Exercises

Nature of Acids and Bases

27.   a. $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$. Only the forward reaction is indicated since $HClO_4$ is a strong acid and is basically 100% dissociated in water. For acids, the dissociation reaction is commonly written without water as a reactant. The common abbreviation for this reaction is: $HClO_4(aq) \rightarrow H^+(aq) + ClO_4^-$ (aq). This reaction is also called the K_a reaction as the equilibrium constant for this reaction is called K_a.

     b. Propanoic acid is a weak acid, so it is only partially dissociated in water. The dissociation reaction is: $CH_3CH_2CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH_2CO_2^-$ (aq) or
$CH_3CH_2CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CH_2CO^-(aq)$.

     c. NH_4^+ is a weak acid. Similar to propanoic acid, the dissociation reaction is:

        $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$ or $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$

28.   The dissociation reaction (the K_a reaction) of an acid in water commonly omits water as a reactant. We will follow this practice. All dissociation reactions produce H^+ and the conjugate base of the acid that is dissociated.

     a. $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ $K_a = \dfrac{[H^+][CN^-]}{[HCN]}$

     b. $C_6H_5OH(aq) \rightleftharpoons H^+(aq) + C_6H_5O^-(aq)$ $K_a = \dfrac{[H^+][C_6H_5O^-]}{[C_6H_5OH]}$

     c. $C_6H_5NH_3^+(aq) \rightleftharpoons H^+(aq) + C_6H_5NH_2(aq)$ $K_a = \dfrac{[H^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$

29.   An acid is a proton (H^+) donor and a base is a proton acceptor. A conjugate acid-base pair differs by only a proton (H^+).

	Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a.	H_2CO_3	H_2O	HCO_3^-	H_3O^+
b.	$C_5H_5NH^+$	H_2O	C_5H_5N	H_3O^+
c.	$C_5H_5NH^+$	HCO_3^-	C_5H_5N	H_2CO_3

30.

	Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a.	$Al(H_2O)_6^{3+}$	H_2O	$Al(H_2O)_5(OH)^{2+}$	H_3O^+

	b.	$HONH_3^+$	H_2O	$HONH_2$	H_3O^+
	c.	$HOCl$	$C_6H_5NH_2$	OCl^-	$C_6H_5NH_3^+$

31. Strong acids have a $K_a \gg 1$ and weak acids have $K_a < 1$. Table 14.2 in the text lists some K_a values for weak acids. K_a values for strong acids are hard to determine so they are not listed in the text. However, there are only a few common strong acids so if you memorize the strong acids, then all other acids will be weak acids. The strong acids to memorize are HCl, HBr, HI, HNO_3, $HClO_4$ and H_2SO_4.

   a. $HClO_4$ is a strong acid.

   b. $HOCl$ is a weak acid ($K_a = 3.5 \times 10^{-8}$).

   c. H_2SO_4 is a strong acid.

   d. H_2SO_3 is a weak diprotic acid with K_{a1} and K_{a2} values less than one.

32. The beaker on the left represents a strong acid in solution; the acid, HA, is 100% dissociated into the H^+ and A^- ions. The beaker on the right represents a weak acid in solution; only a little bit of the acid, HB, dissociates into ions, so the acid exists mostly as undissociated HB molecules in water.

   a. HNO_2: weak acid beaker
   b. HNO_3: strong acid beaker
   c. HCl: strong acid beaker
   d. HF: weak acid beaker
   e. $HC_2H_3O_2$: weak acid beaker

33. The K_a value is directly related to acid strength. As K_a increases, acid strength increases. For water, use K_w when comparing the acid strength of water to other species. The K_a values are:

   $HClO_4$: strong acid ($K_a \gg 1$); $HClO_2$: $K_a = 1.2 \times 10^{-2}$

   NH_4^+: $K_a = 5.6 \times 10^{-10}$; H_2O: $K_a = K_w = 1.0 \times 10^{-14}$

   From the K_a values, the ordering is: $HClO_4 > HClO_2 > NH_4^+ > H_2O$.

34. Except for water, these are the conjugate bases of the acids in the previous exercise. In general, the weaker the acid, the stronger the conjugate base. ClO_4^- is the conjugate base of a strong acid; it is a terrible base (worse than water). The ordering is: $NH_3 > ClO_2^- > H_2O > ClO_4^-$

35. a. HCl is a strong acid and water is a very weak acid with $K_a = K_w = 1.0 \times 10^{-14}$. HCl is a much stronger acid than H_2O.

   b. H_2O, $K_a = K_w = 1.0 \times 10^{-14}$; HNO_2, $K_a = 4.0 \times 10^{-4}$; HNO_2 is a stronger acid than H_2O because K_a for $HNO_2 > K_w$ for H_2O.

   c. HOC_6H_5, $K_a = 1.6 \times 10^{-10}$; HCN, $K_a = 6.2 \times 10^{-10}$; HCN is a stronger acid than HOC_6H_5 because K_a for $HCN > K_a$ for HOC_6H_5.

36. a. H_2O; The conjugate bases of strong acids are terrible bases ($K_b < 10^{-14}$).

b. NO_2^-; The conjugate bases of weak acids are weak bases ($10^{-14} < K_b < 1$).

c. $OC_6H_5^-$; For a conjugate acid-base pair, $K_a \times K_b = K_w$. From this relationship, the stronger the acid the weaker the conjugate base (K_b decreases as K_a increases). Because HCN is a stronger acid than HOC_6H_5 (K_a for HCN > K_a for HOC_6H_5), $OC_6H_5^-$ will be a stronger base than CN^-.

Autoionization of Water and the pH Scale

37. At 25°C, the relationship: $[H^+]\,[OH^-] = K_w = 1.0 \times 10^{-14}$ always holds for aqueous solutions. When $[H^+]$ is greater than $1.0 \times 10^{-7}\,M$, the solution is acidic; when $[H^+]$ is less than $1.0 \times 10^{-7}\,M$, the solution is basic; when $[H^+] = 1.0 \times 10^{-7}\,M$, the solution is neutral. In terms of $[OH^-]$, an acidic solution has $[OH^-] < 1.0 \times 10^{-7}\,M$, a basic solution has $[OH^-] > 1.0 \times 10^{-7}\,M$, and a neutral solution has $[OH^-] = 1.0 \times 10^{-7}\,M$.

a. $[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\,M$; The solution is neutral.

b. $[OH^-] = \dfrac{1.0 \times 10^{-14}}{8.3 \times 10^{-16}} = 12\,M$; The solution is basic.

c. $[OH^-] = \dfrac{1.0 \times 10^{-14}}{12} = 8.3 \times 10^{-16}\,M$; The solution is acidic.

d. $[OH^-] = \dfrac{1.0 \times 10^{-14}}{5.4 \times 10^{-5}} = 1.9 \times 10^{-10}\,M$; The solution is acidic.

