(a) \quad [\text{OH}^-] = 10^{-\text{pOH}}; \text{pOH} = 14 - \text{pH} = 14.00 - 11.33 = 2.67$$

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



$$(b) \quad K_b = \frac{[\text{C}_{10}\text{H}_{15}\text{ONH}^+][\text{OH}^-]}{[\text{C}_{10}\text{H}_{15}\text{ON}]} = \frac{(2.138 \times 10^{-3})^2}{(0.03286)} = 1.4 \times 10^{-4}$$

$$16.76 \quad (a) \quad \text{pOH} = 14.00 - 9.95 = 4.05; [\text{OH}^-] = 10^{-4.05} = 8.91 \times 10^{-5} = 8.9 \times 10^{-5} \text{ M}$$



$$K_b = \frac{[\text{C}_{18}\text{H}_{21}\text{NO}_3\text{H}^+][\text{OH}^-]}{[\text{C}_{18}\text{H}_{21}\text{NO}_3]} = \frac{(8.91 \times 10^{-5})^2}{(0.0050 - 8.91 \times 10^{-5})} = 1.62 \times 10^{-6} = 1.6 \times 10^{-6}$$

$$(b) \quad \text{p}K_b = -\log(K_b) = -\log(1.62 \times 10^{-6}) = 5.79$$

The $K_a - K_b$ Relationship; Acid-Base Properties of Salts (sections 16.8 and 16.9)

16.77 (a) For a conjugate acid/conjugate base pair such as $\text{C}_6\text{H}_5\text{OH}/\text{C}_6\text{H}_5\text{O}^-$, 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.

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

(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 .

16.78 The stronger a base, the weaker its conjugate acid. From the K_a values in Table 16.3, place the conjugate acids of these oxyanions in order of increasing K_a value, increasing acid strength and decreasing conjugate base strength. Use K_{a2} for H_2SO_4 , H_2CO_3 , and H_2SO_3 and K_{a3} for H_3PO_4 .

In order of increasing K_a value and acid strength: $\text{HPO}_4^{2-} < \text{HCO}_3^- < \text{HSO}_3^- < \text{HSO}_4^-$

In order of decreasing base strength: $\text{PO}_4^{3-} > \text{CO}_3^{2-} > \text{SO}_3^{2-} > \text{SO}_4^{2-}$

16.79 *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.

$$(c) \quad K_b \text{ for } \text{CH}_3\text{COO}^- = K_w/K_a \text{ for } \text{CH}_3\text{COOH} = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

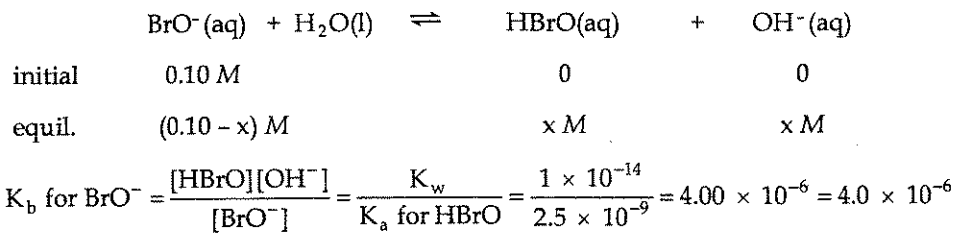
$$K_b \text{ for } \text{ClO}^- = K_w/K_a \text{ for } \text{HClO} = 1 \times 10^{-14} / 3.0 \times 10^{-8} = 3.3 \times 10^{-7}$$

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

- 16.80 (a) Ammonia is the stronger base because it has the larger K_b value.
 (b) Hydroxylammonium is the stronger acid because the weaker base, hydroxylamine, has the stronger conjugate acid.
 (c) K_a for $\text{NH}_4^+ = K_w/K_b$ for $\text{NH}_3 = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$
 K_a for $\text{HONH}_3^+ = K_w/K_b$ for $\text{HONH}_2 = 1.0 \times 10^{-14}/1.1 \times 10^{-8} = 9.1 \times 10^{-7}$
 Note that K_a for HONH_3^+ is larger than K_a for NH_4^+ .

