CHAPTER 14

ACIDS AND BASES

Questions

19. Acids are proton (H^+) donors, and bases are proton acceptors.

HCO_3^- as an acid: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

HCO_3^- as a base: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

$H_2PO_4^-$ as an acid: $H_2PO_4^- + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

$H_2PO_4^-$ as a base: $H_2PO_4^- + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$

20. Acidic solutions (at 25°C) have an $[H^+] > 1.0 \times 10^{-7}$ *M*, which gives a pH < 7.0. Because $[H^+][OH^-] = 1.0 \times 10^{-14}$ and pH + pOH = 14.00 for an aqueous solution at 25°C, an acidic solution must also have $[OH^-] < 1.0 \times 10^{-7}$ *M* and pOH > 7.00. From these relationships, the solutions in parts a, b, and d are acidic. The solution in part c will have a pH > 7.0 (pH = 14.00 – 4.51 = 9.49) and is therefore not acidic (solution is basic).

21. Basic solutions (at 25°C) have an $[OH^-] > 1.0 \times 10^{-7}$ *M*, which gives a pOH < 7.0. Because $[H^+][OH^-] = 1.0 \times 10^{-14}$ and pH + pOH = 14.00 for any aqueous solution at 25°C, a basic solution must also have $[H^+] < 1.0 \times 10^{-7}$ *M* and pH > 7.00. From these relationshis, the solutions in parts b, c, and d are basic solutions. The solution in part a will have a pH < 7.0 (pH = 14.00 – 11.21 = 2.79) and is therefore not basic (solution is acidic).

22. When a strong acid (HX) is added to water, the reaction $HX + H_2O \rightarrow H_3O^+ + X^-$ basically goes to completion. All strong acids in water are completely converted into H_3O^+ and X^-. Thus no acid stronger than H_3O^+ will remain undissociated in water. Similarly, when a strong base (B) is added to water, the reaction $B + H_2O \rightarrow BH^+ + OH^-$ basically goes to completion. All bases stronger than OH^- are completely converted into OH^- and BH^+. Even though there are acids and bases stronger than H_3O^+ and OH^-, in water these acids and bases are completely converted into H_3O^+ and OH^-.

23. 10.78 (4 S.F.); 6.78 (3 S.F.); 0.78 (2 S.F.); a pH value is a logarithm. The numbers to the left of the decimal point identify the power of 10 to which $[H^+]$ is expressed in scientific notation, for example, 10^{-11}, 10^{-7}, 10^{-1}. The number of decimal places in a pH value identifies the number of significant figures in $[H^+]$. In all three pH values, the $[H^+]$ should be expressed only to two significant figures because these pH values have only two decimal places.

24. A Lewis acid must have an empty orbital to accept an electron pair, and a Lewis base must have an unshared pair of electrons.

25. a. These are strong acids like HCl, HBr, HI, HNO_3, H_2SO_4, and $HClO_4$.

b. These are salts of the conjugate acids of the bases in Table 14.3. These conjugate acids are all weak acids. NH_4Cl, $CH_3NH_3NO_3$, and $C_2H_5NH_3Br$ are three examples. Note that the anions used to form these salts are conjugate bases of strong acids; this is so because they have no acidic or basic properties in water (with the exception of HSO_4^-, which has weak acid properties).

c. These are strong bases like LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$.

d. These are salts of the conjugate bases of the neutrally charged weak acids in Table 14.2. The conjugate bases of weak acids are weak bases themselves. Three examples are $NaClO_2$, $KC_2H_3O_2$, and CaF_2. The cations used to form these salts are Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, and Ba^{2+} because these cations have no acidic or basic properties in water. Notice that these are the cations of the strong bases you should memorize.

e. There are two ways to make a neutral salt. The easiest way is to combine a conjugate base of a strong acid (except for HSO_4^-) with one of the cations from a strong base. These ions have no acidic/basic properties in water, so salts of these ions are neutral. Three examples are NaCl, KNO_3, and SrI_2. Another type of strong electrolyte that can produce neutral solutions are salts that contain an ion with weak acid properties combined with an ion of opposite charge having weak base properties. If the K_a for the weak acid ion is equal to the K_b for the weak base ion, then the salt will produce a neutral solution. The most common example of this type of salt is ammonium acetate ($NH_4C_2H_3O_2$). For this salt, K_a for NH_4^+ = K_b for $C_2H_3O_2^-$ = 5.6×10^{-10}. This salt at any concentration produces a neutral solution.

26. $K_a \times K_b = K_w$, $-\log(K_a \times K_b) = -\log K_w$

$-\log K_a - \log K_b = -\log K_w$, $pK_a + pK_b = pK_w = 14.00$ ($K_w = 1.0 \times 10^{-14}$ at 25°C)

27. a. $H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ or

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad K = K_w = [H^+][OH^-]$

b. $HF(aq) + H_2O(l) \rightleftharpoons F^-(aq) + H_3O^+(aq)$ or

$HF(aq) \rightleftharpoons H^+(aq) + F^-(aq) \quad K = K_a = \dfrac{[H^+][F^-]}{[HF]}$

c. $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq) \quad K = K_b = \dfrac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$

28. Only statement a is true (assuming the species is not amphoteric). You cannot add a base to water and get an acidic pH (pH < 7.0). For statement b, you can have negative pH values; this just indicates an $[H^+] > 1.0$ *M*. For statement c, a dilute solution of a strong acid can have a higher pH than a more concentrated weak acid solution. For statement d, the $Ba(OH)_2$ solution will have an $[OH^-]$ twice of the same concentration of KOH, but this does not correspond to a pOH value twice that of the same concentration of KOH (prove it to yourselves).

29. a. This expression holds true for solutions of strong acids having a concentration greater than 1.0×10^{-6} *M*. 0.10 *M* HCl, 7.8 *M* HNO_3, and 3.6×10^{-4} *M* $HClO_4$ are examples where this expression holds true.

b. This expression holds true for solutions of weak acids where the two normal assumptions hold. The two assumptions are that water does not contribute enough H^+ to solution to make a difference, and that the acid is less than 5% dissociated in water (from the assumption that *x* is small compared to some number). This expression will generally hold true for solutions of weak acids having a K_a value less than 1×10^{-4}, as long as there is a significant amount of weak acid present. Three example solutions are 1.5 *M* $HC_2H_3O_2$, 0.10 *M* HOCl, and 0.72 *M* HCN.

c. This expression holds true for strong bases that donate 2 OH^- ions per formula unit. As long as the concentration of the base is above 5×10^{-7} *M*, this expression will hold true. Three examples are 5.0×10^{-3} *M* $Ca(OH)_2$, 2.1×10^{-4} *M* $Sr(OH)_2$, and 9.1×10^{-5} *M* $Ba(OH)_2$.

d. This expression holds true for solutions of weak bases where the two normal assumptions hold. The assumptions are that the OH^- contribution from water is negligible and that and that the base is less than 5% ionized in water (for the 5% rule to hold). For the 5% rule to hold, you generally need bases with $K_b < 1 \times 10^{-4}$, and concentrations of weak base greater than 0.10 *M*. Three examples are 0.10 *M* NH_3, 0.54 *M* $C_6H_5NH_2$, and 1.1 *M* C_5H_5N.

30. H_2CO_3 is a weak acid with $K_{a_1} = 4.3 \times 10^{-7}$ and $K_{a_2} = 5.6 \times 10^{-11}$. The $[H^+]$ concentration in solution will be determined from the K_{a_1} reaction because $K_{a_1} >> K_{a_2}$. Because $K_{a_1} << 1$, the $[H^+] < 0.10$ *M*; only a small percentage of the 0.10 *M* H_2CO_3 will dissociate into HCO_3^- and H^+. So statement a best describes the 0.10 *M* H_2CO_3 solution. H_2SO_4 is a strong acid as well as a very good weak acid ($K_{a_1} >> 1$, $K_{a_2} = 1.2 \times 10^{-2}$). All the 0.10 *M* H_2SO_4 solution will dissociate into 0.10 *M* H^+ and 0.10 *M* HSO_4^-. However, because HSO_4^- is a good weak acid due to the relatively large K_a value, some of the 0.10 *M* HSO_4^- will dissociate into some more H^+ and SO_4^{2-}. Therefore, the $[H^+]$ will be greater than 0.10 *M* but will not reach 0.20 *M* because only some of 0.10 *M* HSO_4^- will dissociate. Statement c is best for a 0.10 *M* H_2SO_4 solution.

31. One reason HF is a weak acid is that the H–F bond is unusually strong and is difficult to break. This contributes significantly to the reluctance of the HF molecules to dissociate in water.

32. a. Sulfur reacts with oxygen to produce SO_2 and SO_3. These sulfur oxides both react with water to produce H_2SO_3 and H_2SO_4, respectively. Acid rain can result when sulfur emissions are not controlled. Note that, in general, nonmetal oxides react with water to produce acidic solutions.

b. CaO reacts with water to produce $Ca(OH)_2$, a strong base. A gardener mixes lime (CaO) into soil in order to raise the pH of the soil. The effect of adding lime is to add $Ca(OH)_2$. Note that, in general, metal oxides react with water to produce basic solutions.

Exercises

Nature of Acids and Bases

33. a. $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$. Only the forward reaction is indicated because $HClO_4$ 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 because the equilibrium constant for this reaction is designated as 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 $CH_3CH_2CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CH_2CO_2^-(aq)$.

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

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

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

b. $HOC_6H_5(aq) \rightleftharpoons H^+(aq) + OC_6H_5^-(aq)$ $\qquad K_a = \dfrac{[H^+][OC_6H_5^-]}{[HOC_6H_5]}$

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

35. 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

36.

	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^-	$C_6H_5NH_3^+$

37. Strong acids have a $K_a >> 1$, 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 because the K_{a1} and K_{a2} values are less than 1.

38. 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

39. 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 ($K_a >> 1$); $HClO_2$: $K_a = 1.2 \times 10^{-2}$

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 $HClO_4 > HClO_2 > NH_4^+ > H_2O$.

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

41. 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 slightly stronger acid than HOC_6H_5 because K_a for HCN > K_a for HOC_6H_5.

42. a. H_2O; the conjugate bases of strong acids are terrible bases ($K_b < 1 \times 10^{-14}$).

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

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 is 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

43. At 25°C, the relationship $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ always holds for aqueous solutions. When $[H^+]$ is greater than 1.0×10^{-7} *M*, the solution is acidic; when $[H^+]$ is less than 1.0×10^{-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. $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\ M$; the solution is neutral.

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

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

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

44. a. $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.5} = 6.7 \times 10^{-15}\ M$; basic

b. $[H^+] = \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-15}} = 2.8\ M$; acidic

c. $[H^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\ M$; neutral

d. $[H^+] = \frac{1.0 \times 10^{-14}}{7.3 \times 10^{-4}} = 1.4 \times 10^{-11}\ M$; basic

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

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

46. a. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad K_w = 2.92 \times 10^{-14} = [H^+][OH^-]$

In pure water: $[H^+] = [OH^-]$, $2.92 \times 10^{-14} = [H^+]^2$, $[H^+] = 1.71 \times 10^{-7}\ M = [OH^-]$

b. $pH = -\log[H^+] = -\log(1.71 \times 10^{-7}) = 6.767$

c. $[H^+] = K_w/[OH^-] = (2.92 \times 10^{-14})/0.10 = 2.9 \times 10^{-13}\ M$; $pH = -\log(2.9 \times 10^{-13}) = 12.54$

47. $pH = -\log[H^+]$; $pOH = -\log[OH^-]$; at 25°C, $pH + pOH = 14.00$; for Exercise 43:

a. $pH = -\log[H^+] = -\log(1.0 \times 10^{-7}) = 7.00$; $pOH = 14.00 - pH = 14.00 - 7.00 = 7.00$

b. $pH = -\log(8.3 \times 10^{-16}) = 15.08$; $pOH = 14.00 - 15.08 = -1.08$

c. $pH = -\log(12) = -1.08$; $pOH = 14.00 - (-1.08) = 15.08$

d. $pH = -\log(5.4 \times 10^{-5}) = 4.27$; $pOH = 14.00 - 4.27 = 9.73$

Note that pH is less than zero when $[H^+]$ is greater than 1.0 *M* (an extremely acidic solution). For Exercise 44:

a. $pOH = -\log[OH^-] = -\log(1.5) = -0.18$; $pH = 14.00 - pOH = 14.00 - (-0.18) = 14.18$

b. $pOH = -\log(3.6 \times 10^{-15}) = 14.44$; $pH = 14.00 - 14.44 = -0.44$

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

d. $pOH = -\log(7.3 \times 10^{-4}) = 3.14$; $pH = 14.00 - 3.14 = 10.86$

Note that pH is greater than 14.00 when $[OH^-]$ is greater than 1.0 *M* (an extremely basic solution).

48. a. $[H^+] = 10^{-pH}$, $[H^+] = 10^{-7.40} = 4.0 \times 10^{-8}\ M$

$pOH = 14.00 - pH = 14.00 - 7.40 = 6.60$; $[OH^-] = 10^{-pOH} = 10^{-6.60} = 2.5 \times 10^{-7}\ M$

or $[OH^-] = \dfrac{K_w}{[H^+]} = \dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-8}} = 2.5 \times 10^{-7}\ M$; this solution is basic since pH > 7.00.

b. $[H^+] = 10^{-15.3} = 5 \times 10^{-16}$ *M*; pOH = 14.00 – 15.3 = –1.3; $[OH^-] = 10^{-(-1.3)} = 20$ *M*; basic

c. $[H^+] = 10^{-(-1.0)} = 10$ *M*; pOH = 14.0 – (–1.0) = 15.0; $[OH^-] = 10^{-15.0} = 1 \times 10^{-15}$ *M*; acidic

d. $[H^+] = 10^{-3.20} = 6.3 \times 10^{-4}$ *M*; pOH = 14.00 – 3.20 = 10.80; $[OH^-] = 10^{-10.80} = 1.6 \times 10^{-11}$ *M*; acidic

e. $[OH^-] = 10^{-5.0} = 1 \times 10^{-5}$ *M*; pH = 14.0 – pOH = 14.0 – 5.0 = 9.0; $[H^+] = 10^{-9.0} = 1 \times 10^{-9}$ *M*; basic

f. $[OH^-] = 10^{-9.60} = 2.5 \times 10^{-10}$ *M*; pH = 14.00 – 9.60 = 4.40; $[H^+] = 10^{-4.40} = 4.0 \times 10^{-5}$ *M*; acidic

49. 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

50. a. pOH = 14.00 – 9.63 = 4.37; $[H^+] = 10^{-9.63} = 2.3 \times 10^{-10}$ *M*

$[OH^-] = 10^{-4.37} = 4.3 \times 10^{-5}$ *M*; basic

b. $[H^+] = \dfrac{1.0 \times 10^{-14}}{3.9 \times 10^{-6}} = 2.6 \times 10^{-9}$ *M*; pH = $-\log(2.6 \times 10^{-9})$ = 8.59

pOH = 14.00 – 8.59 = 5.41; basic

c. pH = –log(0.027) = 1.57; pOH = 14.00 – 1.57 = 12.43

$[OH^-] = 10^{-12.43} = 3.7 \times 10^{-13}$ *M*; acidic

d. pH = 14.0 – 12.2 = 1.8; $[H^+] = 10^{-1.8} = 2 \times 10^{-2}$ *M*

$[OH^-] = 10^{-12.2} = 6 \times 10^{-13}$ *M*; acidic

51. pOH = 14.0 − pH = 14.0 − 2.1 = 11.9; $[H^+] = 10^{-pH} = 10^{-2.1} = 8 \times 10^{-3}$ *M* (1 sig. fig.)

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{8 \times 10^{-3}} = 1 \times 10^{-12}\ M \text{ or } [OH^-] = 10^{-pOH} = 10^{-11.9} = 1 \times 10^{-12}\ M$$

The sample of gastric juice is acidic because the pH is less than 7.00 at 25°C.