39. a. Because the value of the equilibrium constant increases as the temperature increases, the reaction is endothermic. In endothermic reactions, heat is a reactant so an increase in temperature (heat) shifts the reaction to produce more products and increases K in the process.

b. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ $K_w = 5.47 \times 10^{-14} = [H^+][OH^-]$ at 50.°C

In pure water $[H^+] = [OH^-]$, so $5.47 \times 10^{-14} = [H^+]^2$, $[H^+] = 2.34 \times 10^{-7}\,M = [OH^-]$

43. a. pOH = 14.00 - 6.88 = 7.12; $[H^+] = 10^{-6.88} = 1.3 \times 10^{-7}\,M$

$[OH^-] = 10^{-7.12} = 7.6 \times 10^{-8}\,M$; acidic

b. $[H^+] = \dfrac{1.0 \times 10^{-14}}{8.4 \times 10^{-14}} = 0.12\,M$; pH = -log(0.12) = 0.92

pOH = 14.00 – 0.92 = 13.08; acidic

c. pH = 14.00 – 3.11 = 10.89; $[H^+] = 10^{-10.89} = 1.3 \times 10^{-11}\,M$

$[OH^-] = 10^{-3.11} = 7.8 \times 10^{-4}\ M$; basic

d. $pH = -\log(1.0 \times 10^{-7}) = 7.00$; $pOH = 14.00 - 7.00 = 7.00$

$[OH^-] = 10^{-7.00} = 1.0 \times 10^{-7}\ M$; neutral

47. All the acids in this problem are strong acids that are always assumed to completely dissociate in water. The general dissociation reaction for a strong acid is: $HA(aq) \rightarrow H^+(aq) + A^-(aq)$ where A^- is the conjugate base of the strong acid HA. For 0.250 M solutions of these strong acids,
0.250 M H^+ and 0.250 M A^- are present when the acids completely dissociate. The amount of H^+ donated from water will be insignificant in this problem since H_2O is a very weak acid.

a. Major species present after dissociation = H^+, ClO_4^- and H_2O;

$pH = -\log[H^+] = -\log(0.250) = 0.602$

b. Major species = H^+, NO_3^- and H_2O; $pH = 0.602$

49. Both are strong acids.

$0.0500\ L \times 0.050\ mol/L = 2.5 \times 10^{-3}\ mol\ HCl = 2.5 \times 10^{-3}\ mol\ H^+ + 2.5 \times 10^{-3}\ mol\ Cl^-$

$0.1500\ L \times 0.10\ mol/L = 1.5 \times 10^{-2}\ mol\ HNO_3 = 1.5 \times 10^{-2}\ mol\ H^+ + 1.5 \times 10^{-2}\ mol$ NO_3^-

$$[H^+] = \frac{(2.5 \times 10^{-3} + 1.5 \times 10^{-2})\ mol}{0.2000\ L} = 0.088\ M;\quad [OH^-] = \frac{K_w}{[H^+]} = 1.1 \times 10^{-13}\ M$$

$$[Cl^-] = \frac{2.5 \times 10^{-3}\ mol}{0.2000\ L} = 0.013\ M;\quad [NO_3^-] = \frac{1.5 \times 10^{-2}\ mol}{0.2000\ L} = 0.075\ M$$

51. $[H^+] = 10^{-1.50} = 3.16 \times 10^{-2}\ M$ (carrying one extra sig fig); $M_1V_1 = M_2V_2$

$$V_1 = \frac{M_2V_2}{M_1} = \frac{3.16 \times 10^{-2}\ mol/L \times 1.6\ L}{12\ mol/L} = 4.2 \times 10^{-3}\ L$$

To 4.2 mL of 12 M HCl, add enough water to make 1600 mL of solution. The resulting solution will have $[H^+] = 3.2 \times 10^{-2}\ M$ and pH = 1.50.

53. a. HNO_2 ($K_a = 4.0 \times 10^{-4}$) and H_2O ($K_a = K_w = 1.0 \times 10^{-14}$) are the major species. HNO_2 is a much stronger acid than H_2O so it is the major source of H^+. However, HNO_2 is a weak acid ($K_a < 1$) so it only partially dissociates in water. We must solve an equilibrium problem to determine $[H^+]$. In the Solutions Guide, we will summarize the initial, change and equilibrium concentrations into one table called the ICE table. Solving the weak acid problem:
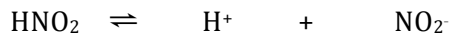
$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

Initial   0.250 M ~0   0
               x mol/L HNO_2 dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil.   0.250 $-x$ x x

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = 4.0 \times 10^{-4} = \frac{x^2}{0.250 - x} ;\ \text{If we assume } x << 0.250, \text{ then:}$$

$$4.0 \times 10^{-4} \approx \frac{x^2}{0.250}, \quad x = \sqrt{4.0 \times 10^{-4}\,(0.250)} = 0.010\ M$$

We must check the assumption: $\dfrac{x}{0.250} \times 100 = \dfrac{0.010}{0.250} \times 100 = 4.0\%$

All the assumptions are good. The H^+ contribution from water $(10^{-7}\ M)$ is negligible, and x is small compared to 0.250 (percent error = 4.0%). If the percent error is less than 5% for an assumption, we will consider it a valid assumption (called the 5% rule). Finishing the problem: $x = 0.010\ M = [H^+]$; pH = -log(0.010) = 2.00

b. CH_3CO_2H ($K_a = 1.8 \times 10^{-5}$) and H_2O ($K_a = K_w = 1.0 \times 10^{-14}$) are the major species. CH_3CO_2H is the major source of H^+. Solving the weak acid problem:
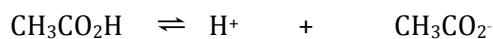
$$CH_3CO_2H \ \rightleftharpoons\ H^+ \ + \ CH_3CO_2^-$$

Initial   0.250 M ~0   0
               x mol/L CH_3CO_2H dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$
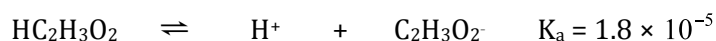Equil.   0.250 $- x$ x x

$$K_a = \frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad (\text{assuming } x << 0.250)$$

$x = 2.1 \times 10^{-3}\ M$; Checking assumption: $\dfrac{2.1 \times 10^{-3}}{0.250} \times 100 = 0.84\%$. Assumptions

good.

