16 Acid-Base Equilibria

Visualizing Concepts

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.*

(a) 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.

(b) If HY is the stronger acid, Y^- is the weaker base and X^- is the stronger base.

(c) 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.*

(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.

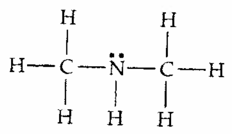
16.4 *Plan.* The definition of % ionization is $\dfrac{[H^+]}{[HA]_{\text{Initial}}} \times 100.$ *Solve.*

(a) Curve C shows the effect of initial concentration on % ionization of a weak acid.

(b) The % ionization is inversely related to initial acid concentration; only curve C shows a decrease in % ionization as acid concentration increases.

16.6 *Plan.* Write the molecular formula so we can count the correct number of valence electrons. Use the atom connectivity shown to draw the Lewis structure. *Solve.*

(a) The molecular formula is $(CH_3)_2NH$, or C_2H_7N. The number of valence electrons is $2(4) + 7 + 5 = 20\ e^-$, $10\ e^-$ pr.



(b) The compound is an amine. It is an ammonia molecule where two H atoms have been replaced by CH_3 groups.

16.7 *Plan.* Evaluate the interactions of Na^+ and X^- with H_2O.

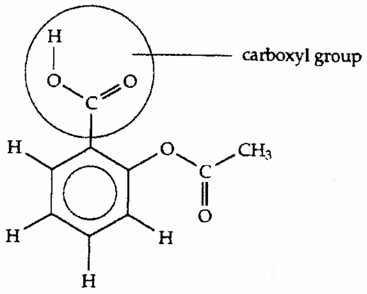
Solve. Na^+ does not affect the $[H^+]$ or $[OH^-]$ of an aqueous solution. It is a "negligible" acid in water (which can be thought of as the conjugate acid of the strong base NaOH).

X^- is the conjugate base of HX. It is not a negligible base in water, because we see from the diagram that one X^- has gained an H^+ to form HX. In this solution, H_2O acts as the Brønsted acid, according to the hydrolysis equilibrium:

$$X^-(aq) + H_2O(l) \rightleftharpoons HX(aq) + OH^-(aq).$$

The missing ion is $OH^-(aq)$. According to the equilibrium reaction, the number of HX molecules and OH^- ions are equal. Since there is 1 HX molecule in the diagram, 1 OH^- should be shown.

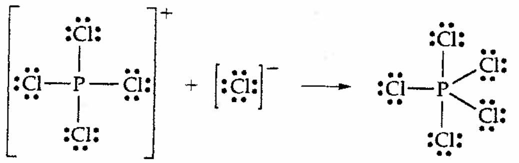
16.9 The carboxyl group in the H-atom group at the "top" of the molecule.



The group on the right of the molecule is not a carboxyl group because it contains no ionizable H.

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

PCl_4^-	+	Cl^-	$\rightarrow$	PCl_5
32 e^-, 16 e^-pr		8 e^-, 4 e^-pr		40 e^-, 20 e^-pr



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

16.12 When NaOH dissolves in water, it completely dissociates to form $Na^+(aq)$ and $OH^-(aq)$. CaO is the oxide of a metal; it dissolves in water according to the following process: $CaO(s) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$. Thus, the properties of both solutions are dominated by the presence of $OH^-(aq)$. Both solutions taste bitter, turn litmus paper blue (are basic), neutralize solutions of acids, and conduct electricity.

16.14 (a) According to the Arrhenius definition, a *base* when dissolved in water increases $[OH^-]$. 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) $NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ When NH_3 dissolves in water, it accepts H^+ from H_2O (B-L definition). In doing so, OH^- is produced (Arrhenius definition).

Note that the OH^- produced was originally part of the H_2O molecule, not part of the NH_3 molecule.