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

- (a) *Plan.* NaBrO is a soluble salt and thus a strong electrolyte. When it is dissolved in H_2O , it dissociates completely into Na^+ and BrO^- . $[\text{NaBrO}] = [\text{Na}^+] = [\text{BrO}^-] = 0.10 \text{ M}$. Na^+ is the conjugate acid of the strong base NaOH and thus does not influence the pH of the solution. BrO^- , on the other hand, is the conjugate base of the weak acid HBrO 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 $[\text{OH}^-]$. *Solve.*



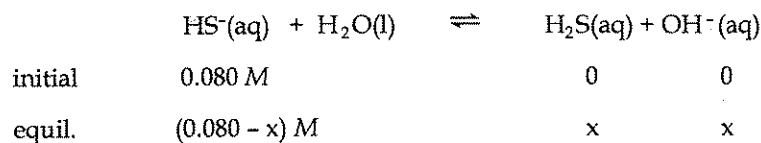
$$4.00 \times 10^{-6} = \frac{(x)(x)}{(0.10 - x)}; \text{ assume the percent of } \text{BrO}^- \text{ that hydrolyzes is small}$$

$$x^2 = 0.10 (4.00 \times 10^{-6}); x = [\text{OH}^-] = 6.32 \times 10^{-4} = 6.3 \times 10^{-4} \text{ M}$$

$$\text{pOH} = 3.20; \text{pH} = 14 - 3.20 = 10.80$$

- (b) *Plan.* $\text{NaHS}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{HS}^-(\text{aq})$

HS^- is the conjugate base of H_2S and its hydrolysis reaction will determine the $[\text{OH}^-]$ and pH of the solution (see similar explanation for NaBrO in part (a)). We will assume the process $\text{HS}^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{S}^-(\text{aq})$ will not significantly affect the $[\text{OH}^-]$ in solution because K_{a2} for H_2S is so small. Solve the equilibrium problem for $[\text{OH}^-]$. *Solve.*



$$K_b = \frac{[\text{H}_2\text{S}][\text{OH}^-]}{[\text{HS}^-]} = \frac{K_w}{K_a \text{ for H}_2\text{S}} = \frac{1.0 \times 10^{-14}}{9.5 \times 10^{-8}} = 1.053 \times 10^{-7} = 1.1 \times 10^{-7}$$

$$1.053 \times 10^{-7} = \frac{x^2}{(0.080 - x)}; x^2 = 0.080 (1.053 \times 10^{-7}); x = 9.177 \times 10^{-5} = 9.2 \times 10^{-5} \text{ M OH}^-$$

(Assume x is small compared to 0.080); $\text{pOH} = 4.04$; $\text{pH} = 14 - 4.04 = 9.96$

Check. $\frac{9.2 \times 10^{-5} \text{ M OH}^-}{0.080 \text{ M HS}^-} \times 100 = 0.12\%$ hydrolysis; the approximation is valid

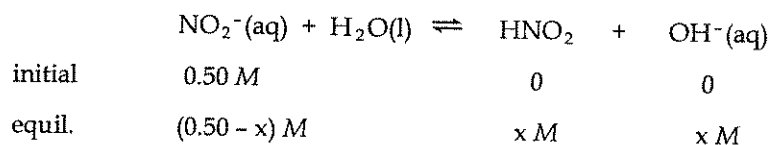
- (c) *Plan.* For the two salts present, Na^+ and Ca^{2+} are negligible acids. NO_2^- is the conjugate base of HNO_2 and will determine the pH of the solution. *Solve.*

Calculate total $[\text{NO}_2^-]$ present initially.

$$[\text{NO}_2^-]_{\text{total}} = [\text{NO}_2^-] \text{ from NaNO}_2 + [\text{NO}_2^-] \text{ from Ca(NO}_2)_2$$

$$[\text{NO}_2^-]_{\text{total}} = 0.10 \text{ M} + 2(0.20 \text{ M}) = 0.50 \text{ M}$$

The hydrolysis equilibrium is:

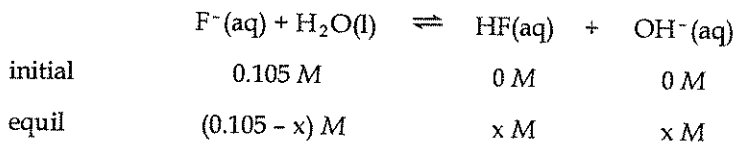


$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{K_w}{K_a \text{ for HNO}_2} = \frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4}} = 2.22 \times 10^{-11} = 2.2 \times 10^{-11}$$

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

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

- 16.82 (a) Proceeding as in Solution 16.81(a):



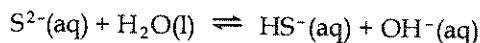
$$K_b \text{ for F}^- = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{K_w}{K_a \text{ for HF}} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.47 \times 10^{-11} = 1.5 \times 10^{-11}$$

$$1.5 \times 10^{-11} = \frac{(x)(x)}{(0.105 - x)}; \text{assume the amount of F}^- \text{ that hydrolyzes is small}$$

$$x^2 = 0.105(1.47 \times 10^{-11}); x = [\text{OH}^-] = 1.243 \times 10^{-6} = 1.2 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.91; \text{pH} = 14 - 5.91 = 8.09$$

- (b) $\text{Na}_2\text{S}(\text{aq}) \rightarrow \text{S}^{2-}(\text{aq}) + 2\text{Na}^+(\text{aq})$



As in part (a) above, $[\text{OH}^-] = [\text{HS}^-] = x$; $[\text{S}^{2-}] = 0.035 \text{ M}$

$$K_b = \frac{[\text{HS}^-][\text{OH}^-]}{[\text{S}^{2-}]} = \frac{K_w}{K_a \text{ for HS}^-} = \frac{1.0 \times 10^{-14}}{1 \times 10^{-19}} = 1 \times 10^5$$

Since $K_b \gg 1$, the equilibrium above lies far to the right and $[\text{OH}^-] = [\text{HS}^-] = 0.035 \text{ M}$. K_b for $\text{HS}^- = 1.05 \times 10^{-7}$; $[\text{OH}^-]$ produced by further hydrolysis of HS^- amounts to $6.1 \times 10^{-5} \text{ M}$. The second hydrolysis step does not make a significant contribution to the total $[\text{OH}^-]$ and pH.

$$[\text{OH}^-] = 0.035 \text{ M}; \text{pOH} = 1.46, \text{pH} = 12.54$$

- (c) As in Solution 16.81(c), calculate $[\text{CH}_3\text{COO}^-]$.

$$[\text{CH}_3\text{COO}^-]_t = [\text{CH}_3\text{COO}^-] \text{ from } \text{CH}_3\text{COONa} + [\text{CH}_3\text{COO}^-] \text{ from } (\text{CH}_3\text{COO})_2\text{Ba}$$

$$[\text{CH}_3\text{COO}^-]_t = 0.045 \text{ M} + 2(0.055 \text{ M}) = 0.155 \text{ M}$$

The hydrolysis equilibrium is $\text{CH}_3\text{COO}^- (\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{aq}) + \text{OH}^- (\text{aq})$

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a \text{ for } \text{CH}_3\text{COOH}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$= 5.6 \times 10^{-10}$$

$$[\text{OH}^-] = [\text{CH}_3\text{COOH}] = x, [\text{CH}_3\text{COO}^-] = 0.155 - x$$

$$K_b = 5.56 \times 10^{-10} = \frac{x^2}{(0.155 - x)}; \text{assume } x \text{ is small compared to } 0.155 \text{ M}$$

$$x^2 = 0.155 (5.56 \times 10^{-10}); x = [\text{OH}^-] = 9.280 \times 10^{-6} = 9.3 \times 10^{-6}$$

$$\text{pH} = 14 + \log (9.280 \times 10^{-6}) = 8.97$$

- 16.83 *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 ($1.0 \times 10^{-14} / 5.9 \times 10^{-2} = 1.7 \times 10^{-13}$).

- 16.84 (a) acidic; Al^{3+} is a highly charged metal cation and a Lewis acid; Cl^- is negligible.
 (b) neutral; both Na^+ and Br^- are negligible.
 (c) basic; ClO^- is the conjugate base of HClO ; Na^+ is negligible.
 (d) acidic; CH_3NH_3^+ is the conjugate acid of CH_3NH_2 ; NO_3^- is negligible.
 (e) basic; SO_3^{2-} is the conjugate base of H_2SO_3 ; Na^+ is negligible.