$[H^+] = x = 2.1 \times 10^{-3}\ M$; pH = -log (2.1×10^{-3}) = 2.68

55. $[CH_3COOH]_0 = [HC_2H_3O_2]_0 = \dfrac{0.0560\ \text{g } HC_2H_3O_2 \times \dfrac{1\ \text{mol } HC_2H_3O_2}{60.05\ \text{g}}}{0.05000\ \text{L}} = 1.87 \times 10^{-2}\ M$

$$HC_2H_3O_2 \ \rightleftharpoons\ H^+ \ + \ C_2H_3O_2^- \qquad K_a = 1.8 \times 10^{-5}$$

Initial   0.0187 M ~0   0
               x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$

Equil.   0.0187 - x x x

$K_a = 1.8 \times 10^{-5} = \dfrac{[H^+][C_2H_3O_2^-]}{[HC_3H_3O_2]} = \dfrac{x^2}{0.0187 - x} \approx \dfrac{x^2}{0.0187}$

$x = [H^+] = 5.8 \times 10^{-4}\ M$; pH = 3.24   Assumptions good (x is 3.1% of 0.0187).

$[H^+] = [C_2H_3O_2^-] = [CH_3COO^-] = 5.8 \times 10^{-4}\ M$; $[CH_3COOH] = 0.0187 - 5.8 \times 10^{-4}$
$= 0.0181\ M$

57.   This is a weak acid in water. Solving the weak acid problem:

HF $\rightleftharpoons$ H+   +   F- $K_a = 7.2 \times 10^{-4}$

Initial   0.020 M ~0   0
            x mol/L HF dissociates to reach equilibrium
Change   -x $\rightarrow$ +x +x
Equil.   0.020 - x x x

$K_a = 7.2 \times 10^{-4} = \dfrac{[H^+][F^-]}{[HF]} = \dfrac{x^2}{0.020 - x} \approx \dfrac{x^2}{0.020}$ (assuming $x \ll 0.020$)

$x = [H^+] = 3.8 \times 10^{-3}\ M$; Check assumptions: $\dfrac{x}{0.020} \times 100 = \dfrac{3.8 \times 10^{-3}}{0.020} = 19\%$

The assumption $x \ll 0.020$ is not good (x is more than 5% of 0.020). We must solve
$x^2/(0.020 - x) = 7.2 \times 10^{-4}$ exactly by using either the quadratic formula or by the method of successive approximations (see Appendix 1.4 of text). Using successive approximations, we let 0.016 M be a new approximation for [HF]. That is, in the denominator, try x = 0.0038 (the value of x we calculated making the normal assumption), so 0.020 - 0.0038 = 0.016, then solve for a new value of x in the numerator.

$\dfrac{x^2}{0.020 - x} \approx \dfrac{x^2}{0.016} = 7.2 \times 10^{-4}$, $x = 3.4 \times 10^{-3}$

We use this new value of x to further refine our estimate of [HF], i.e., 0.020 - x = 0.020 - 0.0034 = 0.0166 (carry extra significant figure).

$\dfrac{x^2}{0.020 - x} \approx \dfrac{x^2}{0.0166} = 7.2 \times 10^{-4}$, $x = 3.5 \times 10^{-3}$

We repeat until we get an answer that repeats itself. This would be the same answer we would get solving exactly using the quadratic equation. In this case it is: $x = 3.5 \times 10^{-3}$

So: $[H^+] = [F^-] = x = 3.5 \times 10^{-3}\ M$; $[OH^-] = K_w/[H^+] = 2.9 \times 10^{-12}\ M$

[HF] = 0.020 - x = 0.020 - 0.0035 = 0.017 M; pH = 2.46

Note: When the 5% assumption fails, use whichever method you are most comfortable with to solve exactly. The method of successive approximations is probably fastest when the percent error is less than ~25% (unless you have a calculator that can solve quadratic equations).

59.   Major species: $HC_2H_2ClO_2$ (K_a = 1.35 × 10^{-3}) and H_2O; Major source of H^+: $HC_2H_2ClO_2$

$$HC_2H_2ClO_2 \;\rightleftharpoons\; H^+ \;+\; C_2H_2ClO_2^-$$

Initial	0.10 M	~0	0

x mol/L $HC_2H_2ClO_2$ dissociates to reach equilibrium

Change	-x	→	+x	+x
Equil.	0.10- x		x	x

K_a = 1.35 × 10^{-3} = $\dfrac{x^2}{0.10 - x}$ ☞ $\dfrac{x^2}{0.10}$, x = 1.2 × 10^{-2} M

Checking the assumptions finds that x is 12% of 0.10 which fails the 5% rule. We must solve 1.35 × 10^{-3} = x^2/(0.10 - x) exactly using either the method of successive approximations or the quadratic equation. Using either method gives x = [H^+] = 1.1 × 10^{-2} M. pH = -log [H^+] = -log (1.1 × 10^{-2}) = 1.96.

61.   a. HCl is a strong acid. It will produce 0.10 M H^+. HOCl is a weak acid. Let's consider the equilibrium:
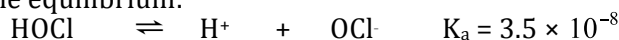
$$HOCl \;\rightleftharpoons\; H^+ \;+\; OCl^- \qquad K_a = 3.5 × 10^{-8}$$

Initial	0.10 M	0.10 M	0

x mol/L HOCl dissociates to reach equilibrium

Change	-x	→	+x	+x
Equil.	0.10 - x	0.10 + x		x

K_a = 3.5 × 10^{-8} = $\dfrac{[H^+][OCl^-]}{[HOCl]}$ = $\dfrac{(0.10 + x)(x)}{0.10 - x}$ ≈ x, x = 3.5 × 10^{-8} M

Assumptions are great (x is 3.5 × 10^{-5}% of 0.10). We are really assuming that HCl is the only important source of H^+, which it is. The [H^+] contribution from HOCl, x, is negligible. There-fore, [H^+] = 0.10 M; pH = 1.00

b. HNO_3 is a strong acid, giving an initial concentration of H^+ equal to 0.050 M. Consider the equilibrium:

$$HC_2H_3O_2 \;\rightleftharpoons\; H^+ \;+\; C_2H_3O_2^- \qquad K_a = 1.8 × 10^{-5}$$
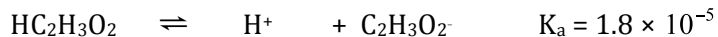
Initial	0.50 M	0.050 M	0

x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium

Change	-x	→	+x	+x
Equil.	0.50 - x	0.050 + x		x

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(0.050 + x)x}{0.50 - x} \approx \frac{0.050\ x}{0.50}$$

$x = 1.8 \times 10^{-4}$; Assumptions are good (well within the 5% rule).