52. pH = 14.00 − pOH = 14.00 − 5.74 = 8.26; $[H^+] = 10^{-pH} = 10^{-8.26} = 5.5 \times 10^{-9}$ *M*

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{5.5 \times 10^{-9}} = 1.8 \times 10^{-6}\ M \text{ or } [OH^-] = 10^{-pOH} = 10^{-5.74} = 1.8 \times 10^{-6}\ M$$

The solution of baking soda is basic because the pH is greater than 7.00 at 25°C.

Solutions of Acids

53. 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

54. Both are strong acids, which are assumed to completely dissociate in water.

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

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

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

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

55. Strong acids are assumed to completely dissociate in water; for example; $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ or $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$.

a. A 0.10 *M* HCl solution gives 0.10 *M* H^+ and 0.10 *M* Cl^- because HCl completely dissociates. The amount of H^+ from H_2O will be insignificant.

$pH = -\log[H^+] = -\log(0.10) = 1.00$

b. 5.0 *M* H^+ is produced when 5.0 *M* $HClO_4$ completely dissociates. The amount of H^+ from H_2O will be insignificant. pH = –log(5.0) = –0.70 (Negative pH values just indicate very concentrated acid solutions.)

c. 1.0×10^{-11} *M* H^+ is produced when 1.0×10^{-11} *M* HI completely dissociates. If you take the negative log of 1.0×10^{-11}, this gives pH = 11.00. This is impossible! We dissolved an acid in water and got a basic pH. What we must consider in this problem is that water by itself donates 1.0×10^{-7} *M* H^+. We can normally ignore the small amount of H^+ from H_2O except when we have a very dilute solution of an acid (as in the case here). Therefore, the pH is that of neutral water (pH = 7.00) because the amount of HI present is insignificant.

56. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$; HNO_3 is a strong acid, which means it is assumed to completely dissociate in water. The initial concentration of HNO_3 will equal the $[H^+]$ donated by the strong acid.

a. $pH = -\log[H^+] = -\log(2.0 \times 10^{-2}) = 1.70$

b. pH = –log(4.0) = –0.60

c. Because the concentration of HNO_3 is so dilute, the pH will be that of neutral water (pH = 7.00). In this problem, water is the major H^+ producer present. Whenever the strong acid has a concentration less than 1.0×10^{-7} *M*, the $[H^+]$ contribution from water must be considered.

57. $[H^+] = 10^{-pH} = 10^{-2.50} = 3.2 \times 10^{-3}$ *M*. Because HI is a strong acid, a 3.2×10^{-3} *M* HI solution will produce 3.2×10^{-3} *M* H^+, giving a pH = 2.50.

58. $[H^+] = 10^{-pH} = 10^{-4.25} = 5.6 \times 10^{-5}$ *M*. Because HBr is a strong acid, a 5.6×10^{-5} *M* HBr solution is necessary to produce a pH = 4.25 solution.

59. HCl is a strong acid. $[H^+] = 10^{-1.50} = 3.16 \times 10^{-2}$ *M* (carrying one extra sig. fig.)

$$M_1V_1 = M_2V_2\,,\quad V_1 = \frac{M_2V_2}{M_1} = \frac{3.16\times 10^{-2}\ \text{mol/L} \times 1.6\ \text{L}}{12\ \text{mol/L}} = 4.2 \times 10^{-3}\ \text{L}$$

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.

60. $$50.0\ \text{mL conc. HCl soln} \times \frac{1.19\ \text{g}}{\text{mL}} \times \frac{38\ \text{g HCl}}{100\ \text{g conc. HCl soln}} \times \frac{1\ \text{mol HCl}}{36.5\ \text{g}} = 0.62\ \text{mol HCl}$$

$$20.0\ \text{mL conc. HNO}_3\ \text{soln} \times \frac{1.42\ \text{g}}{\text{mL}} \times \frac{70.\ \text{g HNO}_3}{100\ \text{g soln}} \times \frac{1\ \text{mol HNO}_3}{63.0\ \text{g HNO}_3} = 0.32\ \text{mol HNO}_3$$

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$ and $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$ (Both are strong acids.)

So we will have 0.62 + 0.32 = 0.94 mol of H^+ in the final solution.

$$[H^+] = \frac{0.94\text{ mol}}{1.00\text{ L}} = 0.94\ M;\ \ pH = -\log[H^+] = -\log(0.94) = 0.027 = 0.03$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.94} = 1.1 \times 10^{-14}\ M$$

61. 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 *i*nitial, *c*hange, and *e*quilibrium 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	$-x$	→	$+x$		$+x$
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: $\frac{x}{0.250} \times 100 = \frac{0.010}{0.250} \times 100 = 4.0\%$

All the assumptions are good. The H^+ contribution from water ($1 \times 10^{-7}\ M$) 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	$-x$	→	$+x$		$+x$
Equil.	$0.250 - x$		x		x

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

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

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

62. a. HOC_6H_5 ($K_a = 1.6 \times 10^{-10}$) and H_2O ($K_a = K_w = 1.0 \times 10^{-14}$) are the major species. The major equilibrium is the dissociation of HOC_6H_5. Solving the weak acid problem:

	HOC_6H_5	$\rightleftharpoons$	H^+	+	$OC_6H_5^-$
Initial	0.250 M		~0		0
	x mol/L HOC_6H_5 dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.250 - x$		x		x

$$K_a = 1.6 \times 10^{-10} = \frac{[H^+][OC_6H_5^-]}{[HOC_6H_5]} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad \text{(assuming } x << 0.250\text{)}$$

$x = [H^+] = 6.3 \times 10^{-6}\ M$; checking assumption: x is $2.5 \times 10^{-3}\%$ of 0.250, so assumption is valid by the 5% rule.

$pH = -\log(6.3 \times 10^{-6}) = 5.20$

b. HCN ($K_a = 6.2 \times 10^{-10}$) and H_2O are the major species. HCN is the major source of H^+.

	HCN	$\rightleftharpoons$	H^+	+	CN^-
Initial	0.250 M		~0		0
	x mol/L HCN dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.250 - x$		x		x

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad \text{(assuming } x << 0.250\text{)}$$

$x = [H^+] = 1.2 \times 10^{-5}\ M$; checking assumption: x is $4.8 \times 10^{-3}\%$ of 0.250.

Assumptions good. $pH = -\log(1.2 \times 10^{-5}) = 4.92$

63. 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	

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

$x = [H^+] = 3.8 \times 10^{-3}\ M$; check assumptions:

$$\frac{x}{0.020} \times 100 = \frac{3.8 \times 10^{-3}}{0.020} \times 100 = 19\%$$

The assumption $x << 0.020$ 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 the method of successive approximations (see Appendix 1 of the text). Using successive approxi-mations, 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 that $0.020 - 0.0038 = 0.016$; then solve for a new value of x in the numerator.

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

We use this new value of x to further refine our estimate of [HF], that is, $0.020 - x = 0.020 - 0.0034 = 0.0166$ (carrying an extra sig. fig.).

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

We repeat until we get a self-consistent answer. This would be the same answer we would get solving exactly using the quadratic equation. In this case it is, $x = 3.5 \times 10^{-3}$.
Thus:

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

$[HF] = 0.020 - x = 0.020 - 0.0035 = 0.017\ M$; 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 graphing calculator).

64. $HClO_2 \rightleftharpoons H^+ + ClO_2^-$ $\quad K_a = 1.2 \times 10^{-2}$

	$HClO_2$		H^+	ClO_2^-
Initial	0.22 M		~0	0
	x mol/L $HClO_2$ dissociates to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.22 - x$		x	x

$$K_a = 1.2 \times 10^{-2} = \frac{[H^+][ClO_2^-]}{[HClO_2]} = \frac{x^2}{0.22 - x} \approx \frac{x^2}{0.22},\ x = 5.1 \times 10^{-2}$$

The assumption that x is small is not good (x is 23% of 0.22). Using the method of successive approximations and carrying extra significant figures:

$$\frac{x^2}{0.22-0.051} \approx \frac{x^2}{0.169} = 1.2 \times 10^{-2},\ x = 4.5 \times 10^{-2}$$

$$\frac{x^2}{0.175} = 1.2 \times 10^{-2},\ x = 4.6 \times 10^{-2} \text{ (consistent answer)}$$

$[H^+] = [ClO_2^-] = x = 4.6 \times 10^{-2}\ M$; percent dissociation = $\dfrac{4.6 \times 10^{-2}}{0.22} \times 100 = 21\%$

65. $HC_3H_5O_2$ ($K_a = 1.3 \times 10^{-5}$) and H_2O ($K_a = K_w = 1.0 \times 10^{-14}$) are the major species present. $HC_3H_5O_2$ will be the dominant producer of H^+ because $HC_3H_5O_2$ is a stronger acid than H_2O. Solving the weak acid problem:

$$HC_3H_5O_2 \rightleftharpoons H^+ + C_3H_5O_2^-$$

	$HC_3H_5O_2$		H^+	$C_3H_5O_2^-$
Initial	0.100 M		~0	0
	x mol/L $HC_3H_5O_2$ dissociates to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.100 - x$		x	x

$$K_a = 1.3 \times 10^{-5} = \frac{[H^+][C_3H_5O_2^-]}{[HC_3H_5O_2]} = \frac{x^2}{0.100-x} \approx \frac{x^2}{0.100}$$

$x = [H^+] = 1.1 \times 10^{-3} M$; pH $= -\log(1.1 \times 10^{-3}) = 2.96$

Assumption follows the 5% rule (x is 1.1% of 0.100).

$[H^+] = [C_3H_5O_2^-] = 1.1 \times 10^{-3} M$; $[OH^-] = K_w/[H^+] = 9.1 \times 10^{-12} M$

$[HC_3H_5O_2] = 0.100 - 1.1 \times 10^{-3} = 0.099\ M$

$$\text{Percent dissociation} = \frac{[H^+]}{[HC_3H_5O_2]_0} \times 100 = \frac{1.1 \times 10^{-3}}{0.100} \times 100 = 1.1\%$$

66. This is a weak acid in water. We must solve a weak acid problem. Let HBz = $C_6H_5CO_2H$.

$$0.56 \text{ g HBz} \times \frac{1 \text{ mol HBz}}{122.1 \text{ g}} = 4.6 \times 10^{-3} \text{ mol};\ [HBz]_0 = 4.6 \times 10^{-3}\ M$$

$$HBz \rightleftharpoons H^+ + Bz^-$$

	HBz		H^+	Bz^-
Initial	$4.6 \times 10^{-3}\ M$		~0	0
	x mol/L HBz dissociates to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$4.6 \times 10^{-3} - x$		x	x

$$K_a = 6.4 \times 10^{-5} = \frac{[H^+][Bz^-]}{[HBz]} = \frac{x^2}{(4.6 \times 10^{-3} - x)} \approx \frac{x^2}{4.6 \times 10^{-3}}$$

$x = [H^+] = 5.4 \times 10^{-4}$; check assumptions: $\frac{x}{4.6 \times 10^{-3}} \times 100 = \frac{5.4 \times 10^{-4}}{4.6 \times 10^{-3}} \times 100 = 12\%$

Assumption is not good (x is 12% of 4.6×10^{-3}). When assumption(s) fail, we must solve exactly using the quadratic formula or the method of successive approximations (see Appendix 1 of text). Using successive approximations:

$$\frac{x^2}{(4.6 \times 10^{-3}) - (5.4 \times 10^{-4})} = 6.4 \times 10^{-5},\ x = 5.1 \times 10^{-4}$$

$$\frac{x^2}{(4.6 \times 10^{-3}) - (5.1 \times 10^{-4})} = 6.4 \times 10^{-5},\ x = 5.1 \times 10^{-4}\ M \quad \text{(consistent answer)}$$

Thus: $x = [H^+] = [Bz^-] = [C_6H_5CO_2^-] = 5.1 \times 10^{-4}\ M$

$[HBz] = [C_6H_5CO_2H] = 4.6 \times 10^{-3} - x = 4.1 \times 10^{-3}\ M$

pH = $-\log(5.1 \times 10^{-4}) = 3.29$; pOH = 14.00 – pH = 10.71; $[OH^-] = 10^{-10.71} = 1.9 \times 10^{-11}\ M$

67. Major species: $HC_2H_2ClO_2$ ($K_a = 1.35 \times 10^{-3}$) 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	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.10 - x$		x		x

$$K_a = 1.35 \times 10^{-3} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10},\ x = 1.2 \times 10^{-2}\ M$$

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

68. This is a weak acid in water, so we solve the weak acid problem.

	HCO_2H	$\rightleftharpoons$	H^+	+	HCO_2^-	$K_a = 1.8 \times 10^{-4}$
Initial	0.025 M		~0		0	
	x mol/L HCO_2H dissociates to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$0.025 - x$		x		x	

$$K_a = 1.8 \times 10^{-4} = \frac{[H^+][HCO_2^-]}{[HCO_2H]} = \frac{x^2}{0.025 - x} \approx \frac{x^2}{0.025}$$

$x = [H^+] = 2.1 \times 10^{-3}$ *M*; check assumptions: $\frac{2.1 \times 10^{-3}}{0.025} \times 100 = 8.4\%$

The assumption that $x << 0.025$ is not good (fails the 5% rule). Solving using the method of successive approximations (see Appendix 1 in text):

$$\frac{x^2}{0.025 - x} = \frac{x^2}{0.025 - 0.0021} = \frac{x^2}{0.023} = 1.8 \times 10^{-4},\ x = 2.0 \times 10^{-3}$$, which we get consistently.

$x = [H^+] = 2.0 \times 10^{-3}$ *M*; pH = 2.70

69. HF and HOC_6H_5 are both weak acids with K_a values of 7.2×10^{-4} and 1.6×10^{-10}, respectively. Since the K_a value for HF is much greater than the K_a value for HOC_6H_5, HF will be the dominant producer of H^+ (we can ignore the amount of H^+ produced from HOC_6H_5 because it will be insignificant).

	HF	$\rightleftharpoons$	H^+	$+$	F^-
Initial	1.0 *M*		~0		0
	x mol/L HF dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$1.0 - x$		x		x

$$K_a = 7.2 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$x = [H^+] = 2.7 \times 10^{-2}$ *M*; pH $= -\log(2.7 \times 10^{-2}) = 1.57$; assumptions good.

Solving for $[OC_6H_5^-]$ using $HOC_6H_5 \rightleftharpoons H^+ + OC_6H_5^-$ equilibrium:

$$K_a = 1.6 \times 10^{-10} = \frac{[H^+][OC_6H_5^-]}{[HOC_6H_5]} = \frac{(2.7 \times 10^{-2})[OC_6H_5^-]}{1.0},\ [OC_6H_5^-] = 5.9 \times 10^{-9}\ M$$

Note that this answer indicates that only 5.9×10^{-9} *M* HOC_6H_5 dissociates, which confirms that HF is truly the only significant producer of H^+ in this solution.

70. a. The initial concentrations are halved since equal volumes of the two solutions are mixed.

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	$+$	$C_2H_3O_2^-$
Initial	0.100 *M*		5.00×10^{-4} *M*		0
Equil.	$0.100 - x$		$5.00 \times 10^{-4} + x$		x

$$K_a = 1.8 \times 10^{-5} = \frac{x(5.00 \times 10^{-4} + x)}{0.100 - x} \approx \frac{x(5.00 \times 10^{-4})}{0.100}$$

$x = 3.6 \times 10^{-3}$; assumption is horrible. Using the quadratic formula:

$$x^2 + (5.18 \times 10^{-4})x - 1.8 \times 10^{-6} = 0$$

$$x = 1.1 \times 10^{-3}\ M;\ [H^+] = 5.00 \times 10^{-4} + x = 1.6 \times 10^{-3}\ M;\ \text{pH} = 2.80$$

b. $x = [C_2H_3O_2^-] = 1.1 \times 10^{-3}\ M$

71. 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.	$HC_2H_3O_2$	$\rightleftharpoons$	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

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

$x = [H^+] = [C_2H_3O_2^-] = 3.0 \times 10^{-3}\ M$; 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 setup for solutions b and c are similar to solution a except that the final equation is different because the new concentration of $HC_2H_3O_2$ is different.