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

(a) HCN (b) OH (c) $H_2PO_4^-$ (d) $C_2H_5NH_3^+$

16.18

	B-L acid	+	B-L base	⇌	Conjugate acid	+	Conjugate base
(a)	$HBrO(aq)$		$H_2O(l)$		$H_3O^+(aq)$		$BrO^-(aq)$
(b)	$HSO_4^-(aq)$		$HCO_3^-(aq)$		$H_2CO_3(aq)$		$SO_4^{2-}(aq)$
(c)	$H_3O^+(aq)$		$HSO_3^-(aq)$		$H_2SO_3(aq)$		$H_2O(l)$

16.20 (a) $H_2C_6H_7O_5^-(aq) + H_2O(l) \rightleftharpoons H_3C_6H_7O_5(aq) + OH^-(aq)$

(b) $H_2C_6H_7O_5^-(aq) + H_2O(l) \rightleftharpoons HC_6H_7O_5^{2-}(aq) + H_3O^+(aq)$

(c) $H_3C_6H_7O_5$ is the conjugate acid of $H_2C_6H_7O_5^-$

$HC_6H_7O_5^{2-}$ is the conjugate base of $H_2C_6H_7O_5^-$

16.22 (a) $C_2H_3O_2^-$, weak base; $HC_2H_3O_2$, 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

16.24 (a) HNO_3. It is one of the seven strong acids (Section 16.5). Also, in a series of oxyacids with the same central atom (N), the acid with more O atoms is stronger (Section 16.10).

(b) NH_3. When NH_3 and H_2O are combined, as in $NH_3(aq)$, NH_3 acts as the B-L base, accepting H^+ from H_2O. NH_3 has the greater tendency to accept H^+. For binary hydrides, base strength increases going to the left across a row of the periodic chart (Section 16.10).

16.26 **Base** + **Acid** ⇌ **Conjugate acid** + **Conjugate base**

(a) $OH^-(aq) + NH_4^+(aq) \rightleftharpoons H_2O(l) + NH_3(aq)$

OH^- is a stronger base than NH_3 (Figure 16.4), so the equilibrium lies to the right.

(b) $C_2H_3O_2^-(aq) + H_3O^+(aq) \rightleftharpoons HC_2H_3O_2(aq) + H_2O(l)$

H_3O^+ is a stronger acid than $HC_2H_3O_2$ (Figure 16.4), so the equilibrium lies to the right.

(c) $F^-(aq) + HCO_3^-(aq) \rightleftharpoons HC_2H_3O_2(aq) + H_2O(l)$

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

Autoionization of Water

16.28 (a) $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

(b) $K_w = [H^+][OH^-]$. The $[H_2O(l)]$ 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^+ ($[OH^-] > [H^+]$).

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

(a) $$[OH^-] = \frac{K_W}{[H^+]} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}\ M} = 1.3 \times 10^{-12}\ M < 1 \times 10^{-7}\ M;\ \text{acidic}$$

(b) $$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{6.5 \times 10^{-10}\ M} = 1.5 \times 10^{-5}\ M > 1 \times 10^{-7}\ M;\ \text{basic}$$

(c) $[H^+] = 10[OH^-]$; $K_w = 10[OH^-][OH^-] = 10[OH^-]^2$

$[OH^-] = (K_w/10)^{1/2} = 3.2 \times 10^{-8}\ M < 1 \times 10^{-7}\ M$; acidic

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

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

The pH Scale

16.34 $[H^+]_A = 500\ [H^+]_B$ From Solution 16.33, $\Delta pH = -\log \frac{[H^+]_B}{[H^+]_A}$

$$\Delta pH = -\log \frac{[H^+]_B}{500\,[H^+]_B} = -\log\left(\frac{1}{500}\right) = 2.70$$

The pH of solution A is 2.70 pH units lower than the pH of solution B, because $[H^+]_A$ is 500 times greater than $[H^+]_B$. The greater $[H^+]$, the lower the pH of the solution.

16.36 (a) $K_w = [H^+][OH^-]$. If HNO_3 is added to water, it ionizes to form $H^+(aq)$ and $NO_3^-(aq)$. This increases $[H^+]$ and necessarily decreases $[OH^-]$. When $[H^+]$ increases, pH decreases.

(b) On Figure 16.5, 1.4×10^{-2} M OH^- is between pH = 12 (1×10^{-2} M OH^-) and pH 13 (1×10^{-1} M OH^-), slightly higher than pH = 12, so we estimate pH = 12.1. If pH > 7, the solution is basic.

(c) pH = 6.6 is midway between pH 6 and pH 7 on Figure 16.5.

At pH = 7, $[H^+] = 1 \times 10^{-7}$; at pH = 6, $[H^+] = 1 \times 10^{-6} = 10 \times 10^{-7}$.