- 16.85 *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.*

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

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

$$[NaX] = [X^-] = 0.050 \text{ mol salt} / 0.500 \text{ L} = 0.10 M$$

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

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

The unknown is NaF.

- 16.86 *Plan.* Estimate pH of salt solution by evaluating the ions in the salts. Calculate to confirm if necessary. *Solve.*

KBr: salt of strong acid and strong base, neutral solution. The unknown is probably KBr. Check the others to be sure.

NH_4Cl : salt of a weak base and a strong acid, acidic solution

KCN: salt of a strong base and a weak acid, basic solution

K_2CO_3 : salt of a strong base and a weak acid (HCO_3^-), basic solution

Only KBr fits the acid-base properties of the unknown.

Acid-Base Character and Chemical Structure (section 16.10)

- 16.87 (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.
- 16.88 (a) For binary compounds where X atoms are in the same period, the more polar the X-H bond, the stronger the acid and the weaker the base. Oxygen is more electronegative than nitrogen, so the O-H bonds in H_2O are more polar than the N-H bonds in NH_3 and NH_3 is the stronger base. Also, less electronegative N is more likely than O to share its nonbonding electrons with an incoming H^+ and NH_3 is a better H^+ acceptor.
- (b) The C-H bonds in CH_4 are essentially nonpolar and the molecule has no nonbonding electron pairs. CH_4 has no acid or base properties, so NH_3 is a stronger base.
- 16.89 (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 .
- 16.90 (a) For binary hydrides, acid strength increases going across a row, so HCl is a stronger acid than H_2S .
- (b) For oxyacids, the more electronegative the central atom, the stronger the acid, so H_3PO_4 is a stronger acid than H_3AsO_4 .
- (c) HBrO_3 has one more nonprotonated oxygen and a higher oxidation number on Br, so it is a stronger acid than HBrO_2 .
- (d) The first dissociation of a polyprotic acid is always stronger because H^+ is more tightly held by an anion, so $\text{H}_2\text{C}_2\text{O}_4$ is a stronger acid than HC_2O_4^- .
- (e) The conjugate base of benzoic acid, $\text{C}_6\text{H}_5\text{COO}^-$, is stabilized by resonance, while the conjugate base of phenol, $\text{C}_6\text{H}_5\text{O}^-$, is not. $\text{C}_6\text{H}_5\text{COOH}$ has greater tendency to form its conjugate base and is the stronger acid.
- 16.91 (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^+)
- 16.92 (a) NO_2^- (HNO_3 is the stronger acid because it has more nonprotonated O atoms, so NO_2^- is the stronger base.)
- (b) PO_4^{3-} (K_a for HAsO_4^{2-} is greater than K_a for HPO_4^{2-} , so K_b for PO_4^{3-} is greater and PO_4^{3-} is the stronger base. Note that P is more electronegative than As and H_3PO_4 is a stronger acid than H_3AsO_4 , which could lead to the conclusion that AsO_4^{3-} is the stronger base. As in all cases, the measurement of base strength, K_b , supercedes the prediction. Chemistry is an experimental science.)
- (c) CO_3^{2-} (The more negative the anion, the stronger the attraction for H^+ .)
- 16.93 (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.

- 16.94 (a) True.
 (b) False. For oxyacids with the same structure but different central atom, the acid strength **increases** as the electronegativity of the central atom increases.
 (c) False. HF is a weak acid, weaker than the other hydrogen halides, primarily because the H-F bond energy is exceptionally high.