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

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

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

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

$x = [H^+] = [C_2H_3O_2^-] = 3.0 \times 10^{-4}\ M$; 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 of the 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 $x = 2.9 \times 10^{-4}$.

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

d. As we dilute a solution, all concentrations are decreased. 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:

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

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

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

72. a. HNO_3 is a strong acid; it is assumed 100% dissociated in solution.

b. $HNO_2 \rightleftharpoons H^+ + NO_2^-$ $K_a = 4.0 \times 10^{-4}$

	HNO_2	$\rightleftharpoons$	H^+	+	NO_2^-
Initial	$0.20\ M$		~ 0		0
	x mol/L HNO_2 dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.20 - x$		x		x

$$K_a = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$x = [H^+] = [NO_2^-] = 8.9 \times 10^{-3}\ M$; assumptions good.

$$\text{Percent dissociation} = \frac{[H^+]}{[HNO_2]_0} \times 100 = \frac{8.9 \times 10^{-3}}{0.20} \times 100 = 4.5\%$$

c. $HOC_6H_5 \rightleftharpoons H^+ + OC_6H_5^-$ $K_a = 1.6 \times 10^{-10}$

	HOC_6H_5	$\rightleftharpoons$	H^+	+	$OC_6H_5^-$
Initial	$0.20\ M$		~ 0		0
	x mol/L HOC_6H_5 dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.20 - x$		x		x

$$K_a = 1.6 \times 10^{-10} = \frac{[H^+][OC_6H_5^-]}{[HOC_6H_5]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$x = [H^+] = [OC_6H_5^-] = 5.7 \times 10^{-6}\,M$; assumptions good.

$$\text{Percent dissociation} = \frac{5.7 \times 10^{-6}}{0.20} \times 100 = 2.9 \times 10^{-3}\,\%$$

d. For the same initial concentration, the percent dissociation increases as the strength of the acid increases (as K_a increases).

73. Let HA symbolize the weak acid. Set up the problem like a typical weak acid equilibrium problem.

	HA	$\rightleftharpoons$	H^+	$+$	A^-
Initial	$0.15\,M$		~0		0
	x mol/L HA 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.

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

74.

	HX	$\rightleftharpoons$	H^+	$+$	X^-	
Initial	I		~0		0	where $I = [HX]_0$
	x mol/L HX dissociates to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$I - x$		x		x	

From the problem, $x = 0.25(I)$ and $I - x = 0.30\,M$.

$I - 0.25(I) = 0.30\,M$, $I = 0.40\,M$ and $x = 0.25(0.40\,M) = 0.10\,M$

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{x^2}{I - x} = \frac{(0.10)^2}{0.30} = 0.033$$

75. Set up 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

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

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

76. Set up the problem using the K_a equilibrium reaction for HOBr.

	$HOBr$	$\rightleftharpoons$	H^+	+	OBr^-
Initial	$0.063\,M$		~0		0
	x mol/L HOBr dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.063 - x$		x		x

$$K_a = \frac{[H^+][OBr^-]}{[HOBr]} = \frac{x^2}{0.063 - x}\text{; from pH = 4.95: } x = [H^+] = 10^{-pH} = 10^{-4.95} = 1.1 \times 10^{-5}\,M$$

$$K_a = \frac{(1.1 \times 10^{-5})^2}{0.063 - 1.1 \times 10^{-5}} = 1.9 \times 10^{-9}$$

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

	$HCOOH$	$\rightleftharpoons$	H^+	+	$HCOO^-$	
Initial	C		~0		0	where $C = [HCOOH]_0$
	x mol/L HCOOH dissociates to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$C - x$		x		x	

$$K_a = 1.8 \times 10^{-4} = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{x^2}{C - x}\text{, where } x = [H^+]$$

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

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

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

78. Major species: $HC_2H_3O_2$ (acetic acid) and H_2O; major source of H^+: $HC_2H_3O_2$

	$HC_2H_3O_2$	$\rightleftharpoons$	H^+	+	$C_2H_3O_2^-$	
Initial	C		~0		0	where $C = [HC_2H_3O_2]_0$
	x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$C - x$		x		x	

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{x^2}{C - x}, \text{ where } x = [H^+]$$

$$1.8 \times 10^{-5} = \frac{[H^+]^2}{C - [H^+]}; \text{ from pH = 3.0: } [H^+] = 10^{-3.0} = 1 \times 10^{-3}\ M$$

$$1.8 \times 10^{-5} = \frac{(1 \times 10^{-3})^2}{C - (1 \times 10^{-3})}, \ C - (1 \times 10^{-3}) = \frac{1 \times 10^{-6}}{1.8 \times 10^{-5}}, \ C = 5.7 \times 10^{-2} \approx 6 \times 10^{-2}\ M$$

A 6×10^{-2} *M* acetic acid solution will have pH = 3.0.

79. $[HA]_0 = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50$ mol/L; solve using the K_a equilibrium reaction.

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial	0.50 *M*		~0		0
Equil.	$0.50 - x$		x		x

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.50 - x}; \text{ in this problem, [HA] = 0.45 } M \text{ so:}$$

$$[HA] = 0.45\ M = 0.50\ M - x, \ x = 0.05\ M; \ K_a = \frac{(0.05)^2}{0.45} = 6 \times 10^{-3}$$

80. Let HSac = saccharin and I = $[HSac]_0$.

	$HSac$	$\rightleftharpoons$	H^+	+	Sac^-
Initial	I		~0		0
Equil.	$I - x$		x		x

$K_a = 10^{-11.70} = 2.0 \times 10^{-12}$

$$K_a = 2.0 \times 10^{-12} = \frac{x^2}{I - x}; \ x = [H^+] = 10^{-5.75} = 1.8 \times 10^{-6}\ M$$

$$2.0 \times 10^{-12} = \frac{(1.8 \times 10^{-6})^2}{I - (1.8 \times 10^{-6})}, \quad I = 1.6\ M = [HSac]_0.$$

$$100.0 \text{ g } HC_7H_4NSO_3 \times \frac{1 \text{ mol}}{183.19 \text{ g}} \times \frac{1 \text{ L}}{1.6 \text{ mol}} \times \frac{1000 \text{ mL}}{\text{L}} = 340 \text{ mL}$$

Solutions of Bases

81. All K_b reactions refer to the base reacting with water to produce the conjugate acid of the base and OH^-.

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

b. $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$ $K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$

82. a. $C_6H_5NH_2(aq) + H_2O(l) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$ $K_b = \frac{[C_6H_5NH_3^+][OH^-]}{[C_6H_5NH_2]}$

b. $(CH_3)_2NH(aq) + H_2O(l) \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^-(aq)$ $K_b = \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]}$

83. NO_3^-: Because HNO_3 is a strong acid, NO_3^- is a terrible base ($K_b << K_w$). 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: $K_b = 1.7 \times 10^{-9}$

Base strength = $NH_3 > C_5H_5N > H_2O > NO_3^-$ (As K_b increases, base strength increases.)

84. Excluding water, these are the conjugate acids of the bases in the preceding exercise. In general, the stronger the base, the weaker is the conjugate acid. *Note*: Even though NH_4^+ and $C_5H_5NH^+$ are conjugate acids of weak bases, they are still weak acids with K_a values between K_w and 1. Prove this to yourself by calculating the K_a values for NH_4^+ and $C_5H_5NH^+$ ($K_a = K_w/K_b$).

Acid strength = $HNO_3 > C_5H_5NH^+ > NH_4^+ > H_2O$

85. 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 ($K_{b,\,C_6H_5NH_2} = 3.8 \times 10^{-10}$, $K_{b,\,CH_3NH_2} = 4.4 \times 10^{-4}$). OH^- is the strongest base possible in water.

86. a. $HClO_4$ (a strong acid) b. $C_6H_5NH_3^+$ c. $C_6H_5NH_3^+$

The acid with the largest K_a value is the strongest acid. To calculate K_a values for $C_6H_5NH_3^+$ and $CH_3NH_3^+$, use $K_a = K_w/K_b$, where K_b refers to the bases $C_6H_5NH_2$ or CH_3NH_2.

87. $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$; NaOH is a strong base that 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 exercise, water is the major OH^- contributor, and $[OH^-] = 1.0 \times 10^{-7}$ *M*.

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

c. $[OH^-] = 2.0$ *M*; $pOH = -\log(2.0) = -0.30$; $pH = 14.00 - (-0.30) = 14.30$

88. a. $Ca(OH)_2 \rightarrow Ca^{2+} + 2\ OH^-$; $Ca(OH)_2$ is a strong base and dissociates completely.

$[OH^-] = 2(0.00040) = 8.0 \times 10^{-4}$ *M*; $pOH = -\log[OH^-] = 3.10$

$pH = 14.00 - pOH = 10.90$

b. $$\frac{25\text{ g KOH}}{\text{L}} \times \frac{1\text{ mol KOH}}{56.11\text{ g KOH}} = 0.45\text{ mol KOH/L}$$

KOH is a strong base, so $[OH^-] = 0.45$ *M*; $pOH = -\log(0.45) = 0.35$; $pH = 13.65$

c. $$\frac{150.0\text{ g NaOH}}{\text{L}} \times \frac{1\text{ mol}}{40.00\text{ g}} = 3.750\ M$$; NaOH is a strong base, so $[OH^-] = 3.750$ *M*.

$pOH = -\log(3.750) = -0.5740$ and $pH = 14.0000 - (-0.5740) = 14.5740$

Although we are justified in calculating the answer to four decimal places, in reality, the pH can only be measured to ±0.01 pH units.

89. 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: Ba^{2+}, OH^-, H_2O; $Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2\ OH^-(aq)$; because each mole of the strong base $Ba(OH)_2$ dissolves in water to produce two mol OH^-, $[OH^-] = 2(0.015\ M) = 0.030\ M$.

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

90. a. Major species: Na^+, Li^+, OH^-, H_2O (NaOH and LiOH are both strong bases.)

$[OH^-] = 0.050 + 0.050 = 0.100$ *M*; $pOH = 1.000$; $pH = 13.000$

b. Major species: Ca^{2+}, Rb^+, OH^-, H_2O; Both $Ca(OH)_2$ and RbOH are strong bases, and $Ca(OH)_2$ donates 2 mol OH^- per mol $Ca(OH)_2$.

$[OH^-] = 2(0.0010) + 0.020 = 0.022$ *M*; $pOH = -\log(0.022) = 1.66$; $pH = 12.34$

91. $pOH = 14.00 - 11.56 = 2.44$; $[OH^-] = [KOH] = 10^{-2.44} = 3.6 \times 10^{-3}$ *M*

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

92. pH = 10.50; pOH = 14.00 - 10.50 = 3.50; $[OH^-] = 10^{-3.50} = 3.2 \times 10^{-4}\ M$

$Sr(OH)_2(aq) \rightarrow Sr^{2+}(aq) + 2\ OH^-(aq)$; $Sr(OH)_2$ donates 2 mol OH^- per mol $Sr(OH)_2$.

$$[Sr(OH)_2] = \frac{3.2 \times 10^{-4}\ \text{mol OH} -}{\text{L}} \times \frac{1\ \text{mol Sr(OH)}_2}{2\ \text{mol OH}^-} = 1.6 \times 10^{-4}\ M\ \text{Sr(OH)}_2$$

A $1.6 \times 10^{-4}\ M$ $Sr(OH)_2$ solution will produce a pH = 10.50 solution.

93. NH_3 is a weak base with $K_b = 1.8 \times 10^{-5}$. The major species present will be NH_3 and H_2O ($K_b = K_w = 1.0 \times 10^{-14}$). Because NH_3 has a much larger K_b value than 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 using the K_b reaction for NH_3.

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

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

$x = [OH^-] = 1.6 \times 10^{-3}\ M$; 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.

94. Major species: H_2NNH_2 ($K_b = 3.0 \times 10^{-6}$) and H_2O ($K_b = K_w = 1.0 \times 10^{-14}$); the weak base H_2NNH_2 will dominate OH^- production. We must perform a weak base equilibrium calculation.

	H_2NNH_2 + H_2O	$\rightleftharpoons$	$H_2NNH_3^+$	+	OH^-	$K_b = 3.0 \times 10^{-6}$
Initial	$2.0\ M$		0		~0	
	x mol/L H_2NNH_2 reacts with H_2O to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$2.0 - x$		x		x	

$$K_b = 3.0 \times 10^{-6} = \frac{[H_2NNH_3^+][OH^-]}{[H_2NNH_2]} = \frac{x^2}{2.0 - x} \approx \frac{x^2}{2.0} \quad \text{(assuming } x << 2.0\text{)}$$

$x = [OH^-] = 2.4 \times 10^{-3}\ M$; pOH = 2.62; pH = 11.38; assumptions good (x is 0.12% of 2.0).

$[H_2NNH_3^+] = 2.4 \times 10^{-3}\ M$; $[H_2NNH_2] = 2.0\ M$; $[H^+] = 10^{-11.38} = 4.2 \times 10^{-12}\ M$

95. These are solutions of weak bases in water. In each case we must solve an equilibrium weak base problem.

a. $$(C_2H_5)_3N + H_2O \rightleftharpoons (C_2H_5)_3NH^+ + OH^- \qquad K_b = 4.0 \times 10^{-4}$$

Initial	0.20 M		0	~0
	x mol/L of $(C_2H_5)_3N$ reacts with H_2O to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.20 - x$		x	x

$$K_b = 4.0 \times 10^{-4} = \frac{[(C_2H_5)_3NH^+][OH^-]}{[(C_2H_5)_3N]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}, \quad x = [OH^-] = 8.9 \times 10^{-3}\,M$$

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

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

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

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

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

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

96. These are solutions of weak bases in water.

a. $$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^- \qquad K_b = 3.8 \times 10^{-10}$$

Initial	0.40 M		0	~0
	x mol/L of $C_6H_5NH_2$ reacts with H_2O to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.40 - x$		x	x

$$3.8 \times 10^{-10} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}, \quad x = [OH^-] = 1.2 \times 10^{-5}\,M;\ \ \text{assumptions good.}$$

$[H^+] = K_w/[OH^-] = 8.3 \times 10^{-10}\ M$; pH = 9.08

b. $$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^- \qquad K_b = 4.38 \times 10^{-4}$$

Initial	0.40 M	0	~0
Equil.	$0.40 - x$	x	x

$$K_b = 4.38 \times 10^{-4} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}, \; x = 1.3 \times 10^{-2}\,M; \quad \text{assumptions good.}$$

$[OH^-] = 1.3 \times 10^{-2}\,M$; $[H^+] = K_w/[OH^-] = 7.7 \times 10^{-13}\,M$; pH = 12.11

97. 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	$-x$	→	$+x$	$+x$	
Equil.	$0.20 - x$		x	x	

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

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

The assumption fails the 5% rule. We must solve exactly using either the quadratic equation or the method of successive approximations (see Appendix 1 of the text). Using successive approximations and carrying extra significant figures:

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

$$x = [OH^-] = 1.0 \times 10^{-2}\,M; \; [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}\,M; \; \text{pH} = 12.00$$

98.

	$(C_2H_5)_2NH$ + H_2O	$\rightleftharpoons$	$(C_2H_5)_2NH_2^+$	+ OH^-	$K_b = 1.3 \times 10^{-3}$
Initial	0.050 *M*		0	~0	
	x mol/L $(C_2H_5)_2NH$ reacts with H_2O to reach equilibrium				
Change	$-x$	→	$+x$	$+x$	
Equil.	$0.050 - x$		x	x	

$$K_b = 1.3 \times 10^{-3} = \frac{[(C_2H_5)_2NH_2^+][OH^-]}{[(C_2H_5)_2NH]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$x = 8.1 \times 10^{-3}$; assumption is bad (x is 16% of 0.20).