A reasonable estimate is 5×10^{-7} M H^+. By calculation:

pH = 6.6, $[H^+] = 10^{-pH} = 10^{-6.6} = 3 \times 10^{-7}$

At pH = 6, $[OH^-] = 1 \times 10^{-9}$; at pH = 7, $[OH^-] = 1 \times 10^{-7} = 10 \times 10^{-8}$.

A reasonable estimate is 5×10^{-8} M OH^-. By calculation:

pOH = 14.0 - 6.6 = 7.4; $[OH^-] = 10^{-pOH} = 10^{-7.4} = 4 \times 10^{-8}$ M OH^-.

16.38

pH	pOH	$[H^+]$	$[OH^-]$	acidic or basic
4.75	9.25	1.8×10^{-5} M	5.6×10^{-10} M	acidic
2.11	11.89	7.8×10^{-3} M	1.3×10^{-12} M	acidic
2.19	11.81	6.5×10^{-3} M	1.5×10^{-12} M	acidic
7.93	6.07	1.2×10^{-8} M	8.6×10^{-7} M	basic

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 6×10^{-6} M to 3×10^{-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 2×10^{-9} M to 4×10^{-9} M.

(The pH has one decimal place, so concentrations are reported to one sig fig.)

Strong Acids and Bases

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.

$Sr(OH)_2(aq) \rightarrow Sr^{2+}(aq) + 2OH^-(aq)$

0.045 M $Sr(OH)_2(aq)$ = 0.090 M OH^-

(c) 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.

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

(a) $0.00835\ M\ HNO_3 = 0.00835\ M\ H^+$; $pH = -\log(0.00835) = 2.08$

(b) $$\frac{0.525\ g\ HClO_4}{2.00\ L\ soln} \times \frac{1\ mol\ HClO_4}{100.5\ g\ HClO_4} = 2.612 \times 10^{-3} = 2.61 \times 10^{-3}\ M\ HClO_4$$

$[H^+] = 2.61 \times 10^{-3}\ M$; $pH = -\log(2.612 \times 10^{-3}) = 2.583$

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

$1.00\ M\ HCl \times 5.00\ mL\ HCl = M_d\ HCl \times 500\ mL\ HCl$

$$M_d\ HCl = \frac{1.00\ M \times 5.00\ mL}{500\ mL} = 1.00 \times 10^{-2}\ M\ HCl = 1.00 \times 10^{-2}\ M\ H^+$$

$pH = -\log(1.00 \times 10^{-2}) = 2.000$

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

$$[H^+]_{total} = \frac{(0.020\ M\ HCl \times 0.0500\ L) + (0.010\ M\ HI \times 0.150\ L)}{0.200\ L}$$

$$[H^+]_{total} = \frac{1.0 \times 10^{-3}\ mol\ H^+ + 1.50 \times 10^{-3}\ mol\ H^+}{0.200\ L} = 0.0125 = 0.013\ M$$

$pH = -\log(0.0125) = 1.90$

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

(a) $0.012\ M\ KOH = 0.012\ M\ OH^-$; $pOH = -\log(0.012) = 1.92$; $pH = 14 - 1.92 = 12.08$

(b) $$\frac{1.565\ g\ KOH}{0.5000\ L} \times \frac{1\ mol\ KOH}{56.106\ g\ KOH} = 0.055787 = 0.05579\ M = [OH^-]$$

$pOH = -\log(0.055787) = 1.2535$; $pH = 14 - pOH = 12.7465$

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

$0.250\ M\ Ca(OH)_2 \times 10.0\ mL = M_d\ Ca(OH)_2 \times 500\ mL$

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

$Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

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

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

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

$$\frac{(7.5 \times 10^{-3}\ M \times 0.0400\ L) + 2(0.015\ M \times 0.0100\ L)}{0.0500\ L}$$

$$[OH^-]_{total} = \frac{3.00 \times 10^{-4}\ mol\ OH^- + 3.0 \times 10^{-4}\ mol\ OH^-}{0.0500\ L} = 0.01200 = 0.012\ M\ OH^-$$

$pOH = -\log(0.0120) = 1.92$; $pH = 14 - pOH = 12.08$

16.48 $pOH = 14 - pH = 14.00 - 12.05 = 1.95$

$pOH = 1.95 = -\log[OH^-]$; $[OH^-] = 10^{-1.95} = 0.01122 = 1.1 \times 10^{-2}\ M$

$[OH^-] = 2[Ca(OH)_2]$; $[Ca(OH)_2] = [OH^-] / 2 = 0.01122/2 = 5.6 \times 10^{-3}\ M$

16.50 Upon dissolving, Li_2O dissociates to form Li^+ and O^{2-}. According to Equation 16.22, O^{2-} is completely protonated in aqueous solution.