Lewis Acids and Bases (section 16.11)

- 16.95 Yes. If a substance is an Arrhenius base, it must also be a Brønsted-Lowry base and a Lewis base. The Arrhenius definition (hydroxide ion) is the most restrictive, the Brønsted-Lowry (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-Lowry and Lewis definitions.
- 16.96 No. If a substance is a Lewis acid, it is not necessarily a Brønsted-Lowry or an Arrhenius acid. The Lewis definition of an acid, an electron pair acceptor, is most general. A Lewis acid does not necessarily fit the more narrow description of a Brønsted-Lowry or Arrhenius acid. An electron pair acceptor isn't necessarily an H^+ donor, nor must it produce H^+ in aqueous solution. An example is Al^{3+} , which is a Lewis acid, but has no ionizable hydrogen.
- 16.97 *Analyze/Plan.* Identify each reactant as an electron pair donor (Lewis base) or electron pair acceptor (Lewis acid). Remember that a Brønsted-Lowry acid is necessarily a Lewis acid, and a Brønsted-Lowry base is necessarily a Lewis base (Solution 16.95). *Solve.*

	<u>Lewis Acid</u>	<u>Lewis Base</u>
(a)	$\text{Fe}(\text{ClO}_4)_3$ or Fe^{3+}	H_2O
(b)	H_2O	CN^-
(c)	BF_3	$(\text{CH}_3)_3\text{N}$
(d)	HIO	NH_2^-

	<u>Lewis Acid</u>	<u>Lewis Base</u>
(a)	HNO_2 (or H^+)	OH^-
(b)	FeBr_3 (Fe^{3+})	Br^-
(c)	Zn^{2+}	NH_3
(d)	SO_2	H_2O

- 16.99 (a) Cu^{2+} , higher cation charge
 (b) Fe^{3+} , higher cation charge
 (c) Al^{3+} , smaller cation radius, same charge
- 16.100 (a) ZnBr_2 , smaller cation radius, same charge
 (b) $\text{Cu}(\text{NO}_3)_2$, higher cation charge
 (c) NiBr_2 , smaller cation radius, same charge

Additional Exercises

16.101 To compare base strength, compare either K_b or pK_b values. The stronger the base, the larger the K_b and the smaller the pK_b . (pK_b is the negative log of K_b ; pK_b increases as base strength decreases.)

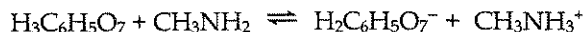
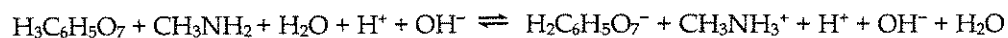
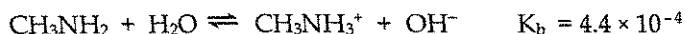
$$pK_b \text{ for } \text{NH}_3 = -\log(1.8 \times 10^{-5}) = 4.74. \quad pK_b \text{ for } (\text{C}_2\text{H}_5)_3\text{N} = 2.99$$

$(\text{C}_2\text{H}_5)_3\text{N}$ is a stronger base than NH_3 by virtue of its smaller pK_b .

- 16.102 (a) Correct.
 (b) Incorrect. A Brønsted-Lowry acid must have ionizable hydrogen. Lewis acids are electron pair acceptors, but need not have ionizable hydrogen.
 (c) Correct.
 (d) Incorrect. K^+ is a negligible Lewis acid because it is the conjugate of strong base KOH . Its relatively large ionic radius and low positive charge render it a poor attractor of electron pairs.
 (e) Correct.
- 16.103 The equilibrium favors the weaker acid and base. That is, the stronger acid will be ionized; the weaker acid will not.
- (a) The equilibrium lies to the right. HPO_4^{2-} is a weaker acid than NH_4^+ , and NH_3 is a weaker base than PO_4^{3-} . The equilibrium favors products and $K > 1$.
 (b) The equilibrium lies to the left. CH_3COOH is a weaker acid than HF , and F^- is a weaker base than CH_3COO^- . The equilibrium favors reactants and $K < 1$.



citric acid methylamine odorless salt



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

- 16.105 (a) A higher O_2 concentration displaces protons from Hb, producing a more acidic solution, with lower pH in the lungs than in the tissues.
 (b) $[\text{H}^+] = \text{antilog}(-7.4) = 4.0 \times 10^{-8} \text{ M}$. At body temperature, 37°C , $K_w = 2.4 \times 10^{-14}$ (see Solution 16.39). At this temperature, a "neutral" solution has $[\text{H}^+] = 1.5 \times 10^{-7}$ and pH 6.81. Even though the frame of reference is a bit different at this temperature, blood at pH 7.4 is slightly basic.