Using successive approximations:

$$1.3 \times 10^{-3} = \frac{x^2}{0.050 - 0.081}, \quad x = 7.4 \times 10^{-3}$$

$$1.3 \times 10^{-3} = \frac{x^2}{0.050 - 0.074}, \quad x = 7.4 \times 10^{-3} \; (\text{consistent answer})$$

$[OH^-] = x = 7.4 \times 10^{-3}\,M$; $[H^+] = K_w/[OH^-] = 1.4 \times 10^{-12}\,M$; pH = 11.85

99. To solve for percent ionization, we first solve the weak base equilibrium problem.

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

	NH_3	NH_4^+	OH^-
Initial	0.10 M	0	~0
Equil.	$0.10 - x$	x	x

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

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

b. $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

	NH_3	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.

c. $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ $K_b = 4.38 \times 10^{-4}$

	CH_3NH_2	$CH_3NH_3^+$	OH^-
Initial	0.10 M	0	~0
Equil.	$0.10 - x$	x	x

$4.38 \times 10^{-4} = \dfrac{x^2}{0.10 - x} \approx \dfrac{x^2}{0.10}$, $x = 6.6 \times 10^{-3}$; assumption fails the 5% rule (x is 6.6% of 0.10). Using successive approximations and carrying extra significant figures:

$$\frac{x^2}{0.10 - 0.0066} = \frac{x^2}{0.093} = 4.38 \times 10^{-4},\ x = 6.4 \times 10^{-3} \quad \text{(consistent answer)}$$

$$\text{Percent ionization} = \frac{6.4 \times 10^{-3}}{0.10} \times 100 = 6.4\%$$

100. $C_5H_5N + H_2O \rightleftharpoons C_5H_5N^+ + OH^-$ $K_b = 1.7 \times 10^{-9}$

	C_5H_5N	$C_5H_5N^+$	OH^-
Initial	0.10 M	0	~0
Equil.	$0.10 - x$	x	x

$$K_b = 1.7 \times 10^{-9} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10},\ x = [C_5H_5N] = 1.3 \times 10^{-5}\ M;\quad \text{assumptions good.}$$

$$\text{Percent } C_5H_5N \text{ reacted} = \frac{1.3 \times 10^{-5}\ M}{0.10\ M} \times 100 = 1.3 \times 10^{-2}\%$$

101. Using the K_b reaction to solve where PT = p-toluidine ($CH_3C_6H_4NH_2$):

	PT	+	H_2O	$\rightleftharpoons$	PTH^+	+	OH^-
Initial	$0.016\ M$				0		~0
	x mol/L of PT reacts with H_2O to reach equilibrium						
Change	$-x$			$\rightarrow$	$+x$		$+x$
Equil.	$0.016 - x$				x		x

$$K_b = \frac{[PTH^+][OH^-]}{[PT]} = \frac{x^2}{0.016 - x}$$

Because pH = 8.60: pOH = 14.00 – 8.60 = 5.40 and $[OH^-] = x = 10^{-5.40} = 4.0 \times 10^{-6}\ M$

$$K_b = \frac{(4.0 \times 10^{-6})^2}{0.016 - (4.0 \times 10^{-6})} = 1.0 \times 10^{-9}$$

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

	$HONH_2$		$HONH_3^+$	OH^-	
Initial	I		0	~0	$I = [HONH_2]_0$
Equil.	$I - x$		x	x	

$$K_b = 1.1 \times 10^{-8} = \frac{x^2}{I - x}$$

From problem, pH = 10.00, so pOH = 4.00 and $x = [OH^-] = 1.0 \times 10^{-4}\ M$.

$$1.1 \times 10^{-8} = \frac{(1.0 \times 10^{-4})^2}{I - (1.0 \times 10^{-4})},\quad I = 0.91\ M$$

$$\text{Mass } HONH_2 = 0.2500\ L \times \frac{0.91\ \text{mol } HONH_2}{L} \times \frac{33.03\ \text{g } HONH_2}{\text{mol } HONH_2} = 7.5\ \text{g } HONH_2$$

Polyprotic Acids

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

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

104. $H_3C_6H_5O_7(aq) \rightleftharpoons H_2C_6H_5O_7^-(aq) + H^+(aq)$ $\quad K_{a_1} = \dfrac{[H_2C_6H_5O_7^-][H^+]}{[H_3C_6H_5O_7]}$

$H_2C_6H_5O_7^-(aq) \rightleftharpoons HC_6H_5O_7^{2-}(aq) + H^+(aq)$ $\quad K_{a_2} = \dfrac{[HC_6H_5O_7^{2-}][H^+]}{[H_2C_6H_5O_7^-]}$

$HC_6H_5O_7^{2-}(aq) \rightleftharpoons C_6H_5O_7^{3-}(aq) + H^+(aq)$ $\quad K_{a_3} = \dfrac{[C_6H_5O_7^{3-}][H^+]}{[HC_6H_5O_7^{2-}]}$

105. For H_3PO_4, $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, and = $K_{a_3} = 4.8 \times 10^{-13}$. Because K_{a_1} is much larger than K_{a_2} and K_{a_3}, the dominant H^+ producer is H_3PO_4, and the H^+ contributed from $H_2PO_4^-$ and HPO_4^{2-} can be ignored Solving the weak acid problem in the typical manner.

	H_3PO_4	$\rightleftharpoons$	$H_2PO_4^-$	+	H^+
Initial	0.007 *M*		0		~0
Equil.	$0.007 - x$		x		x

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} = \frac{x^2}{0.007 - x} \approx \frac{x^2}{0.007}$$

$x = 7.5 \times 10^{-3}$; assumption is horrible because x is 100% of 0.007. We will use the quadratic equation to solve exactly.

$$7.5 \times 10^{-3} = \frac{x^2}{0.007 - x},\ x^2 = 5 \times 10^{-5} - (7.5 \times 10^{-3})x,\ x^2 + (7.5 \times 10^{-3})x - 5 \times 10^{-5} = 0$$

$$x = [H^+] = \frac{-7.5 \times 10^{-3} \pm [(7.5 \times 10^{-3})^2 - 4(1)(-5 \times 10^{-5})]^{1/2}}{2(1)} = 4 \times 10^{-3}\ M$$

$\text{pH} = -\log(4 \times 10^{-3}) = 2.4$

106. The reactions are:

$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^-$ $\quad K_{a_1} = 5 \times 10^{-3}$

$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-}$ $\quad K_{a_2} = 8 \times 10^{-8}$

$HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-}$ $\quad K_{a_3} = 6 \times 10^{-10}$

We will deal with the reactions in order of importance, beginning with the largest K_a, K_{a_1}.

	H_3AsO_4	$\rightleftharpoons$	H^+	+	$H_2AsO_4^-$	$K_{a_1} = 5 \times 10^{-3} = \dfrac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]}$
Initial	0.20 *M*		~0		0	
Equil.	0.20 - *x*		*x*		*x*	

$$5 \times 10^{-3} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20},\ x = 3 \times 10^{-2}\ M;\ \text{assumption fails the 5\% rule.}$$

Solving by the method of successive approximations:

$5 \times 10^{-3} = x^2/(0.20 - 0.03)$, $x = 3 \times 10^{-2}$ (consistent answer)

$[H^+] = [H_2AsO_4^-] = 3 \times 10^{-2}\ M$; $[H_3AsO_4] = 0.20 - 0.03 = 0.17\ M$

Because $K_{a_2} = \dfrac{[H^+][HAsO_4^{2-}]}{[H_2AsO_4^-]} = 8 \times 10^{-8}$ is much smaller than the K_{a_1} value, very little of $H_2AsO_4^-$ (and $HAsO_4^{2-}$) dissociates compared to H_3AsO_4. Therefore, $[H^+]$ and $[H_2AsO_4^-]$ will not change significantly by the K_{a_2} reaction. Using the previously calculated concentrations of H^+ and $H_2AsO_4^-$ to calculate the concentration of $HAsO_4^{2-}$:

$$8 \times 10^{-8} = \frac{(3 \times 10^{-2})[HAsO_4^{2-}]}{3 \times 10^{-2}},\ [HAsO_4^{2-}] = 8 \times 10^{-8}\ M$$

The assumption that the K_{a_2} reaction does not change $[H^+]$ and $[H_2AsO_4^-]$ is good. We repeat the process using K_{a_3} to get $[AsO_4^{3-}]$.

$$K_{a_3} = 6 \times 10^{-10} = \frac{[H^+][AsO_4^{3-}]}{[HAsO_4^{2-}]} = \frac{(3 \times 10^{-2})[AsO_4^{3-}]}{8 \times 10^{-8}}$$

$[AsO_4^{3-}] = 1.6 \times 10^{-15} \approx 2 \times 10^{-15}\ M$; assumption good.

So in 0.20 *M* analytical concentration of H_3AsO_4:

$[H_3AsO_4] = 0.17\ M$; $[H^+] = [H_2AsO_4^-] = 3 \times 10^{-2}\ M$

$[HAsO_4^{2-}] = 8 \times 10^{-8}\ M$; $[AsO_4^{3-}] = 2 \times 10^{-15}\ M$; $[OH^-] = K_w/[H^+] = 3 \times 10^{-13}\ M$

107. Because K_{a_2} for H_2S is so small, we can ignore the H^+ contribution from the K_{a_2} reaction.

	H_2S	$\rightleftharpoons$	H^+	HS^-	$K_{a_1} = 1.0 \times 10^{-7}$
Initial	0.10 *M*		~0	0	
Equil.	0.10 − *x*		*x*	*x*	

$$K_{a_1} = 1.0 \times 10^{-7} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, \quad x = [H^+] = 1.0 \times 10^{-4}; \quad \text{assumptions good.}$$

$pH = -\log(1.0 \times 10^{-4}) = 4.00$

Use the K_{a_2} reaction to determine $[S^{2-}]$.

	HS^-	$\rightleftharpoons$	H^+	$+$	S^{2-}
Initial	$1.0 \times 10^{-4}\ M$		$1.0 \times 10^{-4}\ M$		0
Equil.	$1.0 \times 10^{-4} - x$		$1.0 \times 10^{-4} + x$		x

$$K_{a_2} = 1.0 \times 10^{-19} = \frac{(1.0 \times 10^{-4} + x)x}{(1.0 \times 10^{-4} - x)} \approx \frac{(1.0 \times 10^{-4})x}{1.0 \times 10^{-4}}$$

$x = [S^{2-}] = 1.0 \times 10^{-19}\ M$; assumptions good.

108. The relevant reactions are:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad K_{a_1} = 4.3 \times 10^{-7}; \quad HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad K_{a_2} = 5.6 \times 10^{-11}$$

Initially, we deal only with the first reaction (since $K_{a_1} >> K_{a_2}$), and then let those results control values of concentrations in the second reaction.

	H_2CO_3	$\rightleftharpoons$	H^+	$+$	HCO_3^-
Initial	$0.010\ M$		~0		0
Equil.	$0.010 - x$		x		x

$$K_{a_1} = 4.3 \times 10^{-7} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010}$$

$x = 6.6 \times 10^{-5}\ M = [H^+] = [HCO_3^-]$; assumptions good.

	HCO_3^-	$\rightleftharpoons$	H^+	$+$	CO_3^{2-}
Initial	$6.6 \times 10^{-5}\ M$		$6.6 \times 10^{-5}\ M$		0
Equil.	$6.6 \times 10^{-5} - y$		$6.6 \times 10^{-5} + y$		y

If y is small, then $[H^+] = [HCO_3^-]$, and $K_{a_2} = 5.6 \times 10^{-11} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \approx y$.

$y = [CO_3^{2-}] = 5.6 \times 10^{-11}\ M$; assumptions good.

The amount of H^+ from the second dissociation is $5.6 \times 10^{-11}\ M$ or:

$$\frac{5.6 \times 10^{-11}}{6.6 \times 10^{-5}} \times 100 = 8.5 \times 10^{-5}\%$$

This result justifies our treating the equilibria separately. If the second dissociation contributed a significant amount of H^+, we would have to treat both equilibria simultaneously.

The reaction that occurs when acid is added to a solution of HCO_3^- is:

$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

The bubbles are $CO_2(g)$ and are formed by the breakdown of unstable H_2CO_3 molecules. We should write $H_2O(l) + CO_2(aq)$ or $CO_2(aq)$ for what we call carbonic acid. It is for convenience, however, that we write $H_2CO_3(aq)$.

109. 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 that 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

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

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} *M*. 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 usually the case in more dilute solutions of H_2SO_4.

110. For H_2SO_4, the first dissociation occurs to completion. The hydrogen sulfate ion (HSO_4^-) is a weak acid with $K_{a_2} = 1.2 \times 10^{-2}$. We will consider this equilibrium for additional H^+ production:

	HSO_4^-	$\rightleftharpoons$	H^+	+	SO_4^{2-}
Initial	0.0050 *M*		0.0050 *M*		0
	x mol/L HSO_4^- dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.0050 - x$		$0.0050 + x$		x

$$K_{a_2} = 0.012 = \frac{(0.0050+x)x}{0.0050-x} \approx x,\ x = 0.012;\ \ \text{assumption is horrible (240\% error).}$$

Using the quadratic formula:

$$6.0 \times 10^{-5} - (0.012)x = x^2 + (0.0050)x,\ \ x^2 + (0.017)x - 6.0 \times 10^{-5} = 0$$

$$x = \frac{-0.017 \pm (2.9 \times 10^{-4} + 2.4 \times 10^{-4})^{1/2}}{2} = \frac{-0.017 \pm 0.023}{2},\ \ x = 3.0 \times 10^{-3}\,M$$

$$[H^+] = 0.0050 + x = 0.0050 + 0.0030 = 0.0080\ M;\ \ pH = 2.10$$

Note: We had to consider both H_2SO_4 and HSO_4^- for H^+ production in this problem.

Acid-Base Properties of Salts

111. One difficult aspect of acid-base chemistry is recognizing what types of species are present in solution, that is, 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, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$

c. Weak acids have a K_a value of less than 1 but greater than K_w. Some weak acids are listed in Table 14.2 of the text. Weak bases have a K_b value of less than 1 but greater than K_w. Some weak bases are listed in Table 14.3 of the text.

d. Conjugate bases of weak acids are weak bases; that is, all have a K_b value of less than 1 but greater than K_w. Some examples of these are the conjugate bases of the weak acids listed in Table 14.2 of the text.

e. Conjugate acids of weak bases are weak acids; that is, all have a K_a value of less than 1 but greater than K_w. Some examples of these are the conjugate acids of the weak bases listed 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^-, NO_3^-, ClO_4^-, HSO_4^-) have no basic properties in water ($K_b << K_w$), 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 that identifies the species.

KOH: Strong base (b)

KNO_3: Neutral; K^+ and NO_3^- have no acidic/basic properties (f and g).

KCN: CN^- is a weak base, $K_b = K_w/K_{a,\,HCN} = 1.0 \times 10^{-14}/6.2 \times 10^{-10} = 1.6 \times 10^{-5}$ (c and d). Ignore K^+ (f).

NH_4Cl: 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 solution, with the weak acid solution less acidic. The most basic solution will be the strong base solution, with the weak base solution less basic. The KNO_3 solution will be neutral at pH = 7.00.

Most acidic → most basic: $HCl > NH_4Cl > KNO_3 > KCN > KOH$

112. See Exercise 111 for some generalizations on acid-base properties of salts. The letters in parenthesis is(are) the generalization(s) listed in Exercise 111 that identifies the species.

$CaBr_2$:	Neutral; Ca^{2+} and Br^- have no acidic/basic properties (f and g).
KNO_2:	NO_2^- is a weak base, $K_b = K_w/K_{a,\ HNO_2} = (1.0 \times 10^{-14})/(4.0 \times 10^{-4}) = 2.5 \times 10^{-11}$ (c and d). Ignore K^+ (f).
$HClO_4$:	Strong acid (a)
HNO_2:	Weak acid, $K_a = 4.0 \times 10^{-4}$ (c)
$HONH_3ClO_4$:	$HONH_3^+$ is a weak acid, $K_a = K_w/K_{b,\ HONH_2} = (1.0 \times 10^{-14})/(1.1 \times 10^{-8}) = 9.1 \times 10^{-7}$ (c and e). Ignore ClO_4^- (g). Note that HNO_2 has a larger K_a value than $HONH_3^+$, so HNO_2 is a stronger weak acid than $HONH_3^+$.