$[H^+] = 0.050 + x = 0.050\ M$ and pH = 1.30

63. In all parts of this problem, acetic acid ($HC_2H_3O_2$) is the best weak acid present. We must solve a weak acid problem.
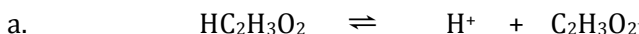
a. $\qquad HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$

Initial	0.50 M	~0	0

x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	0.50 - x		x	x

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

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

$$\text{Percent dissociation} = \frac{[H^+]}{[HC_2H_3O_2]_0} \times 100 = \frac{3.0 \times 10^{-3}}{0.50} \times 100 = 0.60\%$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

65. Let HX symbolize the weak acid. Setup the problem like a typical weak acid equilibrium problem.

	HX	$\rightleftharpoons$	H+	+	X-
Initial	0.15 M		~0		0

x mol/L HX dissociates to reach equilibrium

Change	-x	$\rightarrow$	+x		+x
Equil.	0.15 - x		x		x

If the acid is 3.0% dissociated, then $x = [H^+]$ is 3.0% of 0.15: $x = 0.030 \times (0.15\ M) = 4.5 \times 10^{-3}\ M$. Now that we know the value of x, we can solve for K_a.

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{x^2}{0.15 - x} = \frac{(4.5 \times 10^{-3})^2}{0.15 - 4.5 \times 10^{-3}} = 1.4 \times 10^{-4}$$

67. Setup the problem using the K_a equilibrium reaction for HOCN.

	HOCN	$\rightleftharpoons$	H+	+	OCN-
Initial	0.0100 M		~0		0

x mol/L HOCN dissociates to reach equilibrium

Change	-x	$\rightarrow$	+x		+x
Equil.	0.0100 - x		x		x

$$K_a = \frac{[H^+][OCN^-]}{[HOCN]} = \frac{x^2}{0.0100 - x} \quad ; \quad pH = 2.77: \quad x = [H^+] = 10^{-pH} = 10^{-2.77} = 1.7 \times 10^{-3}\ M$$

$$K_a = \frac{(1.7 \times 10^{-3})^2}{0.0100 - 1.7 \times 10^{-3}} = 3.5 \times 10^{-4}$$

69.   Major species: HCOOH and H_2O; Major source of H^+: HCOOH

	HCOOH	$\rightleftharpoons$	H^+	+	$HCOO^-$

Initial   C   ~0   0   where C = $[HCOOH]_o$
                    x mol/L HCOOH dissociates to reach equilibrium
Change   -x $\rightarrow$ +x +x
Equil.   C - x x x
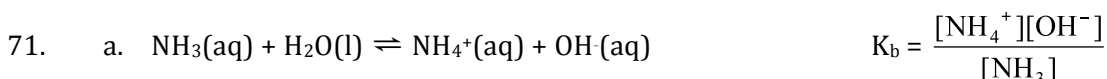
$$K_a = 1.8 \times 10^{-4} = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{x^2}{C - x} \text{ where } x = [H^+]$$

$$1.8 \times 10^{-4} = \frac{[H^+]^2}{C - [H^+]}; \quad pH = 2.70, \text{ so: } [H^+] = 10^{-2.70} = 2.0 \times 10^{-3} M$$

$$1.8 \times 10^{-4} = \frac{(2.0 \times 10^{-3})^2}{C - (2.0 \times 10^{-3})}, \quad C - (2.0 \times 10^{-3}) = \frac{4.0 \times 10^{-6}}{1.8 \times 10^{-4}}, \quad C = 2.4 \times 10^{-2} M$$

A 0.024 M formic acid solution will have pH = 2.70.

Solutions of Bases

71.   a. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ $K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$

       b. $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$ $K_b =$

$$\frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

73. NO_3^-: $K_b << K_w$ since HNO_3 is a strong acid. All conjugate bases of strong acids have
       no base strength. H_2O: $K_b = K_w = 1.0 \times 10^{-14}$; NH_3: $K_b = 1.8 \times 10^{-5}$; C_5H_5N: $K_b = 1.7 \times 10^{-9}$

       $NH_3 > C_5H_5N > H_2O > NO_3^-$ (As K_b increases, base strength increases.)
75.   a. $C_6H_5NH_2$ b. $C_6H_5NH_2$ c. OH^- d. CH_3NH_2

       The base with the largest K_b value is the strongest base ($K_{b, C_6H_5NH_2} = 3.8 \times 10^{-10}$,

K_{b, CH_3NH_2} = 4.4 10^{-4}. OH⁻ is the strongest base possible in water.

77.   NaOH(aq) → Na⁺(aq) + OH⁻ (aq); NaOH is a strong base which completely dissociates into Na⁺ and OH⁻. The initial concentration of NaOH will equal the concentration of OH⁻ donated by NaOH.

   a.   [OH⁻] = 0.10 M; pOH = -log[OH⁻] = -log(0.10) = 1.00

   pH = 14.00 - pOH = 14.00 - 1.00 = 13.00

   Note that H_2O is also present, but the amount of OH⁻ produced by H_2O will be insignificant compared to the 0.10 M OH⁻ produced from the NaOH.

   b.   The [OH⁻] concentration donated by the NaOH is 1.0 × 10^{-10} M. Water by itself donates
   1.0 × 10^{-7} M. In this problem, water is the major OH⁻ contributor and [OH⁻] = 1.0 × 10^{-7} M.

   pOH = -log (1.0 × 10^{-7}) = 7.00; pH = 14.00 - 7.00 = 7.00

   c.   [OH⁻] = 2.0 M; pOH = -log (2.0) = -0.30; pH = 14.00 - (-0.30) = 14.30

79.   a.   Major species: K⁺, OH⁻, H_2O (KOH is a strong base.)