$Li_2O(s) + H_2O(l) \rightarrow 2Li^+(aq) + 2OH^-(aq)$

Thus, initial $[Li_2O] = [O_2^-]$; $[OH^-] = 2[O^{2-}] = 2[Li_2O]$

$$[Li_2O] = \frac{\text{mol } Li_2O}{\text{L solution}} = 2.50\text{ g } Li_2O \times \frac{1\text{ mol } Li_2O}{29.88\text{ g } Li_2O} \times \frac{1}{1.500\text{ L}} = 0.0558 = 0.0558\ M$$

$[OH^-] = 0.11156 = 0.112\ M$; $pOH = 0.9525 = 0.958$ $pH = 14.00 - pOH = 13.0475 = 13.048$

Weak Acids

16.52 (a) $$HC_6H_5O\,(aq) \rightleftharpoons H^+(aq) + C_6H_5O^-(aq);\quad K_a = \frac{[H^+][C_6H_5O^-]}{[HC_6H_5O]}$$

$$HC_6H_5O\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + C_6H_5O^-(aq);\quad K_a = \frac{[H_3O^+][C_6H_5O^-]}{[HC_6H_5O]}$$

(b) $$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq);\quad K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$HCO_3^-(aq) + H_2O\,(aq) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq);\quad K_a = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

16.54 $$HC_8H_7O_2\,(aq) \rightleftharpoons H^+(aq) + C_8H_7O_2^-(aq);\quad K_a = \frac{[H^+][C_8H_7O_2^-]}{[HC_8H_7O_2]}$$

$[H^+] = [C_8H_7O_2^-] = 10^{-2.68} = 2.09 \times 10^{-3} = 2.1 \times 10^{-3}\ M$

$[HC_8H_7O_2] = 0.085 - 2.09 \times 10^{-3} = 0.0829 = 0.083\ M$

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

16.56 $[H^+] = 0.132 \times [BrCH_2COOH]_{\text{initial}} = 0.0132\ M$

	$BrCH_2COOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$BrCH_2COO^-(aq)$
initial	0.100 *M*		0		0
equil.	0.087		0.0132 *M*		0.0132 *M*

$$K_a = \frac{[H^+][BrCH_2COO^-]}{[BrCH_2COOH]} = \frac{(0.0132)^2}{0.087} = 2.0 \times 10^{-3}$$

16.58 $[H^+] = 10^{-pH} = 10^{-3.25} = 5.623 \times 10^{-4} = 5.62 \times 10^{-4}\ M$

$$K_a = 6.8 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{(5.623 \times 10^{-4})^2}{x - 5.623 \times 10^{-4}}$$

$6.8 \times 10^{-4}(x - 5.623 \times 10^{-4}) = (5.623 \times 10^{-4})^2$;

$6.8 \times 10^{-4}\,x = 3.824 \times 10^{-7} + 3.162 \times 10^{-7} = 6.986 \times 10^{-7}$

$x = 1.027 \times 10^{-3} = 1.0 \times 10^{-3}\ M$ HF

mol = $M \times L = 1.027 \times 10^{-3}\ M \times 0.200\ L = 2.055 \times 10^{-4} = 2.1 \times 10^{-4}$ mol HF

16.60

	$HClO(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$ClO^-(aq)$
initial	$0.0075\ M$		0		0
equil.	$(0.0075 - x)\ M$		$x\ M$		$x\ M$

$$K_a = \frac{[H^+][ClO^-]}{[HClO]} = \frac{x^2}{(0.0075 - x)} \approx \frac{x^2}{0.0075} = 3.0 \times 10^{-5}$$

$x^2 = 0.0075\ (3.0 \times 10^{-8})$; $x = 1.5 \times 10^{-5}\ M = [H^+] = [H_3O^+] = [ClO^-]$

$[HClO] = 7.5 \times 10^{-3} - 1.5 \times 10^{-6} = 7.485 \times 10^{-3} = 7.5 \times 10^{-3}\ M$