Using the information above (identity and the K_a or K_b values), the ordering is:

Most acidic → most basic: $HClO_4 > HNO_2 > HONH_3ClO_4 > CaBr_2 > KNO_2$

113. 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.

114. Because NH_3 is a weaker base (smaller K_b value) than CH_3NH_2, the conjugate acid of NH_3 will be a stronger acid than the conjugate acid of CH_3NH_2. Thus NH_4^+ is a stronger acid than $CH_3NH_3^+$.

115. a. KCl is a soluble ionic compound that dissolves in water to produce $K^+(aq)$ and $Cl^-(aq)$. K^+ (like the other alkali metal cations) has no acidic or basic properties. Cl^- is the conjugate base of the strong acid HCl. Cl^- has no basic (or acidic) properties. Therefore, a solution of KCl will be neutral because neither of the ions has any acidic or basic properties. The 1.0 *M* KCl solution has $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ *M* and pH = pOH = 7.00.

b. KF is also a soluble ionic compound that dissolves in water to produce $K^+(aq)$ and $F^-(aq)$. The difference between the KCl solution and the KF solution is that F^- does have basic properties in water, unlike Cl^-. F^- is the conjugate base of the weak acid HF, and as is true for all conjugate bases of weak acids, F^- is a weak base in water. We must solve an equilibrium problem in order to determine the amount of OH^- this weak base produces in water.

$$F^- + H_2O \rightleftharpoons HF + OH^- \qquad K_b = \frac{K_w}{K_{a,\,HF}} = \frac{1.0\times10^{-14}}{7.2\times10^{-4}}$$

Initial	1.0 M		0	~0
	x mol/L of F^- reacts with H_2O to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$1.0 - x$		x	x

$$K_b = 1.4\times10^{-11} = \frac{[HF][OH^-]}{[F^-]},\ 1.4\times10^{-11} = \frac{x^2}{1.0-x} \approx \frac{x^2}{1.0}$$

$x = [OH^-] = 3.7\times10^{-6}\ M$; assumptions good

pOH = 5.43; pH = 14.00 – 5.43 = 8.57; $[H^+] = 10^{-8.57} = 2.7\times10^{-9}\ M$

116. $C_2H_5NH_3Cl \rightarrow C_2H_5NH_3^+ + Cl^-$; $C_2H_5NH_3^+$ is the conjugate acid of the weak base $C_2H_5NH_2$ ($K_b = 5.6\times10^{-4}$). As is true for all conjugate acids of weak bases, $C_2H_5NH_3^+$ is a weak acid. Cl^- has no basic (or acidic) properties. Ignore Cl^-. Solving the weak acid problem:

$$C_2H_5NH_3^+ \rightleftharpoons C_2H_5NH_2 + H^+ \qquad K_a = K_w/5.6\times10^{-4} = 1.8\times10^{-11}$$

Initial	0.25 M		0	~0
	x mol/L $C_2H_5NH_3^+$ dissociates to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.25 - x$		x	x

$$K_a = 1.8\times10^{-11} = \frac{[C_2H_5NH_2][H^+]}{[C_2H_5NH_3^+]} = \frac{x^2}{0.25-x} \approx \frac{x^2}{0.25} \quad (\text{assuming } x << 0.25)$$

$x = [H^+] = 2.1\times10^{-6}\ M$; pH = 5.68; assumptions good.

$[C_2H_5NH_2] = [H^+] = 2.1\times10^{-6}\ M$; $[C_2H_5NH_3^+] = 0.25\ M$; $[Cl^-] = 0.25\ M$

$[OH^-] = K_w/[H^+] = 4.8\times10^{-9}\ M$

117. 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.

$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+ \quad K_a = \frac{[CH_3NH_2][H^+]}{[CH_3NH_3^+]} = \frac{K_w}{K_b} = \frac{1.00\times10^{-14}}{4.38\times10^{-4}} = 2.28\times10^{-11}$$

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

Initial	0.10 M		0	~0
	x mol/L $CH_3NH_3^+$ dissociates to reach equilibrium			
Change	$-x$	→	$+x$	$+x$
Equil.	$0.10 - x$		x	x

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

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.

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

	CN^-		HCN	OH^-	
Initial	0.050 *M*		0	~0	$K_b = 1.6 \times 10^{-5}$
	x mol/L CN^- reacts with H_2O to reach equilibrium				
Change	$-x$	→	$+x$	$+x$	
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.

118. a. $KNO_2 \rightarrow K^+ + NO_2^-$: NO_2^- is a weak base. Ignore K^+.

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

	NO_2^-	HNO_2	OH^-
Initial	0.12 *M*	0	~0
Equil.	$0.12 - x$	x	x

$$K_b = 2.5 \times 10^{-11} = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.12 - x} \approx \frac{x^2}{0.12}$$

$x = [OH^-] = 1.7 \times 10^{-6}$ *M*; pOH = 5.77; pH = 8.23; assumptions good.

b. $NaOCl \rightarrow Na^+ + OCl^-$: OCl^- is a weak base. Ignore Na^+.

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

	OCl^-	$HOCl$	OH^-
Initial	0.45 *M*	0	~0
Equil.	$0.45 - x$	x	x

$$K_b = 2.9 \times 10^{-7} = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{x^2}{0.45 - x} \approx \frac{x^2}{0.45}$$

$x = [OH^-] = 3.6 \times 10^{-4}$ *M*; pOH = 3.44; pH = 10.56; assumptions good.

c. $NH_4ClO_4 \rightarrow NH_4^+ + ClO_4^-$: NH_4^+ is a weak acid. ClO_4^- is the conjugate base of a strong acid. ClO_4^- has no basic (or acidic) properties.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

	NH_4^+	NH_3	H^+
Initial	0.40 *M*	0	~0
Equil.	0.40 − *x*	*x*	*x*

$$K_a = 5.6 \times 10^{-10} = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}$$

$x = [H^+] = 1.5 \times 10^{-5}\,M$; pH = 4.82; assumptions good.

119. 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 since K_b values for these species are between K_w and 1. 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.

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

	A^-		HA	OH^-
Initial	0.100 mol/1.00 L		0	~0
	x mol/L A^- reacts with H_2O to reach equilibrium			
Change	−*x*	→	+*x*	+*x*
Equil.	0.100 − *x*		*x*	*x*

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{0.100 - x};$$ 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.

120. $BHCl \rightarrow BH^+ + Cl^-$; Cl^- is the conjugate base of the strong acid HCl, so Cl^- has no acidic/basic properties. BH^+ is a weak acid because it is the conjugate acid of a weak base B. Determining the K_a value for BH^+:

	BH^+	$\rightleftharpoons$	B	+	H^+
Initial	$0.10\ M$		0		~ 0
	x mol/L BH^+ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.10 - x$		x		x

$$K_a = \frac{[B][H^+]}{[BH^+]} = \frac{x^2}{0.10 - x}; \text{ from the problem, pH} = 5.82:$$

$$[H^+] = x = 10^{-5.82} = 1.5 \times 10^{-6}\ M; \quad K_a = \frac{(1.5 \times 10^{-6})^2}{0.10 - (1.5 \times 10^{-6})} = 2.3 \times 10^{-11}$$

K_b for the base B = $K_w/K_a = (1.0 \times 10^{-14})/(2.3 \times 10^{-11}) = 4.3 \times 10^{-4}$.

From Table 14.3 of the text, this K_b value is closest to CH_3NH_2, so the unknown salt is CH_3NH_3Cl.

121. B^- is a weak base. Use the weak base data to determine K_b for B^-.

	B^- + H_2O	$\rightleftharpoons$	HB	+	OH^-
Initial	$0.050\ M$		0		~ 0
Equil.	$0.050 - x$		x		x

From pH = 9.00: pOH = 5.00, $[OH^-] = 10^{-5.00} = 1.0 \times 10^{-5}\ M = x$.

$$K_b = \frac{[HB][OH^-]}{[B^-]} = \frac{x^2}{0.050 - x} = \frac{(1.0 \times 10^{-5})^2}{0.050 - (1.0 \times 10^{-5})} = 2.0 \times 10^{-9}$$

Because B^- is a weak base, HB will be a weak acid. Solving the weak acid problem:

	HB	$\rightleftharpoons$	H^+	+	B^-
Initial	$0.010\ M$		~ 0		0
Equil.	$0.010 - x$		x		x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-9}}, \quad 5.0 \times 10^{-6} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010}$$

$x = [H^+] = 2.2 \times 10^{-4}\ M$; pH = 3.66; assumptions good.

122. From the pH, $C_7H_4ClO_2^-$ is a weak base. Use the weak base data to determine K_b for $C_7H_4ClO_2^-$ (which we will abbreviate as CB^-).

	CB^- + H_2O	$\rightleftharpoons$	HCB	+	OH^-
Initial	$0.20\ M$		0		~ 0
Equil.	$0.20 - x$		x		x

Because pH = 8.65, pOH = 5.35 and $[OH^-] = 10^{-5.35} = 4.5 \times 10^{-6} = x$.

$$K_b = \frac{[HCB][OH^-]}{[CB^-]} = \frac{x^2}{0.20 - x} = \frac{(4.5 \times 10^{-6})^2}{0.20 - (4.5 \times 10^{-6})} = 1.0 \times 10^{-10}$$

Because CB^- is a weak base, HCB, chlorobenzoic acid, is a weak acid. Solving the weak acid problem:

	HCB	$\rightleftharpoons$	H^+	+	CB^-
Initial	0.20 *M*		~0		0
Equil.	$0.20 - x$		x		x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-10}},\ 1.0 \times 10^{-4} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$x = [H^+] = 4.5 \times 10^{-3}$ *M*; pH = 2.35; assumptions good.

123. 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	$-x$	$\longrightarrow$	$+x$	$+x$
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.

124. Major species: $Co(H_2O)_6^{3+}$ ($K_a = 1.0 \times 10^{-5}$), Cl^- (neutral), and H_2O ($K_w = 1.0 \times 10^{-14}$); $Co(H_2O)_6^{3+}$ will determine the pH because it is a stronger acid than water. Solving the weak acid problem in the usual manner:

	$Co(H_2O)_6^{3+}$	$\rightleftharpoons$	$Co(H_2O)_5(OH)^{2+}$	+	H^+	$K_a = 1.0 \times 10^{-5}$
Initial	0.10 *M*		0		~0	
Equil.	$0.10 - x$		x		x	

$$K_a = 1.0 \times 10^{-5} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10},\quad x = [H^+] = 1.0 \times 10^{-3}\ M$$

$pH = -\log(1.0 \times 10^{-3}) = 3.00$; assumptions good.

125. Reference Table 14.6 of the text and the solution to Exercise 111 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.

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

126. a. $KCl \rightarrow K^+ + Cl^-$ neutral; K^+ and Cl^- have no effect on pH.

b. $NH_4C_2H_3O_2 \rightarrow NH_4^+ + C_2H_3O_2^-$ neutral; NH_4^+ is a weak acid, and $C_2H_3O_2^-$ is a weak base.

Because $K_{a,\,NH_4^+} = K_{b,\,C_2H_3O_2^-}$, pH = 7.00.

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad K_a = \frac{K_w}{K_{b,\,NH_3}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \quad K_b = \frac{K_w}{K_{b,\,HC_2H_3O_2}} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

c. $CH_3NH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$ acidic; $CH_3NH_3^+$ is a weak acid, and Cl^- has no effect on pH.

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

d. $KF \rightarrow K^+ + F^-$ basic; F^- is a weak base, and K^+ has no effect on pH.

$$F^- + H_2O \rightleftharpoons HF + OH^- \quad K_b = \frac{K_w}{K_{a,\,HF}} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

e. $NH_4F \rightarrow NH_4^+ + F^-$ acidic; NH_4^+ is a weak acid, and F^- is a weak base. Because $K_{a,\,NH_4^+} > K_{b,\,F^-}$, the solution is acidic.

$$NH_4^+ \rightleftharpoons H^+ + NH_3 \quad K_a = 5.6 \times 10^{-10}; \quad F^- + H_2O \rightleftharpoons HF + OH^- \quad K_b = 1.4 \times 10^{-11}$$

f. $CH_3NH_3CN \rightarrow CH_3NH_3^+ + CN^-$ basic; $CH_3NH_3^+$ is a weak acid, and CN^- is a weak base. Because $K_{b,\,CN^-} > K_{a,\,CH_3NH_3^+}$, the solution is basic.

$$CH_3NH_3^+ \rightleftharpoons H^+ + CH_3NH_2 \quad K_a = 2.28 \times 10^{-11}$$

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

Relationships Between Structure and Strengths of Acids and Bases

127. 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.

128. a. $BrO_3^- < IO_3^-$; these are the conjugate bases of the acids in Exercise 127a. Since $HBrO_3$ is the stronger acid, the conjugate base of $HBrO_3$ (BrO_3^-) will be the weaker base. IO_3^- will be the stronger base because HIO_3 is the weaker acid.

b. $NO_3^- < NO_2^-$; these are the conjugate bases of the acids in Exercise 127b. Conjugate base strength is inversely related to acid strength.

c. $OCl^- < OI^-$; these are the conjugate bases of the acids in Exercise 127c.

129. 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.

130. In general, the stronger the acid, the weaker is the conjugate base.

a. $SeH^- < SH^- < OH^-$; these are the conjugate bases of the acids in Exercise 129a. The ordering of the base strength is the opposite of the acids.

b. $PH_3 < NH_3$ (See Exercise 129d.)

c. $HONH_2 < NH_3$ (See Exercise129c.)

131. 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.

132. a. Basic; $Li_2O(s) + H_2O(l) \rightarrow 2\ LiOH(aq)$; LiOH is a strong base.

b. Acidic; $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$; H_2CO_3 is a weak diprotic acid.

c. Basic; $SrO(s) + H_2O(l) \rightarrow Sr(OH)_2(aq)$; $Sr(OH)_2$ is a strong base.

Lewis Acids and Bases

133. 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

134. a. Fe^{3+}, acid; H_2O, base
b. H_2O, acid; CN^-, base
c. HgI_2, acid; I^-, base

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

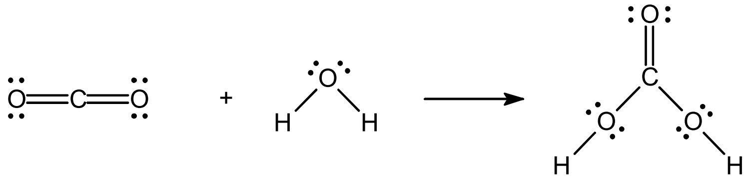
$Al(OH)_3(s) + OH^-(aq) \rightarrow Al(OH)_4^-(aq)$ (Lewis acid, electron pair acceptor)

136. $Zn(OH)_2(s) + 2\ H^+(aq) \rightarrow Zn^{2+}(aq) + 2\ H_2O(l)$ (Brønsted-Lowry base)

$Zn(OH)_2(s) + 2\ OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq)$ (Lewis acid)

137. 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+}.

138. The Lewis structures for the reactants and products are:



In this reaction, H_2O donates a pair of electrons to carbon in CO_2, which is followed by a proton shift to form H_2CO_3. H_2O is the Lewis base, and CO_2 is the Lewis acid.