   [OH⁻] = 0.015 M, pOH = -log (0.015) = 1.82; pH = 14.00 - pOH = 12.18

   b.   Major species: Ba²⁺, OH⁻, H_2O; Ba(OH)₂(aq) → Ba²⁺(aq) + 2 OH⁻ (aq); Since each mol of the strong base Ba(OH)₂ dissolves in water to produce two mol OH⁻, then [OH⁻] =
   2(0.015 M) = 0.030 M.

   pOH = -log (0.030) = 1.52; pH =14.00 - 1.52 = 12.48

81.   pOH = 14.00 – 11.56 = 2.44; [OH⁻] = [KOH] = $10^{-2.44}$ = 3.6 × 10^{-3} M

   $$0.8000 \text{ L} \times \frac{3.6 \times 10^{-3} \text{ mol KOH}}{\text{L}} \times \frac{56.11 \text{ g KOH}}{\text{mol KOH}} = 0.16 \text{ g KOH}$$

83. NH_3 is a weak base with K_b = 1.8 × 10^{-5}. The major species present will be NH_3 and H_2O (K_b = K_w = 1.0 × 10^{-14}). Since NH_3 has a much larger K_b value compared to H_2O, NH_3 is the stronger base present and will be the major producer of OH⁻. To determine the amount of OH⁻ produced from NH_3, we must perform an equilibrium calculation.

$$NH_3(aq) \ + \ H_2O(l) \ \rightleftharpoons \ NH_4^+(aq) \ + \ OH^-(aq)$$
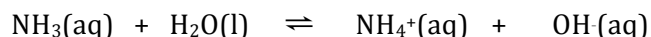
Initial	0.150 M	0	~0
	x mol/L NH_3 reacts with H_2O to reach equilibrium		
Change	-x	→ +x	+x
Equil.	0.150 - x	x	x

$K_b = 1.8 \times 10^{-5} = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{x^2}{0.150 - x} \approx \dfrac{x^2}{0.150}$ (assuming $x \ll 0.150$)

$x = [OH^-] = 1.6 \times 10^{-3} M$; Check assumptions: x is 1.1% of 0.150 so the assumption $0.150 - x \approx 0.150$ is valid by the 5% rule. Also, the contribution of OH- from water will be insignificant (which will usually be the case). Finishing the problem, pOH = -log $[OH^-]$ = -log $(1.6 \times 10^{-3} M)$ = 2.80; pH = 14.00 - pOH = 14.00 - 2.80 = 11.20.

85.   These are solutions of weak bases in water. We must solve the equilibrium weak base problem.

a. $(C_2H_5)_3N$ + H_2O $\rightleftharpoons$ $(C_2H_5)_3NH^+$ +   OH- $K_b = 4.0 \times 10^{-4}$
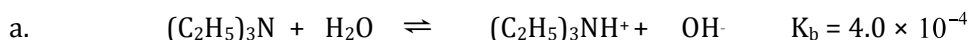
        Initial   0.20 M 0   ~0
                     x mol/L of $(C_2H_5)_3N$ reacts with H_2O to reach equilibrium
        Change   -x $\rightarrow$ +x +x
        Equil.   0.20 - x x x

              $K_b = 4.0 \times 10^{-4} = \dfrac{[(C_2H_5)_3NH^+][OH^-]}{[(C_2H_5)_3N]} = \dfrac{x^2}{0.20 - x} \approx \dfrac{x^2}{0.20}$, $x = [OH^-] = 8.9 \times$

$10^{-3} M$

        Assumptions good (x is 4.5% of 0.20). $[OH^-] = 8.9 \times 10^{-3}$ M

        $[H^+] = \dfrac{K_w}{[OH^-]} = \dfrac{1.0 \times 10^{-14}}{8.9 \times 10^{-3}} = 1.1 \times 10^{-12} M$; pH = 11.96

b. $HONH_2$ + H_2O $\rightleftharpoons$ $HONH_3^+$ +   OH- $K_b = 1.1 \times 10^{-8}$

        Initial   0.20 M 0   ~0
        Equil.   0.20 - x x x

        $K_b = 1.1 \times 10^{-8} = \dfrac{x^2}{0.20 - x} \approx \dfrac{x^2}{0.20}$, $x = [OH^-] = 4.7 \times 10^{-5} M$; Assumptions good.

        $[H^+] = 2.1 \times 10^{-10} M$; pH = 9.68

87.   This is a solution of a weak base in water. We must solve the weak base equilibrium problem.
                     $C_2H_5NH_2$ + H_2O $\rightleftharpoons$ $C_2H_5NH_3^+$ + OH- $K_b = 5.6 \times 10^{-4}$

        Initial   0.20 M 0   ~0
                     x mol/L $C_2H_5NH_2$ reacts with H_2O to reach equilibrium
        Change   -x $\rightarrow$ +x +x
        Equil.   0.20 - x x x

$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{x^2}{0.20-x} \approx \frac{x^2}{0.20} \quad \text{(assuming } x << 0.20)$$

$$x = 1.1 \times 10^{-2}; \text{ Checking assumption: } \frac{1.1 \times 10^{-2}}{0.20} \times 100 = 5.5\%$$

Assumption fails the 5% rule. We must solve exactly using either the quadratic equation or the method of successive approximations (see Appendix 1.4 of the text). Using successive approximations and carrying extra significant figures:

$$\frac{x^2}{0.20 - 0.011} = \frac{x^2}{0.189} = 5.6 \times 10^{-4}, \; x = 1.0 \times 10^{-2} \, M \quad \text{(consistent answer)}$$

$$x = [OH^-] = 1.0 \times 10^{-2} \, M; \; [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \, M; \; pH = 12.00$$
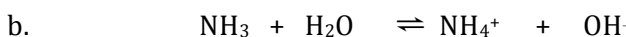
89.   To solve for percent ionization, just solve the weak base equilibrium problem.

    a. $NH_3 \; + \; H_2O \; \rightleftharpoons NH_4^+ \; + \; OH^- \qquad K_b = 1.8 \times 10^{-5}$

Initial 0.10 M   0   ~0
Equil. 0.10 - x x x

$$K_b = 1.8 \times 10^{-5} = \frac{x^2}{0.10-x} \approx \frac{x^2}{0.10}, \; x = [OH^-] = 1.3 \times 10^{-3} \, M; \; \text{Assumptions good.}$$

$$\text{Percent ionization} = \frac{[OH^-]}{[NH_3]_0} \times 100 = \frac{1.3 \times 10^{-3} \, M}{0.10 \, M} \times 100 = 1.3\%$$

    b. $NH_3 \; + \; H_2O \; \rightleftharpoons NH_4^+ \; + \; OH^-$
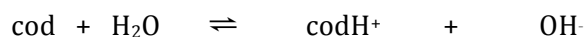
Initial   0.010 M   0   ~0
Equil.   0.010 - x x x

$$1.8 \times 10^{-5} = \frac{x^2}{0.010-x} \approx \frac{x^2}{0.010}, \; x = [OH^-] = 4.2 \times 10^{-4} \, M; \text{Assumptions good.}$$

$$\text{Percent ionization} = \frac{4.2 \times 10^{-4}}{0.010} \times 100 = 4.2\%$$

Note: For the same base, the percent ionization increases as the initial concentration of base decreases.