Check. $\frac{4.7 \times 10^{-5}\ MH^+}{0.0075\ M\ HClO} \times 100 = 0.20\%$ ionization; the assumption is valid

16.62 (a)

	$HOCl(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$OCl^-(aq)$
initial	$0.125\ M$		0		0
equil	$(0.125 - x)\ M$		$x\ M$		$x\ M$

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} = \frac{x^2}{(0.125 - x)} \approx \frac{x^2}{0.125} = 3.0 \times 10^{-8}$$

$x^2 = 0.125\ (3.0 \times 10^{-8})$; $x = [H^+] = 6.1 \times 10^{-5}\ M$, pH = 4.21

Check. $\frac{6.1 \times 10^{-5}\ M\ H^+}{0.125\ M\ HOCl} \times 100 = 0.049\%$ ionization; the assumption is valid

(b) $$K_a = \frac{[H^+][C_6H_5O^-]}{[C_6H_5OH]} = \frac{x^2}{(0.0085 - x)} \approx \frac{x^2}{0.0085} = 1.3 \times 10^{-10}$$

$x^2 = 0.0085\ (1.3 \times 10^{-10})$; $x = [H^+] = 1.1 \times 10^{-6}\ M$, pH = 5.98

Check. Clearly $1.1 \times 10^{-6}\ M\ H^+$ is small compared to $8.5 \times 10^{-3}\ M\ C_6H_5OH$, and the assumption is valid.

(c)

	$HONH_2(aq) + H_2O(l)$	$\rightleftharpoons$	$HONH_3^+(aq)$	+	$OH^-(aq)$
initial	$0.095\ M$		0		0
equil	$(0.095 - x)\ M$		$x\ M$		$x\ M$

$$K_b = \frac{[HONH_3^+][OH^-]}{[HONH_2]} = \frac{x^2}{(0.095-x)} \approx \frac{x^2}{0.095} = 1.1 \times 10^{-8}$$

$x^2 = 0.095\ (1.1 \times 10^{-8})$; $x = [OH^-] = 3.2 \times 10^{-5}\ M$, pH = 9.51

Check. $\dfrac{3.2 \times 10^{-5}\ M\ OH^-}{0.095\ M\ HONH_2} \times 100 = 0.034\%$ ionization; the assumption is valid

16.64 Calculate the initial concentration of $HC_9H_7O_4$.

$$2 \text{ tablets} \times \frac{500 \text{ mg}}{\text{tablet}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol } HC_9H_7O_4}{180.2 \text{ g } HC_9H_7O_4} = 0.005549 = 0.00555 \text{ mol } HC_9H_7O_4$$

$$\frac{0.005549 \text{ mol } HC_9H_7O_4}{0.250 \text{ L}} = 0.02220 = 0.0222\ M\ HC_9H_7O_4$$

	$HC_9H_7O_4$ (aq)	⇌	$C_9H_7O_4^-$ +	H^+ (aq)
Initial	0.0222 *M*		0 *M*	0 *M*
equil	(0.0222 - x)		x *M*	x *M*

$$K_a = 3.3 \times 10^{-4} = \frac{[H^+][C_7H_9O_4^-]}{[HC_7H_9O_4]} = \frac{x^2}{(0.0222-x)}$$

Assuming x is small compared to 0.0222,

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

$\dfrac{2.7 \times 10^{-3}\ M\ H^+}{0.0222\ M\ HC_9H_7O_4} \times 100 = 12\%$ ionization; the assumption is not valid

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

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

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

16.66 (a) $HC_3H_5O_2(aq) \rightleftharpoons H^+(aq) + C_3H_5O_2^-(aq)$

$$K_a = 1.3 \times 10^{-5} = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{x^2}{0.250-x}$$

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

$$\% \text{ ionization} = \frac{1.803 \times 10^{-3}\ M H^+}{0.250\ M\ HC_3H_5O_2} \times 100 = 0.721\%$$

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

$$\% \text{ ionization} = \frac{1.020 \times 10^{-3}\ M H^+}{0.0800\ M HC_3H_5O_2} \times 100 = 1.27\%$$

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

$$\%\ \text{ionization} = \frac{5.099 \times 10^{-4}\ M\ H^+}{0.0200\ M\ HC_3H_5O_2} \times 100 = 2.55\%$$

16.68 $HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$; $K_a = \frac{[H^+][X^-]}{[HX]}$

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

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

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 $\log [HX]$.