Connecting to Biochemistry

139. $$[HC_9H_7O_4] = \frac{2\text{ tablets} \times \frac{0.325\text{ g } HC_9H_7O_4}{\text{tablet}} \times \frac{1\text{ mol } HC_9H_7O_4}{180.15\text{ g}}}{0.237\text{ L}} = 0.0152\ M$$

	$HC_9H_7O_4$	$\rightleftharpoons$	H^+	+	$C_9H_7O_4^-$
Initial	0.0152 M		~0		0
	x mol/L $HC_9H_7O_4$ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.0152 - x$		x		x

$$K_a = 3.3 \times 10^{-4} = \frac{[H^+][C_9H_7O_4^-]}{[HC_9H_7O_4]} = \frac{x^2}{0.0152 - x} \approx \frac{x^2}{0.0152},\ x = 2.2 \times 10^{-3}\ M$$

Assumption that $0.0152 - x \approx 0.0152$ fails the 5% rule: $\frac{2.2 \times 10^{-3}}{0.0152} \times 100 = 14\%$

Using successive approximations or the quadratic equation gives an exact answer of $x = 2.1 \times 10^{-3}\ M$.

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

140. $HClO_4$ is a strong acid with $[H^+] = 0.040\ M$. This equals the $[H^+]$ in the trichloroacetic acid solution. Set up the problem using the K_a equilibrium reaction for CCl_3CO_2H.

	CCl_3CO_2H	$\rightleftharpoons$	H^+	+	$CCl_3CO_2^-$
Initial	0.050 M		~0		0
Equil.	$0.050 - x$		x		x

$$K_a = \frac{[H^+][CCl_3CO_2^-]}{[CCl_3CO_2H]} = \frac{x^2}{0.050 - x};$$ from the problem, $x = [H^+] = 4.0 \times 10^{-2}\ M$.

$$K_a = \frac{(4.0 \times 10^{-2})^2}{0.050 - (4.0 \times 10^{-2})} = 0.16$$

141. For $H_2C_6H_6O_6$. $K_{a_1} = 7.9 \times 10^{-5}$ and $K_{a_2} = 1.6 \times 10^{-12}$. Because $K_{a_1} >> K_{a_2}$, the amount of H^+ produced by the K_{a_2} reaction will be negligible.

$$[H_2C_6H_6O_6]_0 = \frac{0.500\text{ g} \times \frac{1\text{ mol } H_2C_6H_6O_6}{176.12\text{ g}}}{0.2000\text{ L}} = 0.0142\ M$$

	$H_2C_6H_6O_6(aq)$	$\rightleftharpoons$	$HC_6H_6O_6^-(aq)$	+	$H^+(aq)$	$K_{a_1} = 7.9 \times 10^{-5}$
Initial	$0.0142\ M$		0		~0	
Equil.	$0.0142 - x$		x		x	

$$K_{a_1} = 7.9 \times 10^{-5} = \frac{x^2}{0.0142 - x} \approx \frac{x^2}{0.0142},\ x = 1.1 \times 10^{-3};\quad \text{assumption fails the 5\% rule.}$$

Solving by the method of successive approximations:

$$7.9 \times 10^{-5} = \frac{x^2}{0.0142 - 1.1 \times 10^{-3}},\ x = 1.0 \times 10^{-3}\ M\ \text{(consistent answer)}$$

Because H^+ produced by the K_{a_2} reaction will be negligible, $[H^+] = 1.0 \times 10^{-3}$ and pH = 3.00.

142. $$\frac{1.0 \text{ g quinine}}{1.9000 \text{ L}} \times \frac{1 \text{ mol quinine}}{324.4 \text{ g quinine}} = 1.6 \times 10^{-3}\ M \text{ quinine; let Q = quinine} = C_{20}H_{24}N_2O_2.$$

	$Q + H_2O$	$\rightleftharpoons$	QH^+	+	OH^-	$K_b = 10^{-5.1} = 8 \times 10^{-6}$
Initial	$1.6 \times 10^{-3}\ M$		0		~0	
	x mol/L quinine reacts with H_2O to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$1.6 \times 10^{-3} - x$		x		x	

$$K_b = 8 \times 10^{-6} = \frac{[QH^+][OH^-]}{[Q]} = \frac{x^2}{(1.6 \times 10^{-3} - x)} \approx \frac{x^2}{1.6 \times 10^{-3}}$$

$x = 1 \times 10^{-4}$; assumption fails 5% rule (x is 6% of 0.0016). Using successive approximations:

$$\frac{x^2}{(1.6 \times 10^{-3} - 1 \times 10^{-4})} = 8 \times 10^{-6},\ x = 1 \times 10^{-4}\ M\ \text{(consistent answer)}$$

$x = [OH^-] = 1 \times 10^{-4}\ M$; pOH = 4.0; pH = 10.0

143. 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

$K_b = \dfrac{x^2}{1.7 \times 10^{-3} - x}$; pH = 9.59; pOH = 14.00 − 9.59 = 4.41.

$[OH^-] = x = 10^{-4.41} = 3.9 \times 10^{-5}\,M$; $K_b = \dfrac{(3.9\times10^{-5})^2}{1.7 \times 10^{-3} - (3.9\times10^{-5})} = 9.2 \times 10^{-7}$

144. Codeine = $C_{18}H_{21}NO_3$; codeine sulfate = $C_{36}H_{44}N_2O_{10}S$

The formula for codeine sulfate works out to $(\text{codeineH}^+)_2SO_4^{2-}$, where $\text{codeineH}^+ = HC_{18}H_{21}NO_3^+$. Two codeine molecules are protonated by H_2SO_4, forming the conjugate acid of codeine. The SO_4^{2-} then acts as the counter ion to give a neutral compound. Codeine sulfate is an ionic compound that is more soluble in water than codeine, allowing more of the drug into the bloodstream.

145. $NaN_3 \rightarrow Na^+ + N_3^-$; azide ($N_3^-$) is a weak base because 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^+.

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

	N_3^-		HN_3	OH^-
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

$K_b = \dfrac{[HN_3][OH^-]}{[N_3^-]}$, $5.3 \times 10^{-10} = \dfrac{x^2}{0.010-x} \approx \dfrac{x^2}{0.010}$ (assuming $x << 0.010$)

$x = [OH^-] = 2.3 \times 10^{-6}\,M$; $[H^+] = \dfrac{1.0 \times 10^{-14}}{2.3 \times 10^{-6}} = 4.3 \times 10^{-9}\,M$; assumptions good.

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

146. $$\frac{30.0\text{ mg papH}^+\text{Cl}^-}{\text{mL soln}} \times \frac{1000\text{ mL}}{\text{L}} \times \frac{1\text{ g}}{1000\text{ mg}} \times \frac{1\text{ mol papH}^+\text{Cl}^-}{378.85\text{ g}} \times \frac{1\text{ mol papH}^+}{\text{mol papH}^+\text{Cl}^-} = 0.0792\,M$$

$$\text{papH}^+ \rightleftharpoons \text{pap} + H^+ \qquad K_a = \frac{K_w}{K_{b,\text{ pap}}} = \frac{2.1 \times 10^{-14}}{8.33 \times 10^{-9}} = 2.5 \times 10^{-6}$$

	papH^+	pap	H^+
Initial	0.0792 *M*	0	~0
Equil.	$0.0792 - x$	x	x

$K_a = 2.5 \times 10^{-6} = \dfrac{x^2}{0.0792 - x} \approx \dfrac{x^2}{0.0792}$, $x = [H^+] = 4.4 \times 10^{-4}\,M$

$pH = -\log(4.4 \times 10^{-4}) = 3.36$; assumptions good.

147. a. In the lungs there is a lot of O_2, and the equilibrium favors $Hb(O_2)_4$. In the cells there is a deficiency of O_2, and the equilibrium favors HbH_4^{4+}.

b. CO_2 is a weak acid, $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$. Removing CO_2 essentially decreases H^+. $Hb(O_2)_4$ is then favored, and O_2 is not released by hemoglobin in the cells. Breathing into a paper bag increases CO_2 in the blood, thus increasing $[H^+]$, which shifts the reaction left.

c. CO_2 builds up in the blood, and it becomes too acidic, driving the equilibrium to the left. Hemoglobin can't bind O_2 as strongly in the lungs. Bicarbonate ion acts as a base in water and neutralizes the excess acidity.

148. $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \qquad K = \dfrac{[H_2CO_3]}{[CO_2]}$

During exercise: $[H_2CO_3] = 26.3$ m*M* and $[CO_2] = 1.63$ m*M*, so: $K = \dfrac{26.3\text{ m}M}{1.63\text{ m}M} = 16.1$

At rest: $K = 16.1 = \dfrac{24.9\text{ m}M}{[CO_2]}$, $[CO_2] = 1.55$ m*M*

Additional Exercises

149. 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 $= 0.0100\text{ L} \times \dfrac{0.0100\text{ mol H}^+}{\text{L}} = 1.00 \times 10^{-4}\text{ mol H}^+$

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

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

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

150. 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-}.

151. The light bulb is bright because a strong electrolyte is present; that is, a solute is present that dissolves 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 ~1.0 *M*. NH_4Cl is the solute.

152. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$; $Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$

$$[OH^-] = \frac{0.25\ \text{g CaO} \times \dfrac{1\ \text{mol CaO}}{56.08\ \text{g}} \times \dfrac{1\ \text{mol Ca(OH)}_2}{1\ \text{mol CaO}} \times \dfrac{2\ \text{mol OH}^-}{\text{mol Ca(OH)}_2}}{1.5\ \text{L}} = 5.9 \times 10^{-3}\ M$$

$$\text{pOH} = -\log(5.9 \times 10^{-3}) = 2.23,\ \ \text{pH} = 14.00 - 2.23 = 11.77$$

153.

	HBz	$\rightleftharpoons$	H^+	+	Bz^-
Initial	C		~0		0
	x mol/L HBz dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$C - x$		x		x

$HBz = C_6H_5CO_2H$

$C = [HBz]_0$ = concentration of HBz that dissolves to give saturated solution.

$$K_a = \frac{[H^+][Bz^-]}{[HBz]} = 6.4 \times 10^{-5} = \frac{x^2}{C - x}\text{, where } x = [H^+]$$

$$6.4 \times 10^{-5} = \frac{[H^+]^2}{C - [H^+]};\ \text{pH} = 2.80;\ [H^+] = 10^{-2.80} = 1.6 \times 10^{-3} M$$

$$C - (1.6 \times 10^{-3}) = \frac{(1.6 \times 10^{-3})^2}{6.4 \times 10^{-5}} = 4.0 \times 10^{-2}$$

$$C = (4.0 \times 10^{-2}) + (1.6 \times 10^{-3}) = 4.2 \times 10^{-2} M$$

The molar solubility of $C_6H_5CO_2H$ is 4.2×10^{-2} mol/L.

154. $[H^+]_0 = (1.0 \times 10^{-2}) + (1.0 \times 10^{-2}) = 2.0 \times 10^{-2} M$ from strong acids HCl and H_2SO_4.

HSO_4^- is a good weak acid ($K_a = 0.012$). However, HCN is a poor weak acid ($K_a = 6.2 \times 10^{-10}$) and can be ignored. Calculating the H^+ contribution from HSO_4^-:

	HSO_4^-	$\rightleftharpoons$	H^+	+	SO_4^{2-}	$K_a = 0.012$
Initial	0.010 *M*		0.020 *M*		0	
Equil.	$0.010 - x$		$0.020 + x$		x	

$$K_a = \frac{x(0.020 + x)}{0.010 - x},\ \ 0.012 \approx \frac{x(0.020)}{0.010},\ \ x = 0.0060;\ \text{assumption poor (60\% error).}$$

Using the quadratic formula: $x^2 + (0.032)x - 1.2 \times 10^{-4} = 0$, $x = 3.4 \times 10^{-3} M$

$[H^+] = 0.020 + x = 0.020 + (3.4 \times 10^{-3}) = 0.023\ M$; pH = 1.64

155. For this problem we will abbreviate $CH_2{=}CHCO_2H$ as Hacr and $CH_2{=}CHCO_2^-$ as acr^-.

a. Solving the weak acid problem:

$$\text{Hacr} \rightleftharpoons H^+ + acr^- \qquad K_a = 5.6 \times 10^{-5}$$

	Hacr	H^+	acr^-
Initial	0.10 *M*	~0	0
Equil.	0.10 - x	x	x

$$\frac{x^2}{0.10 - x} = 5.6 \times 10^{-5} \approx \frac{x^2}{0.10}, \; x = [H^+] = 2.4 \times 10^{-3}\,M; \; pH = 2.62; \text{ assumptions good.}$$

b. Percent dissociation = $\dfrac{[H^+]}{[\text{Hacr}]_0} \times 100 = \dfrac{2.4 \times 10^{-3}}{0.10} \times 100 = 2.4\%$

c. acr^- is a weak base and the major source of OH^- in this solution.

$$acr^- + H_2O \rightleftharpoons \text{Hacr} + OH^- \qquad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-5}}$$

	acr^-	Hacr	OH^-	
Initial	0.050 *M*	0	~0	$K_b = 1.8 \times 10^{-10}$
Equil.	0.050 − x	x	x	

$$K_b = \frac{[\text{Hacr}][OH^-]}{[acr^-]}, \quad 1.8 \times 10^{-10} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$x = [OH^-] = 3.0 \times 10^{-6}\,M$; pOH = 5.52; pH = 8.48; assumptions good.

156. In deciding whether a substance is an acid or a base, strong or weak, you should keep in mind a couple of ideas:

(1) There are only a few common strong acids and strong bases, all of which should be memorized. Common strong acids = HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4. Common strong bases = LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$.

(2) All other acids and bases are weak and will have K_a and K_b values of less than 1 but greater than K_w (10^{-14}). Reference Table 14.2 for K_a values for some weak acids and Table 14.3 for K_b values for some weak bases. There are too many weak acids and weak bases to memorize them all. Therefore, use the tables of K_a and K_b values to help you identify weak acids and weak bases. Appendix 5 contains more complete tables of K_a and K_b values.

a. weak acid ($K_a = 4.0 \times 10^{-4}$)

b. strong acid

c. weak base ($K_b = 4.38 \times 10^{-4}$)

d. strong base

e. weak base ($K_b = 1.8 \times 10^{-5}$)

f. weak acid ($K_a = 7.2 \times 10^{-4}$)

g. weak acid ($K_a = 1.8 \times 10^{-4}$)

h. strong base

i. strong acid

157. a. $Fe(H_2O)_6^{3+} + H_2O \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H_3O^+$

	$Fe(H_2O)_6^{3+}$	$Fe(H_2O)_5(OH)^{2+}$	H_3O^+
Initial	0.10 M	0	~0
Equil.	$0.10 - x$	x	x

$$K_a = \frac{[Fe(H_2O)_5(OH)^{2+}][H_3O^+]}{[Fe(H_2O)_6^{3+}]},\ 6.0 \times 10^{-3} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$x = 2.4 \times 10^{-2}$; assumption is poor (x is 24% of 0.10). Using successive approximations:

$$\frac{x^2}{0.10 - 0.024} = 6.0 \times 10^{-3},\ x = 0.021$$

$$\frac{x^2}{0.10 - 0.021} = 6.0 \times 10^{-3},\ x = 0.022;\quad \frac{x^2}{0.10 - 0.022} = 6.0 \times 10^{-3},\ x = 0.022$$

$x = [H^+] = 0.022\ M$; pH = 1.66

b. Because of the lower charge, $Fe^{2+}(aq)$ will not be as strong an acid as $Fe^{3+}(aq)$. A solution of iron(II) nitrate will be less acidic (have a higher pH) than a solution with the same concentration of iron(III) nitrate.

158. One difficult aspect of acid-base chemistry is recognizing what types of species are present in solution, that is, 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, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$

c. Weak acids have a K_a value of less than 1 but greater than K_w. Some weak acids are listed in Table 14.2 of the text. Weak bases have a K_b value of less than 1 but greater than K_w. Some weak bases are listed in Table 14.3 of the text.

d. Conjugate bases of weak acids are weak bases; that is, all have a K_b value of less than 1 but greater than K_w. Some examples of these are the conjugate bases of the weak acids listed in Table 14.2 of the text.

e. Conjugate acids of weak bases are weak acids; that is, all have a K_a value of less than 1 but greater than K_w. Some examples of these are the conjugate acids of the weak bases listed in Table 14.3 of the text.

f. Alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and some alkaline earth metal ions (Ca^{2+}, Sr^{2+}, Ba^{2+}) have no acidic or basic properties in water.

g. Conjugate bases of strong acids (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-) have no basic properties in water ($K_b << K_w$), and only HSO_4^- has any acidic properties in water.