91.   Let cod = codeine, $C_{18}H_{21}NO_3$; using the K_b reaction to solve:

                $cod \; + \; H_2O \; \rightleftharpoons \; codH^+ \; + \; OH^-$

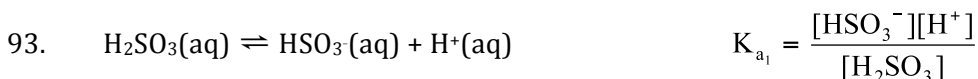Initial $1.7 \times 10^{-3} M$ 0   ~0

           x mol/L codeine reacts with H_2O to reach equilibrium

Change $-x$ $\rightarrow$ $+x$ $+x$

Equil. $1.7 \times 10^{-3} - x$ x x

$$K_b = \frac{x^2}{1.7 \times 10^{-3} - x}; \quad pH = 9.59; \text{ so: } pOH = 14.00 - 9.59 = 4.41.$$

$$[OH^-] = x = 10^{-4.41} = 3.9 \times 10^{-5} M; \; K_b = \frac{(3.9 \times 10^{-5})^2}{1.7 \times 10^{-3} - 3.9 \times 10^{-5}} = 9.2 \times 10^{-7}$$

Polyprotic Acids

93. $H_2SO_3(aq) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$ $K_{a_1} = \dfrac{[HSO_3^-][H^+]}{[H_2SO_3]}$

        $HSO_3^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H^+(aq)$ $K_{a_2} = \dfrac{[SO_3^{2-}][H^+]}{[HSO_3^-]}$

95.   In both these polyprotic acid problems, the dominate equilibrium is the K_{a_1} reaction. The amount of H^+ produced from the subsequent K_a reactions will be minimal since they are all have much smaller K_a values.

     a. H_3PO_4 $\rightleftharpoons H^+$ $+$ $H_2PO_4^-$ $K_{a_1} = 7.5 \times 10^{-3}$

        Initial $0.10 \, M$ ~0   0

             x mol/L H_3PO_4 dissociates to reach equilibrium

        Change $-x$ $\rightarrow$ $+x$ $+x$

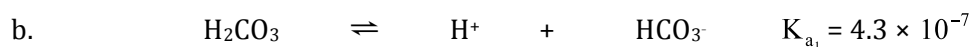   Equil. $0.10 - x$ x x

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, \; x = 2.7 \times 10^{-2}$$

        Assumption is bad (x is 27% of 0.10). Using successive approximations:

$$\frac{x^2}{0.10 - 0.027} = 7.5 \times 10^{-3}, \; x = 2.3 \times 10^{-2}; \; \frac{x^2}{0.10} = 7.5 \times 10^{-3}, \; x = 2.4 \times 10^{-2}$$

(consistent answer)

$$x = [H^+] = 2.4 \times 10^{-2} M; \; pH = -\log(2.4 \times 10^{-2}) = 1.62$$

     b. H_2CO_3 $\rightleftharpoons$ H^+ $+$ HCO_3^- $K_{a_1} = 4.3 \times 10^{-7}$
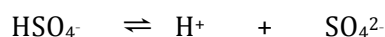
        Initial $0.10 \, M$ ~0   0

        Equil. $0.10 - x$ x x

$$K_{a_1} = 4.3 \times 10^{-7} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$x = [H^+] = 2.1 \times 10^{-4}\ M$; pH = 3.68; Assumptions good.

97. The dominant H^+ producer is the strong acid H_2SO_4. A 2.0 M H_2SO_4 solution produces 2.0 M HSO_4^- and 2.0 M H^+. However, HSO_4^- is a weak acid which could also add H^+ to the solution.

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$

Initial   2.0 M 2.0 M 0
            x mol/L HSO_4^- dissociates to reach equilibrium
Change   -x $\rightarrow$ +x +x
Equil.   2.0 - x 2.0 + x x

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(2.0 + x)(x)}{2.0 - x} \approx \frac{2.0\,(x)}{2.0}, \; x = 1.2 \times 10^{-2}$$

Because x is 0.60% of 2.0, the assumption is valid by the 5% rule. The amount of additional H^+ from HSO_4^- is 1.2×10^{-2}. The total amount of H^+ present is:

$$[H^+] = 2.0 + 1.2 \times 10^{-2} = 2.0\ M; \; pH = -\log(2.0) = -0.30$$

Note: In this problem, H^+ from HSO_4^- could have been ignored. However, this is not always the case, especially in more dilute solutions of H_2SO_4.

Acid-Base Properties of Salts

99. One difficult aspect of acid-base chemistry is recognizing what types of species are present in solution, i.e., whether a species is a strong acid, strong base, weak acid, weak base or a neutral species. Below are some ideas and generalizations to keep in mind that will help in recognizing types of species present.

   a. Memorize the following strong acids: HCl, HBr, HI, HNO_3, $HClO_4$ and H_2SO_4
   b. Memorize the following strong bases: LiOH, NaOH, KOH, RbOH, $Ca(OH)_2$, $Sr(OH)_2$ and $Ba(OH)_2$
   c. All weak acids have a K_a value less than 1 but greater than K_w. Some weak acids are in Table 14.2 of the text. All weak bases have a K_b value less than 1 but greater than K_w. Some weak bases are in Table 14.3 of the text.
   d. All conjugate bases of weak acids are weak bases, i.e., all have a K_b value less than 1 but greater than K_w. Some examples of these are the conjugate bases of the weak acids in Table 14.2 of the text.
   e. All conjugate acids of weak bases are weak acids, i.e., all have a K_a value less than 1 but greater than K_w. Some examples of these are the conjugate acids of the weak bases in Table 14.3 of the text.
   f. Alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and heavier alkaline earth metal ions (Ca^{2+}, Sr^{2+}, Ba^{2+}) have no acidic or basic properties in water.

g. All conjugate bases of strong acids (Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻, HSO₄⁻) have no basic
    properties in water ($K_b \ll K_w$) and only HSO_4^- has any acidic properties in water.