16.70 $H_2C_4H_4O_6(aq) \rightleftharpoons H^+(aq) + HC_4H_4O_6^-(aq)$ $K_{a1} = 1.0 \times 10^{-3}$

$HC_4H_4O_6^-(aq \rightleftharpoons H^+(aq) + C_4H_4O_6^{2-}(aq)$ $K_{a2} = 4.6 \times 10^{-5}$

Begin by calculating the $[H^+]$ from the first ionization. The equilibrium concentrations are $[H^+] = [HC_4H_4O_6^-] = x$, $[H_2C_4H_4O_6] = 0.25 - x$.

$$K_{a1} = \frac{[H^+][HC_4H_4O_6^-]}{[H_2C_4H_4O_8]} = \frac{x^2}{0.25 - x};\ x^2 + 1.0 \times 10^{-3}\ x - 2.5 \times 10^{-4} = 0$$

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

	$HC_4H_4O_6^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$C_4H_4O_6^{2-}(aq)$
initial	0.015		0.015		0
equil.	(0.015 – y)		(0.015 + y)		y

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

$y = 4.6 \times 10^{-5}\ M\ HC_4H_4O_6^{2-}(aq)$

This assumption is reasonable, since 4.6×10^{-5} is only 0.3% of 0.015. $[H^+] = 0.015\ M$ (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 $[H^+]$. Thus, 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 $[H^+]$ and pH.

Weak Bases

16.72 Organic amines (neutral molecules with nonbonded pairs on N atoms) and anions that are the conjugate bases of weak acids function as weak bases.

16.74 (a) $C_3H_7NH_2(aq) + H_2O(l) \rightleftharpoons C_3H_7NH_3^+(aq) + OH^-(aq)$; $K_b = \dfrac{[C_3H_7NH_3^+][OH^-]}{[C_3H_7NH_2]}$

(b) $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$; $K_b = \dfrac{[H_2PO_4][OH^-]}{[HPO_4^{2-}]}$

(c) $C_6H_5CO_2^-(aq) + H_2O(l) \rightleftharpoons C_6H_5CO_2H(aq) + OH^-(aq)$; $K_b = \dfrac{[C_6H_5CO_2H][OH^-]}{[C_6H_5CO_2^-]}$

16.76

	$BrO^-(aq) + H_2O(l)$	$\rightleftharpoons$	$HOBr(aq)$	+	$OH^-(aq)$
initial	1.15 *M*		0		0
equil.	(1.15 – x) *M*		x *M*		x *M*

$$K_b = \frac{[HOBr][OH^-]}{[BrO^-]} = \frac{x^2}{1.15 - x} \approx \frac{x^2}{1.15} = 4.0 \times 10^{-6}$$

$x^2 = 1.15\,(4.0 \times 10^{-6})$; $x = [OH^-] = 2.14 \times 10^{-3} = 2.1 \times 10^{-3}\ M$; pH = 11.33

Check. $\dfrac{2.1 \times 10^{-3}\ M\ OH^-}{1.15\ M\ C_3H_5O_2^-} \times 100 = 0.19\%$ hydrolysis; the assumption is valid

16.78 (a) pOH = 14.00 - 9.95 = 4.05; $[OH^-] = 10^{-4.05} = 8.91 \times 10^{-6} = 8.9 \times 10^{-5}\ M$

	$C_{18}H_{21}NO_3(aq) + H_2O(1)$	$\rightleftharpoons$	$C_{18}H_{21}NO_3H^+(aq)$	+	$OH^-(aq)$
initial	0.0050 *M*		0		0
equil.	$(0.0050 - 8.9 \times 10^{-5})$		$8.9 \times 10^{-5}\ M$		$8.9 \times 10^{-5}\ M$

$$K_b = \frac{[C_{18}H_{21}NO_3H^+][OH^-]}{[C_{18}H_{21}NO_3]} = \frac{(8.91 \times 10^{-5})^2}{(0.0050 - 8.91 \times 10^{-5})} = 1.62 \times 10^{-5} = 1.6 \times 10^{-6}$$

(b) $pK_b = -\log(K_b) = -\log(1.62 \times 10^{-5}) = 5.79$

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

16.80 (a) We need K_a for the conjugate acid of CO_3^{2-}, K_a for HCO_3^-. K_a for HCO_3^- is K_{a2}.