Let's apply these ideas to this problem to see what types of species are present.

a. HI: Strong acid; HF: weak acid ($K_a = 7.2 \times 10^{-4}$)

NaF: F^- is the conjugate base of the weak acid HF, so F^- is a weak base. The K_b value for $F^- = K_w/K_{a,\,HF} = 1.4 \times 10^{-11}$. Na^+ has no acidic or basic properties.

NaI: Neutral (pH = 7.0); Na^+ and I^- have no acidic/basic properties.

In order of increasing pH, we place the compounds from most acidic (lowest pH) to most basic (highest pH). Increasing pH: HI < HF < NaI < NaF.

b. NH_4Br: NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$), and Br^- is a neutral species.

HBr: Strong acid

KBr: Neutral; K^+ and Br^- have no acidic/basic properties.

NH_3: Weak base, $K_b = 1.8 \times 10^{-5}$

Increasing pH: HBr < NH_4Br < KBr < NH_3
Most acidic ... Most basic

c. $C_6H_5NH_3NO_3$: $C_6H_5NH_3^+$ is a weak acid ($K_a = K_w/K_{b,\,C_6H_5NH_2} = 1.0 \times 10^{-14}/3.8 \times 10^{-10} = 2.6 \times 10^{-5}$), and NO_3^- is a neutral species.

$NaNO_3$: Neutral; Na^+ and NO_3^- have no acidic/basic properties.

NaOH: Strong base

HOC_6H_5: Weak acid ($K_a = 1.6 \times 10^{-10}$)

KOC_6H_5: $OC_6H_5^-$ is a weak base ($K_b = K_w/K_{a,\,HOC_6H_5} = 6.3 \times 10^{-5}$), and K^+ is a neutral species.

$C_6H_5NH_2$: Weak base ($K_b = 3.8 \times 10^{-10}$)

HNO_3: Strong acid

This is a little more difficult than the previous parts of this problem because two weak acids and two weak bases are present. Between the weak acids, $C_6H_5NH_3^+$ is a stronger weak acid than HOC_6H_5 since the K_a value for $C_6H_5NH_3^+$ is larger than the K_a value for HOC_6H_5. Between the two weak bases, because the K_b value for $OC_6H_5^-$ is larger than the K_b value for $C_6H_5NH_2$, $OC_6H_5^-$ is a stronger weak base than $C_6H_5NH_2$.

Increasing pH: HNO_3 < $C_6H_5NH_3NO_3$ < HOC_6H_5 < $NaNO_3$ < $C_6H_5NH_2$ < KOC_6H_5 < NaOH
Most acidic ... Most basic

159. The solution is acidic from $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$. Solving the weak acid problem:

	HSO_4^-	$\rightleftharpoons$	H^+	+	SO_4^{2-}	$K_a = 1.2 \times 10^{-2}$
Initial	0.10 *M*		~0		0	
Equil.	$0.10 - x$		x		x	

$$1.2 \times 10^{-2} = \frac{[H^+][SO_4^{\,2-}]}{[HSO_4^{\,-}]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, \quad x = 0.035$$

Assumption is not good (x is 35% of 0.10). Using successive approximations:

$$\frac{x^2}{0.10 - x} = \frac{x^2}{0.10 - 0.035} = 1.2 \times 10^{-2}, \ x = 0.028$$

$$\frac{x^2}{0.10 - 0.028} = 1.2 \times 10^{-2}, \ x = 0.029; \quad \frac{x^2}{0.10 - 0.029} = 1.2 \times 10^{-2}, \ x = 0.029$$

$x = [H^+] = 0.029\ M$; pH = 1.54

160. a. $NH_3 + H_3O^+ \rightleftharpoons NH_4^{\,+} + H_2O$

$$K_{eq} = \frac{[NH_4^{\,+}]}{[NH_3][H^+]} = \frac{1}{K_a \text{ for } NH_4^{\,+}} = \frac{K_b \text{ for } NH_3}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^9$$

b. $NO_2^{\,-} + H_3O^+ \rightleftharpoons HNO_2 + H_2O$ $\quad K_{eq} = \frac{[HNO_2]}{[NO_2^{\,-}][H^+]} = \frac{1}{K_a \text{ for } HNO_2} = \frac{1}{4.0 \times 10^{-4}}$

$= 2.5 \times 10^3$

c. $NH_4^{\,+} + OH^- \rightleftharpoons NH_3 + H_2O$ $\quad K_{eq} = \frac{1}{K_b \text{ for } NH_3} = \frac{1}{1.8 \times 10^{-5}} = 5.6 \times 10^4$

d. $HNO_2 + OH^- \rightleftharpoons H_2O + NO_2^{\,-}$

$$K_{eq} = \frac{[NO_2^{\,-}]}{[HNO_2][OH^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_a \text{ for } HNO_2}{K_w} = \frac{4.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 4.0 \times 10^{10}$$

161. a. H_2SO_3 b. $HClO_3$ c. H_3PO_3

NaOH and KOH are soluble ionic compounds composed of Na^+ and K^+ cations and OH^- anions. All soluble ionic compounds dissolve to form the ions from which they are formed. In oxyacids, the compounds are all covalent compounds in which electrons are shared to form bonds (unlike ionic compounds). When these compounds are dissolved in water, the covalent bond between oxygen and hydrogen breaks to form H^+ ions.

Challenge Problems

162. The pH of this solution is not 8.00 because water will donate a significant amount of H^+ from the autoionization of water. You can't add an acid to water and get a basic pH. The pertinent equations are:

$H_2O \rightleftharpoons H^+ + OH^-$ $\quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

$HCl \rightarrow H^+ + Cl^-$ $\quad K_a$ is very large, so we assume that only the forward reaction occurs.

In any solution, the overall net positive charge must equal the overall net negative charge (called the charge balance). For this problem:

[positive charge] = [negative charge], so $[H^+] = [OH^-] + [Cl^-]$

From K_w, $[OH^-] = K_w/[H^+]$, and from 1.0×10^{-8} *M* HCl, $[Cl^-] = 1.0 \times 10^{-8}$ *M*. Substituting into the charge balance equation:

$$[H^+] = \frac{1.0 \times 10^{-14}}{[H^+]} + 1.0 \times 10^{-8}, \ [H^+]^2 - (1.0 \times 10^{-8})[H^+] - 1.0 \times 10^{-14} = 0$$

Using the quadratic formula to solve:

$$[H^+] = \frac{-(-1.0\times10^{-8}) \pm [(-1.0\times10^{-8})^2 - 4(1)(-1.0\times10^{-14})]^{1/2}}{2(1)}, \ [H^+] = 1.1 \times 10^{-7}\,M$$

$$\text{pH} = -\log(1.1 \times 10^{-7}) = 6.96$$

163. Because this is a very dilute solution of NaOH, we must worry about the amount of OH^- donated from the autoionization of water.

$NaOH \rightarrow Na^+ + OH^-$

$H_2O \rightleftharpoons H^+ + OH^- \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

This solution, like all solutions, must be charged balanced; that is, [positive charge] = [negative charge]. For this problem, the charge balance equation is:

$[Na^+] + [H^+] = [OH^-]$, where $[Na^+] = 1.0 \times 10^{-7}$ *M* and $[H^+] = \dfrac{K_w}{[OH^-]}$

Substituting into the charge balance equation:

$$1.0 \times 10^{-7} + \frac{1.0 \times 10^{-14}}{[OH^-]} = [OH^-], \ [OH^-]^2 - (1.0 \times 10^{-7})[OH^-] - 1.0 \times 10^{-14} = 0$$

Using the quadratic formula to solve:

$$[OH^-] = \frac{-(-1.0 \times 10^{-7}) \pm [(-1.0 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})]^{1/2}}{2(1)}$$

$[OH^-] = 1.6 \times 10^{-7}$ *M*; $\text{pOH} = -\log(1.6 \times 10^{-7}) = 6.80$; pH = 7.20

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

This is a very dilute solution of $Ca(OH)_2$, so we can't ignore the OH^- contribution from H_2O. From the dissociation of $Ca(OH)_2$ alone, $2[Ca^{2+}] = [OH^-]$. Including the H_2O autoionization into H^+ and OH^-, the overall charge balance is:

$$2[Ca^{2+}] + [H^+] = [OH^-]$$

$$2(3.0 \times 10^{-7}\ M) + K_w/[OH^-] = [OH^-],\ \ [OH^-]^2 = (6.0 \times 10^{-7})[OH^-] + K_w$$

$[OH^-]^2 - (6.0 \times 10^{-7})[OH^-] - 1.0 \times 10^{-14} = 0$; using quadratic formula: $[OH^-] = 6.2 \times 10^{-7}\ M$

165.

	HA	$\rightleftharpoons$	H^+	+	A^-	$K_a = 1.00 \times 10^{-6}$
Initial	C		~0		0	$C = [HA]_0$, for pH = 4.000,
Equil.	$C - 1.00 \times 10^{-4}$		1.00×10^{-4}		1.00×10^{-4}	$x = [H^+] = 1.00 \times 10^{-4}\ M$

$$K_a = \frac{(1.00 \times 10^{-4})^2}{(C - 1.00 \times 10^{-4})} = 1.00 \times 10^{-6};\ \text{solving: } C = 0.0101\ M$$

The solution initially contains 50.0×10^{-3} L × 0.0101 mol/L = 5.05×10^{-4} mol HA. We then dilute to a total volume V in liters. The resulting pH = 5.000, so $[H^+] = 1.00 \times 10^{-5}$. In the typical weak acid problem, $x = [H^+]$, so:

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial	5.05×10^{-4} mol/V		~0		0
Equil.	$(5.05 \times 10^{-4}/V) - (1.00 \times 10^{-5})$		1.00×10^{-5}		1.00×10^{-5}

$$K_a = \frac{(1.00 \times 10^{-5})^2}{(5.05 \times 10^{-4}/V) - (1.00 \times 10^{-5})} = 1.00 \times 10^{-6}$$

$$1.00 \times 10^{-4} = (5.05 \times 10^{-4}/V) - 1.00 \times 10^{-5}$$

V = 4.59 L; 50.0 mL are present initially, so we need to add 4540 mL of water.

166.

	HBrO	$\rightleftharpoons$	H^+	+	BrO^-	$K_a = 2 \times 10^{-9}$
Initial	$1.0 \times 10^{-6}\ M$		~0		0	
	x mol/L HBrO dissociates to reach equilibrium					
Change	$-x$	$\rightarrow$	$+x$		$+x$	
Equil.	$1.0 \times 10^{-6} - x$		x		x	

$$K_a = 2 \times 10^{-9} = \frac{x^2}{(1.0 \times 10^{-6} - x)} \approx \frac{x^2}{1.0 \times 10^{-6}},\ \ x = [H^+] = 4 \times 10^{-8}\ M;\ \text{pH} = 7.4$$

Let's check the assumptions. This answer is impossible! We can't add a small amount of an acid to water and get a basic solution. The highest possible pH for an acid in water is 7.0. In the correct solution we would have to take into account the autoionization of water.

167. Major species present are H_2O, $C_5H_5NH^+$ [$K_a = K_w/K_{b,\,C_5H_5N} = (1.0 \times 10^{-14)}/(1.7 \times 10^{-9}) = 5.9 \times 10^{-6}$], and F^- [$K_b = K_w/K_{a,\,HF} = (1.0 \times 10^{-14})/(7.2 \times 10^{-4}) = 1.4 \times 10^{-11}$]. The reaction to consider is the best acid present ($C_5H_5NH^+$) reacting with the best base present (F^-). Let's solve by first setting up an ICE table.

$$C_5H_5NH^+(aq) \;+\; F^-(aq) \;\rightleftharpoons\; C_5H_5N(aq) \;+\; HF(aq)$$

Initial	0.200 *M*	0.200 *M*		0	0
Change	$-x$	$-x$	→	$+x$	$+x$
Equil.	$0.200 - x$	$0.200 - x$		x	x

$$K = K_{a,\,C_5H_5NH^+} \times \frac{1}{K_{a,\,HF}} = 5.9 \times 10^{-6} \times \frac{1}{7.2 \times 10^{-4}} = 8.2 \times 10^{-3}$$

$$K = \frac{[C_5H_5N][HF]}{[C_5H_5NH^+][F^-]},\quad 8.2 \times 10^{-3} = \frac{x^2}{(0.200 - x)^2}\ ;\ \text{taking the square root of both sides:}$$

$$0.091 = \frac{x}{0.200 - x},\quad x = 0.018 - (0.091)x,\ \ x = 0.016\ M$$

From the setup to the problem, $x = [C_5H_5N] = [HF] = 0.016$ *M*, and $0.200 - x = 0.200 - 0.016 = 0.184$ *M* $= [C_5H_5NH^+] = [F^-]$. To solve for the $[H^+]$, we can use either the K_a equilibrium for $C_5H_5NH^+$ or the K_a equilibrium for HF. Using $C_5H_5NH^+$ data:

$$K_{a,\,C_5H_5NH^+} = 5.9 \times 10^{-6} = \frac{[C_5H_5N][H^+]}{[C_5H_5NH^+]} = \frac{(0.016)[H^+]}{0.184},\ [H^+] = 6.8 \times 10^{-5}\ M$$

$pH = -\log(6.8 \times 10^{-5}) = 4.17$

As one would expect, because the K_a for the weak acid is larger than the K_b for the weak base, a solution of this salt should be acidic.

168. Major species: NH_4^+, OCl^-, and H_2O; K_a for $NH_4^+ = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$ and K_b for $OCl^- = (1.0 \times 10^{-14})/(3.5 \times 10^{-8}) = 2.9 \times 10^{-7}$.

Because OCl^- is a better base than NH_4^+ is an acid, the solution will be basic. The dominant equilibrium is the best acid (NH_4^+) reacting with the best base (OCl^-) present.

$$NH_4^+ \;+\; OCl^- \;\rightleftharpoons\; NH_3 \;+\; HOCl$$

Initial	0.50 *M*	0.50 *M*		0	0
Change	$-x$	$-x$	→	$+x$	$+x$
Equil.	$0.50 - x$	$0.50 - x$		x	x

$$K = K_{a,\,NH_4^+} \times \frac{1}{K_{a,\,HOCl}} = (5.6 \times 10^{-10})/(3.5 \times 10^{-8}) = 0.016$$

$$K = 0.016 = \frac{[NH_3][HOCl]}{[NH_4^+][OCl^-]} = \frac{x(x)}{(0.50-x)(0.50-x)}$$

$$\frac{x^2}{(0.50-x)^2} = 0.016, \quad \frac{x}{0.50-x} = (0.016)^{1/2} = 0.13, \ x = 0.058\ M$$

To solve for the H^+, use any pertinent K_a or K_b value. Using K_a for NH_4^+:

$$K_{a,\,NH_4^+} = 5.6 \times 10^{-10} = \frac{[NH_3][H^+]}{[NH_4^+]} = \frac{(0.058)[H^+]}{0.50-0.058}, \ [H^+] = 4.3 \times 10^{-9}\ M, \ pH = 8.37$$

169. Because NH_3 is so concentrated, we need to calculate the OH^- contribution from the weak base NH_3.

	NH_3 + H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-	$K_b = 1.8 \times 10^{-5}$
Initial	15.0 M		0		0.0100 M	(Assume no volume change.)
Equil.	$15.0 - x$		x		$0.0100 + x$	

$$K_b = 1.8 \times 10^{-5} = \frac{x(0.0100+x)}{15.0-x} \approx \frac{x(0.0100)}{15.0}, \ x = 0.027;$$ assumption is horrible (x is 270% of 0.0100).