Let's apply these ideas to this problem to see what type of species are present. The
letters in parenthesis is/are the generalization(s) above which identifies the species.

KOH: strong base (b)
KCl: neutral; K^+ and Cl^- have no acidic/basic properties (f and g).
KCN: CN^- is a weak base, $K_b = 1.0 \times 10^{-14}/6.2 \times 10^{-10} = 1.6 \times 10^{-5}$ (c and d). Ignore
K^+ (f).
NH₄Cl: NH_4^+ is a weak acid, $K_a = 5.6 \times 10^{-10}$ (c and e). Ignore Cl^- (g).
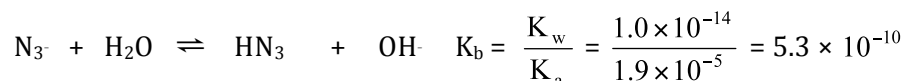HCl: strong acid (a)

The most acidic solution will be the strong acid followed by the weak acid. The most
basic solu-tion will be the strong base followed by the weak base. The KCl solution
will be between the acidic and basic solutions at pH = 7.00.

Most acidic → most basic: HCl > NH₄Cl > KCl > KCN > KOH

101. From the K_a values, acetic acid is a stronger acid than hypochlorous acid.
      Conversely, the conjugate base of acetic acid, $C_2H_3O_2^-$, will be a weaker base than the
      conjugate base of hypochlorous acid, OCl^-. Thus, the hypochlorite ion, OCl^-, is a
      stronger base than the acetate ion, $C_2H_3O_2^-$. In general, the stronger the acid, the
      weaker the conjugate base. This statement comes from the relationship $K_w = K_a \times K_b$,
      which holds for all conjugate acid-base pairs.

103. $NaN_3 \rightarrow Na^+ + N_3^-$; Azide, N_3^-, is a weak base since it is the conjugate base of a weak
      acid. All conjugate bases of weak acids are weak bases ($K_w < K_b < 1$). Ignore Na^+.

$$N_3^- + H_2O \rightleftharpoons HN_3 + OH^- \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-5}} = 5.3 \times 10^{-10}$$

Initial   0.010 M 0   ~0
            x mol/L of N_3^- reacts with H_2O to reach equilibrium
Change   -x →   +x +x
Equil.   0.010 - x x x

$$K_b = 5.3 \times 10^{-10} = \frac{[HN_3][OH^-]}{[N_3^-]} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} \quad \text{(assuming } x \ll 0.010)$$

$$x = [OH^-] = 2.3 \times 10^{-6} M; \quad [H^+] = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-6}} = 4.3 \times 10^{-9} M \quad \text{Assumptions good.}$$

$[HN_3] = [OH^-] = 2.3 \times 10^{-6} M$; $[Na^+] = 0.010 M$; $[N_3^-] = 0.010 - 2.3 \times 10^{-6} = 0.010 M$

105. a. $CH_3NH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$: $CH_3NH_3^+$ is a weak acid. Cl^- is the conjugate base of a
          strong acid. Cl^- has no basic (or acidic) properties.

$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+ \quad K_a = \frac{[CH_3NH_2][H^+]}{[CH_3NH_3^+]} = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{4.38 \times 10^{-4}} = 2.28 \times 10^{-11}$$

$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+$$

Initial   0.10 M 0   ~0

x mol/L $CH_3NH_3^+$ dissociates to reach equilibrium

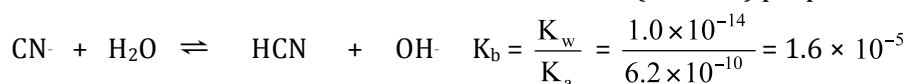Change $-x$ $\rightarrow$ $+x$ $+x$

Equil.   0.10 - x x x

$$K_a = 2.28 \times 10^{-11} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} \quad (\text{assuming } x \ll 0.10)$$

$x = [H^+] = 1.5 \times 10^{-6} M$; pH = 5.82   Assumptions good.

b. $NaCN \rightarrow Na^+ + CN^-$: CN^- is a weak base. Na^+ has no acidic (or basic) properties.

$$CN^- + H_2O \rightleftharpoons HCN + OH^- \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

Initial   0.050 M 0   ~0

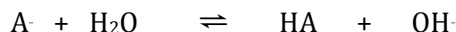x mol/L CN^- reacts with H_2O to reach equilibrium

Change $-x$ $\rightarrow$ $+x$ $+x$

Equil.   0.050 - x x x

$$K_b = 1.6 \times 10^{-5} = \frac{[HCN][OH^-]}{[CN^-]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$x = [OH^-] = 8.9 \times 10^{-4} M$; pOH = 3.05; pH = 10.95 Assumptions good.

107.   All these salts contain Na^+, which has no acidic/basic properties, and a conjugate base of a weak acid (except for NaCl where Cl^- is a neutral species.). All conjugate bases of weak acids are weak bases because the K_b values for these species are between 1 and K_w. To identify the species, we will use the data given to determine the K_b value for the weak conjugate base. From the K_b value and data in Table 14.2 of the text, we can identify the conjugate base present by calculating the K_a value for the weak acid. We will use A^- as an abbreviation for the weak conjugate base.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Initial   0.100 mol/1.00 L   0   ~0

x mol/L A^- reacts with H_2O to reach equilibrium

Change $-x$ $\rightarrow$ $+x$ $+x$

Equil.   0.100 - x x x

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{0.100 - x}; \quad \text{From the problem, pH = 8.07:}$$

pOH = 14.00 - 8.07 = 5.93; $[OH^-] = x = 10^{-5.93} = 1.2 \times 10^{-6} M$

$$K_b = \frac{(1.2 \times 10^{-6})^2}{0.100 - 1.2 \times 10^{-6}} = 1.4 \times 10^{-11} = K_b \text{ value for the conjugate base of a weak acid.}$$

The K_a value for the weak acid equals K_w/K_b: $K_a = \dfrac{1.0 \times 10^{-14}}{1.4 \times 10^{-11}} = 7.1 \times 10^{-4}$

From Table 14.2 of the text, this K_a value is closest to HF. Therefore, the unknown salt is NaF.