(b) $K_b = K_w/K_a = 1.0 \times 10^{-14}/5.6 \times 10^{-11} = 1.8 \times 10^{-4}$

(c) K_b for CO_3^{2-} (1.8×10^{-4}) > K_b for NH_3 (1.8×10^{-5}).

CO_3^{2-} is a stronger base than NH_3.

16.82 (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 $NH_4^+ = K_w/K_b$ for $NH_3 = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

K_a for $HONH_3^+ = K_w/K_b$ for $HONH_2 = 1.0 \times 10^{-14}/1.1 \times 10^{-8} = 9.1 \times 10^{-7}$

Note that K_a for $HONH_3^+$ is larger than K_a for NH_4^+.

16.84 (a) Proceeding as in Solution 16.83(a):

	$F^-(aq) + H_2O(l)$	$\rightleftharpoons$	$HF(aq)$	+	$OH^-(aq)$
initial	0.085 *M*		0 *M*		0 *M*
equil	(0.085 – x) *M*		x *M*		x *M*

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

$$1.5 \times 10^{-11} = \frac{(x)(x)}{(0.085 - x)}; \text{ assume the amount of } F^- \text{ that hydrolyzes is small}$$

$x^2 = 0.085(1.47 \times 10^{-11})$; $x = [OH^-] = 1.118 \times 10^{-6} = 1.1 \times 10^{-6}$ *M*

pOH = 5.95; pH = 14 - 5.95 = 8.05

(b) $Na_2S(aq) \rightarrow S^{2-}(aq) + 2Na^+(aq)$

$S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$

As in part (a) above, $[OH^-] = [HS^-] = x$; $[S^{2-}] = 0.055$ *M*

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

Since $K_b >> 1$, the equilibrium above lies far to the right and $[OH^-] = [S^{2-}] = 0.055$ *M*. K_b for $HS^- = 1.05 \times 10^{-7}$; $[OH^-]$ produced by further hydrolysis of HS^- amounts to 7.6×10^{-5} *M*. The second hydrolysis step does not make a significant contribution to the total $[OH^-]$ and pH.

$[OH^-] = 0.055$ *M*; pOH = 1.26, pH = 12.74

(c) As in Solution 16.83(c), calculate total $[C_2H_3O_2^-]$.

$[C_2H_3O_2^-]_t = [C_2H_3O_2^-]$ from $NaC_2H_3O_2$ + $[C_2H_3O_2^-]$ from $Ba(C_2H_3O_2)_2$

$[C_2H_3O_2^-]_t = 0.045\ M + 2(0.055\ M) = 0.155\ M$

The hydrolysis equilibrium is $C_2H_3O_2^-(aq) + H_2O(l) \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{K_w}{K_a \text{ for } HC_2H_3O_2} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

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

$[OH^-] = [HC_2H_3O_2] = x$, $[C_2H_3O_2^-] = 0.155 - x$

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

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

pH = 14 + log (9.280×10^{-6}) = 8.97

16.86 (a) acidic; Cr^{3+} is a highly charged metal cation and a Lewis acid; Br^- is negligible.

(b) neutral; both Li^+ and I^- are negligible.

(c) basic; PO_4^{3-} is the conjugate base of HPO_4^{2-}; K^+ is negligible.

(d) acidic; $CH_3NH_3^+$ is the conjugate acid of CH_3NH_2; Cl^- is negligible.

(e) acidic; HSO_4^- is a negligible base, but a fairly strong acid ($K_a = 1.2 \times 10^{-2}$). K^+ is negligible.

16.88 *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.

16.90 The solution is basic because of the hydrolysis of PO_4^{3-}. The molarity of PO_4^{3-} is

$$\frac{45.0\text{ g Na}_3\text{PO}_4}{1.00\text{ L soln}} \times \frac{1\text{ mol Na}_3\text{PO}_4}{163.9\text{ g Na}_3\text{PO}_4} = 0.2746 = 0.275\ M\ \text{PO}_4^{3-}$$

$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq)$$

$$K_b = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = \frac{K_w}{K_a \text{ for } HPO_4^{2-}} = \frac{1.0 \times 10^{-14}}{4.2 \times 10^{-13}} = 0.0238 = 2.4 \times 10^{-2}$$

Ignoring the further hydrolysis of HPO_4^{2-},

$[OH^-] = [HPO_4^{2-}] = x$, $[PO_4^{3-}] = 0.275 - x$

$$2.4 \times 10^{-2} = \frac{x^2}{(0.275 - x)};\ x^2 + 2.4 \times 10^{-2}\,x - 0.0065 = 0$$

Since K_b is relatively large, we will not assume x is small compared to 0.275.

$$x = \frac{-0.024 \pm \sqrt{(0.024)^2 - 4(1)(-0.0065)}}{2(1)} = \frac{-0.024 \pm \sqrt{0.0267}}{2(1)}$$

$x = 0.070\ M\ OH^-$; pH = 14 + log (0.070) = 12.84

Acid-Base Character and Chemical Structure

16.92 (a) Acid strength increases as the polarity of the X–H bond increases and decreases as the strength of the X–H bond increases.

(b) Assuming the element, X, is more electronegative than H, as the electronegativity of X increases, the X–H bond becomes more polar and the strength of the acid increases. This trend holds true as electronegativity increases across a row of the periodic chart. However, as electronegativity decreases going down a family, acid strength increases because the strength of the H–X bond decreases, even though the H–X bond becomes less polar.

16.94 (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 $H_2C_2O_4$ is a stronger acid than $HC_2O_4^-$.

(e) The conjugate base of benzoic acid, $C_7H_5O_2^-$, is stabilized by resonance, while the conjugate base of phenol, $C_6H_5O^-$, is not. $HC_7H_5O_2$ has greater tendency to form its conjugate base and is the stronger acid.

16.96 (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^+.)

16.98 (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

16.100 No. If a substance is a Lewis acid, it is not necessarily a Brønsted 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 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.

16.102

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

16.104 (a) $ZnBr_2$, smaller cation radius, same charge

(b) $Cu(NO_3)_2$, higher cation charge

(c) $NiBr_2$, smaller cation radius, same charge

Additional Exercises

16.106 (a) Correct.

(b) Incorrect. A Brønsted 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.

16.108 Assume T = 25°C. For acid or base solute concentrations less than 1×10^{-6} *M*, we must consider the autoionization of water as a source of $[OH^-]$ and $[H^+]$.

	$H_2O(l)$	$\rightleftharpoons$	$[H^+]$	+	$[OH^-]$
initial	C		0		$2.5 \times 10^{-9}\ M$
equil	C		x		$(x + 2.5 \times 10^{-9})\ M$

$K_w = 1.0 \times 10^{-14} = [H^+][OH^-] = (x)(x + 2.5 \times 10^{-9});\ x^2 + 2.5 \times 10^{-9}\,x - 1.0 \times 10^{-14} = 0$

From the quadratic formula, $x = \dfrac{-2.5 \times 10^{-9} \pm \sqrt{(2.5 \times 10^{-9})^2 - 4(-1 \times 10^{-14})}}{2}$

$= 9.876 \times 10^{-6} = 9.9 \times 10^{-6}\ M\ H^+$

$[H^+] = 9.9 \times 10^{-8}\ M;\ [OH^-] = (9.9 \times 10^{-8} + 2.5 \times 10^{-9}) = 1.013 \times 10^{-7} = 1.0 \times 10^{-7}\ M$

pH = 7.0054 = 7.01

Check: $[9.876 \times 10^{-8}][1.013 \times 10^{-7}] = 1.0 \times 10^{-14}$. Our answer makes sense. The very small concentration of OH^- from the solute raises the solution pH to slightly more than 7.

16.109 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 $K_a = 8 \times 10^{-5}$ 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.

16.111 (a) $H_2X \rightarrow H^+ + HX^-$

Assuming HX^- does not ionize, $[H^+] = 0.050\ M$, pH = 1.30

(b) $H_2X \rightarrow 2H^+ + X^-$; $0.050\ M\ H_2X = 0.10\ M\ H^+$; pH = 1.00

(c) The observed pH of a 0.050 *M* solution of H_2X is only slightly less than 1.30, the pH assuming no ionization of HX^-. HX^- is not completely ionized; H_2X, which is completely ionized, is a stronger acid than HX^-.