109.   Major species present: $Al(H_2O)_6^{3+}$ ($K_a = 1.4 \times 10^{-5}$), NO_3^- (neutral) and H_2O ($K_w = 1.0 \times 10^{-14}$);

   $Al(H_2O)_6^{3+}$ is a stronger acid than water so it will be the dominant H^+ producer.

$$Al(H_2O)_6^{3+} \rightleftharpoons Al(H_2O)_5(OH)^{2+} + H^+$$

   Initial   0.050 M 0   ~0
             x mol/L $Al(H_2O)_6^{3+}$ dissociates to reach equilibrium
   Change $-x$ $\rightarrow$ $+x$ $+x$
   Equil.   0.050 - x x x

$$K_a = 1.4 \times 10^{-5} = \frac{[Al(H_2O)_5(OH)^{2+}][H^+]}{[Al(H_2O)_6^{3+}]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

   $x = 8.4 \times 10^{-4} M = [H^+]$; pH = -log $(8.4 \times 10^{-4}) = 3.08$; Assumptions good.

111.   Reference Table 14.6 of the text and the solution to Exercise 14.99 for some generalizations on acid-base properties of salts.

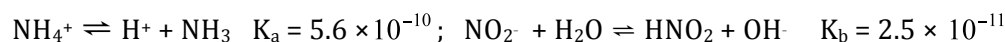   a. $NaNO_3 \rightarrow Na^+ + NO_3^-$ neutral; Neither species has any acidic/basic properties.

   b. $NaNO_2 \rightarrow Na^+ + NO_2^-$ basic; NO_2^- is a weak base and Na^+ has no effect on pH.

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^- \quad K_b = \frac{K_w}{K_{a, HNO_2}} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$$

   c. $C_5H_5NHClO_4 \rightarrow C_5H_5NH^+ + ClO_4^-$ acidic; $C_5H_5NH^+$ is a weak acid and ClO_4^- has no effect on pH.

$$C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N \quad K_a = \frac{K_w}{K_{b, C_5H_5N}} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

   d. $NH_4NO_2 \rightarrow NH_4^+ + NO_2^-$ acidic; NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$) and NO_2^- is a weak base ($K_b = 2.5 \times 10^{-11}$). Because $K_{a, NH_4^+} > K_{b, NO_2^-}$, the solution is acidic.

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \quad K_a = 5.6 \times 10^{-10}; \quad NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^- \quad K_b = 2.5 \times 10^{-11}$$

   e. $KOCl \rightarrow K^+ + OCl^-$ basic; OCl^- is a weak base and K^+ has no effect on pH.

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad K_b = \frac{K_w}{K_{a, HOCl}} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}$$

f. $NH_4OCl \rightarrow NH_4^+ + OCl^-$ basic; NH_4^+ is a weak acid and OCl^- is a weak base. Because $K_{b, OCl^-} > K_{a, NH_4^+}$, the solution is basic.

$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad K_a = 5.6 \times 10^{-10}$; $OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad K_b = 2.9 \times 10^{-7}$

## Relationships Between Structure and Strengths of Acids and Bases

113.　a.　$HIO_3 < HBrO_3$; As the electronegativity of the central atom increases, acid strength increases.

b.　$HNO_2 < HNO_3$; As the number of oxygen atoms attached to the central nitrogen atom increases, acid strength increases.

c.　$HOI < HOCl$; Same reasoning as in a.

d.　$H_3PO_3 < H_3PO_4$; Same reasoning as in b.

115.　a.　$H_2O < H_2S < H_2Se$; As the strength of the H–X bond decreases, acid strength increases.

b.　$CH_3CO_2H < FCH_2CO_2H < F_2CHCO_2H < F_3CCO_2H$; As the electronegativity of neighboring atoms increases, acid strength increases.

c.　$NH_4^+ < HONH_3^+$; Same reason as in b.

d.　$NH_4^+ < PH_4^+$; Same reason as in a.

117.　In general, metal oxides form basic solutions when dissolved in water and nonmetal oxides form acidic solutions in water.

a.　basic;　$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$;　$Ca(OH)_2$ is a strong base.

b.　acidic;　$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$;　H_2SO_3 is a weak diprotic acid.

c.　acidic;　$Cl_2O(g) + H_2O(l) \rightarrow 2\ HOCl(aq)$;　$HOCl$ is a weak acid.

Lewis Acids and Bases
119.　A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor.

a.　$B(OH)_3$, acid; H_2O, base　　　b.　Ag^+, acid; NH_3, base　　　c.　BF_3, acid; F^-, base

121.　$Al(OH)_3(s) + 3\ H^+(aq) \rightarrow Al^{3+}(aq) + 3\ H_2O(l)$　　(Brønsted-Lowry base, H^+ acceptor)

$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$ (Lewis acid, electron pair acceptor)
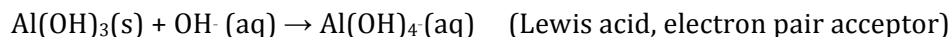
123. Fe^{3+} should be the stronger Lewis acid. Fe^{3+} is smaller and has a greater positive charge. Because of this, Fe^{3+} will be more strongly attracted to lone pairs of electrons as compared to Fe^{2+}.

Additional Exercises

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

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

Let V = total volume of solution at pH = 4.000:

1.00×10^{-4} mol/L = $\dfrac{1.00 \times 10^{-4} \text{ mol } H^+}{V}$, V = 1.00 L

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

126.   Conjugate acid-base pairs differ by an H^+ in the formula. Pairs in parts a, c, and d are conjugate acid-base pairs. For part b, HSO_4^- is the conjugate base of H_2SO_4. In addition, HSO_4^- is the conjugate acid of SO_4^{2-}

129.   The light bulb is bright because a strong electrolyte is present, i.e., a solute is present that dis-solves to produce a lot of ions in solution. The pH meter value of 4.6 indicates that a weak acid is present. (If a strong acid were present, the pH would be close to zero.) Of the possible substances, only HCl (strong acid), NaOH (strong base) and NH_4Cl are strong electrolytes. Of these three substances, only NH_4Cl contains a weak acid (the HCl solution would have a pH close to zero and the NaOH solution would have a pH close to 14.0). NH_4Cl dissociates into NH_4^+ and Cl^- ions when dissolved in water. Cl^- is the conjugate base of a strong acid, so it has no basic (or acidic properties) in water. NH_4^+, however, is the conjugate acid of the weak base NH_3, so NH_4^+ is a weak acid and would produce a solution with a pH = 4.6 when the concentration is ~1 M.