Using the quadratic formula:

$(1.8 \times 10^{-5})(15.0 - x) = (0.0100)x + x^2, \ x^2 + (0.0100)x - 2.7 \times 10^{-4} = 0$

$x = 1.2 \times 10^{-2}\ M, \ [OH^-] = (1.2 \times 10^{-2}) + 0.0100 = 0.022\ M$

170. For 0.0010% dissociation: $[NH_4^+] = 1.0 \times 10^{-5}(0.050) = 5.0 \times 10^{-7}\ M$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b = \frac{(5.0 \times 10^{-7})[OH^-]}{0.050 - 5.0 \times 10^{-7}} = 1.8 \times 10^{-5}$$

Solving: $[OH^-] = 1.8\ M$; assuming no volume change:

$$1.0\ L \times \frac{1.8\ mol\ NaOH}{L} \times \frac{40.00\ g\ NaOH}{mol\ NaOH} = 72\ g\ of\ NaOH$$

171. $1.000\ L \times \frac{1.00 \times 10^{-4}\ mol\ HA}{L} = 1.00 \times 10^{-4}\ mol\ HA$

25.0% dissociation gives:

mol $H^+ = 0.250 \times (1.00 \times 10^{-4}) = 2.50 \times 10^{-5}$ mol

mol $A^- = 0.250 \times (1.00 \times 10^{-4}) = 2.50 \times 10^{-5}$ mol

mol $HA^- = 0.750 \times (1.00 \times 10^{-4}) = 7.50 \times 10^{-5}$ mol

$$1.00 \times 10^{-4} = K_a = \frac{[H^+][A^-]}{[HA]} = \frac{\left(\frac{2.50 \times 10^{-5}}{V}\right)\left(\frac{2.50 \times 10^{-5}}{V}\right)}{\left(\frac{7.50 \times 10^{-5}}{V}\right)}$$

$$1.00 \times 10^{-4} = \frac{(2.50 \times 10^{-5})^2}{(7.50 \times 10^{-5})(V)},\quad V = \frac{(2.50 \times 10^{-5})^2}{(1.00 \times 10^{-4})(7.50 \times 10^{-5})} = 0.0833 \text{ L} = 83.3 \text{ mL}$$

The volume goes from 1000. mL to 83.3 mL, so 917 mL of water evaporated.

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

	$HC_2H_3O_2$	H^+	$C_2H_3O_2^-$
Initial	1.00 *M*	~0	0
Equil.	$1.00 - x$	x	x

$$1.8 \times 10^{-5} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00},\quad x = [H^+] = 4.24 \times 10^{-3}\, M \text{ (using one extra sig. fig.)}$$

$pH = -\log(4.24 \times 10^{-3}) = 2.37$; assumptions good.

We want to double the pH to 2(2.37) = 4.74 by addition of the strong base NaOH. As is true with all strong bases, they are great at accepting protons. In fact, they are so good that we can assume they accept protons 100% of the time. The best acid present will react the strong base. This is $HC_2H_3O_2$. The initial reaction that occurs when the strong base is added is:

$$HC_2H_3O_2 + OH^- \rightarrow C_2H_3O_2^- + H_2O$$

Note that this reaction has the net effect of converting $HC_2H_3O_2$ into its conjugate base, $C_2H_3O_2^-$.

For a pH = 4.74, let's calculate the ratio of $[C_2H_3O_2^-]/[HC_2H_3O_2]$ necessary to achieve this pH.

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^- \quad K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

When pH = 4.74, $[H^+] = 10^{-4.74} = 1.8 \times 10^{-5}$.

$$K_a = 1.8 \times 10^{-5} = \frac{(1.8 \times 10^{-5})[C_2H_3O_2^-]}{[HC_2H_3O_2]},\quad \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.0$$

For a solution having pH = 4.74, we need to have equal concentrations (equal moles) of $C_2H_3O_2^-$ and $HC_2H_3O_2$. Therefore, we need to add an amount of NaOH that will convert one-half of the $HC_2H_3O_2$ into $C_2H_3O_2^-$. This amount is 0.50 *M* NaOH.

	$HC_2H_3O_2$	+ OH^-	→	$C_2H_3O_2^-$ + H_2O
Before	1.00 *M*	0.50 *M*		0
Change	−0.50	−0.50	→	+0.50
After completion	0.50 *M*	0		0.50 *M*

From the preceding stoichiometry problem, adding enough NaOH(s) to produce a 0.50 *M* OH^- solution will convert one-half the $HC_2H_3O_2$ into $C_2H_3O_2^-$; this results in a solution with pH = 4.74.

$$\text{Mass NaOH} = 1.00\text{ L} \times \frac{0.50\text{ mol NaOH}}{\text{L}} \times \frac{40.00\text{ g NaOH}}{\text{mol}} = 20.\text{ g NaOH}$$

173. PO_4^{3-} is the conjugate base of HPO_4^{2-}. The K_a value for HPO_4^{2-} is $K_{a_3} = 4.8 \times 10^{-13}$.

$$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + OH^-(aq) \quad K_b = \frac{K_w}{K_{a_3}} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.021$$

HPO_4^{2-} is the conjugate base of $H_2PO_4^-$ ($K_{a_2} = 6.2 \times 10^{-8}$).

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \quad K_b = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$$

$H_2PO_4^-$ is the conjugate base of H_3PO_4 ($K_{a_1} = 7.5 \times 10^{-3}$).

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^- \quad K_b = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}$$

From the K_b values, PO_4^{3-} is the strongest base. This is expected because PO_4^{3-} is the conjugate base of the weakest acid (HPO_4^{2-}).

174. Major species: Na^+, PO_4^{3-} (a weak base), H_2O; From the K_b values calculated in Exercise 173, the dominant producer of OH^- is the K_b reaction for PO_4^{3-}. We can ignore the contribution of OH^- from the K_b reactions for HPO_4^{2-} and $H_2PO_4^-$. From Exercise 173, K_b for PO_4^{3-} = 0.021.

	PO_4^{3-} + H_2O	$\rightleftharpoons$	HPO_4^{2-}	+ OH^-	$K_b = 0.021$
Initial	0.10 *M*		0	~0	
Equil.	0.10 − *x*		*x*	*x*	

$K_b = 0.021 = \dfrac{x^2}{0.10 - x}$; because K_b is so large, the 5% assumption will not hold. Solving using the quadratic equation:

$$x^2 + (0.021)x - 0.0021 = 0, \quad x = [OH^-] = 3.7 \times 10^{-2}\,M, \quad \text{pOH} = 1.43, \quad \text{pH} = 12.57$$

175. a. $NH_4(HCO_3) \rightarrow NH_4^+ + HCO_3^-$

$$K_{a,\,NH_4^+} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10};\ K_{b,\,HCO_3^-} = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

The solution is basic because HCO_3^- is a stronger base than NH_4^+ is as an acid. The acidic properties of HCO_3^- were ignored because K_{a_2} is very small (4.8×10^{-11}).

b. $NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$; ignore Na^+.

$$K_{a_2,\,H_2PO_4^-} = 6.2 \times 10^{-8};\ K_{b,\,H_2PO_4^-} = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}$$

Solution is acidic because $K_a > K_b$.

c. $Na_2HPO_4 \rightarrow 2\ Na^+ + HPO_4^{2-}$; ignore Na^+.

$$K_{a_3,\,HPO_4^{2-}} = 4.8 \times 10^{-13};\ K_{b,\,HPO_4^{2-}} = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$$

Solution is basic because $K_b > K_a$.

d. $NH_4(H_2PO_4) \rightarrow NH_4^+ + H_2PO_4^-$

NH_4^+ is weak acid, and $H_2PO_4^-$ is also acidic (see part b). Solution with both ions present will be acidic.

e. $NH_4(HCO_2) \rightarrow NH_4^+ + HCO_2^-$; from Appendix 5, $K_{a,\,HCO_2H} = 1.8 \times 10^{-4}$.

$$K_{a,\,NH_4^+} = 5.6 \times 10^{-10};\ K_{b,\,HCO_2^-} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

Solution is acidic because NH_4^+ is a stronger acid than HCO_2^- is a base.

176. a. $HCO_3^- + HCO_3^- \rightleftharpoons H_2CO_3 + CO_3^{2-}$

$$K_{eq} = \frac{[H_2CO_3][CO_3^{2-}]}{[HCO_3^-][HCO_3^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_{a_2}}{K_{a_1}} = \frac{5.6 \times 10^{-11}}{4.3 \times 10^{-7}} = 1.3 \times 10^{-4}$$

b. $[H_2CO_3] = [CO_3^{2-}]$ since the reaction in part a is the principal equilibrium reaction.

c. $H_2CO_3 \rightleftharpoons 2\ H^+ + CO_3^{2-}$ $\quad K_{eq} = \dfrac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]} = K_{a_1} \times K_{a_2}$

Because $[H_2CO_3] = [CO_3^{2-}]$ from part b, $[H^+]^2 = K_{a_1} \times K_{a_2}$.

$[H^+] = (K_{a_1} \times K_{a_2})^{1/2}$, or taking the –log of both sides: $pH = \dfrac{pK_{a_1} + pK_{a_2}}{2}$

d. $[H^+] = [(4.3 \times 10^{-7}) \times (5.6 \times 10^{-11})]^{1/2}$, $[H^+] = 4.9 \times 10^{-9}\ M$; pH = 8.31

177. Molality = $m = \dfrac{0.100\text{ g} \times \dfrac{1\text{ mol}}{100.0\text{ g}}}{0.5000\text{ kg}} = 2.00 \times 10^{-3}\text{ mol/kg} \approx 2.00 \times \text{mol/L}$ (dilute solution)

$\Delta T_f = iK_f m$, $0.0056°\text{C} = i(1.86°\text{C/molal})(2.00 \times 10^{-3}\text{ molal})$, $i = 1.5$

If i = 1.0, the percent dissociation of the acid = 0%, and if i = 2.0, the percent dissociation of the acid = 100%. Because i = 1.5, the weak acid is 50.% dissociated.

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

Because the weak acid is 50.% dissociated:

$[H^+] = [A^-] = [HA]_0 \times 0.50 = 2.00 \times 10^{-3}\,M \times 0.50 = 1.0 \times 10^{-3}\,M$

$[HA] = [HA]_0 - \text{amount HA reacted} = 2.00 \times 10^{-3}\,M - 1.0 \times 10^{-3}\,M = 1.0 \times 10^{-3}\,M$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(1.0 \times 10^{-3})(1.0 \times 10^{-3})}{1.0 \times 10^{-3}} = 1.0 \times 10^{-3}$$

178. a. Assuming no ion association between $SO_4^{2-}(aq)$ and $Fe^{3+}(aq)$, then i = 5 for $Fe_2(SO_4)_3$.

$\pi = iMRT = 5(0.0500\text{ mol/L})(0.08206\text{ L atm/K•mol})(298\text{ K}) = 6.11\text{ atm}$

b. $Fe_2(SO_4)_3(aq) \rightarrow 2\,Fe^{3+}(aq) + 3\,SO_4^{2-}(aq)$

Under ideal circumstances, 2/5 of π calculated above results from Fe^{3+} and 3/5 results from SO_4^{2-}. The contribution to π from SO_4^{2-} is 3/5 × 6.11 atm = 3.67 atm. Because SO_4^{2-} is assumed unchanged in solution, the SO_4^{2-} contribution in the actual solution will also be 3.67 atm. The contribution to the actual osmotic pressure from the $Fe(H_2O)_6^{3+}$ dissociation reaction is 6.73 − 3.67 = 3.06 atm.

The initial concentration of $Fe(H_2O)_6^{2+}$ is 2(0.0500) = 0.100 M. The set up for the weak acid problem is:

$$Fe(H_2O)_6^{3+} \rightleftharpoons H^+ + Fe(OH)(H_2O)_5^{2+} \qquad K_a = \frac{[H^+][Fe(OH)(H_2O)_5^{2+}]}{[Fe(H_2O)_6^{3+}]}$$

Initial $0.100\,M$ ~0 0

x mol/L of $Fe(H_2O)_6^{3+}$ reacts to reach equilibrium

Equil. $0.100 - x$ x x

$$\pi = iMRT;\ \text{total ion concentration} = iM = \frac{\pi}{RT} = \frac{3.06\text{ atm}}{0.8206\text{ L atm/K}\bullet\text{mol}(298)} = 0.125\,M$$

$0.125\,M = 0.100 - x + x + x = 0.100 + x$, $x = 0.025\,M$

$$K_a = \frac{[H^+][Fe(OH)(H_2O)_5^{2+}]}{[Fe(H_2O)_6^{3+}]} = \frac{x^2}{0.100 - x} = \frac{(0.025)^2}{(0.100 - 0.025)} = \frac{(0.025)^2}{0.075}$$

$K_a = 8.3 \times 10^{-3}$

Integrative Problems

179. $$[\text{IO}^-] = \frac{2.14\text{ g NaIO} \times \dfrac{1\text{ mol NaIO}}{165.89\text{ g}} \times \dfrac{1\text{ mol IO}^-}{\text{mol NaIO}}}{1.25\text{ L}} = 1.03 \times 10^{-2}\ M\ \text{IO}^-$$

$$\text{IO}^- + \text{H}_2\text{O} \rightleftharpoons \text{HIO} + \text{OH}^- \qquad \text{K}_\text{b} = \frac{[\text{HIO}][\text{OH}^-]}{[\text{IO}^-]}$$

$$\begin{array}{llll} \text{Initial} & 1.03 \times 10^{-2}\ M & 0 & \sim 0 \\ \text{Equil.} & 1.03 \times 10^{-2} - x & x & x \end{array}$$

$\text{K}_\text{b} = \dfrac{x^2}{1.03 \times 10^{-2} - x}$; from the problem, pOH = 14.00 – 11.32 = 2.68.

$[\text{OH}^-] = 10^{-2.68} = 2.1 \times 10^{-3}\ M = x$; $\text{K}_\text{b} = \dfrac{(2.1 \times 10^{-3})^2}{1.03 \times 10^{-2} - 2.1 \times 10^{-3}} = 5.4 \times 10^{-4}$

180. $$10.0\text{ g NaOCN} \times \frac{1\text{ mol}}{65.01\text{ g}} = 0.154\text{ mol NaOCN}$$

$$10.0\text{ g H}_2\text{C}_2\text{O}_4 \times \frac{1\text{ mol}}{90.04\text{ g}} = 0.111\text{ mol H}_2\text{C}_2\text{O}_4$$

$$\frac{\text{Mol NaOCN}}{\text{Mol H}_2\text{SO}_4}(\text{actual}) = \frac{0.154\text{ mol}}{0.111\text{ mol}} = 1.39$$

The balanced equation requires a larger 2 : 1 mole ratio. Therefore, NaOCN in the numerator is limiting. Because there is a 2 : 2 mole correspondence between mole NaOCN reacted and mole HNCO produced, 0.154 mol of HNCO will be produced.

$$\text{HNCO} \rightleftharpoons \text{H}^+ + \text{NCO}^- \qquad \text{K}_\text{a} = 1.2 \times 10^{-4}$$

$$\begin{array}{llll} \text{Initial} & 0.154\text{ mol}/0.100\text{ L} & \sim 0 & 0 \\ \text{Equil.} & 1.54 - x & x & x \end{array}$$

$$\text{K}_\text{a} = 1.2 \times 10^{-4} = \frac{x^2}{1.54 - x} \approx \frac{x^2}{1.54}, \quad x = [\text{H}^+] = 1.4 \times 10^{-2}\ M$$

$\text{pH} = -\log(1.4 \times 10^{-2}) = 1.85$; assumptions good.

181. $$\text{Molar mass} = \frac{\text{dRT}}{\text{P}} = \frac{5.11\text{ g/L} \times \dfrac{0.08206\text{ L atm}}{\text{K mol}} \times 298\text{ K}}{1.00\text{ atm}} = 125\text{ g/mol}$$

$$[\text{HA}]_0 = \frac{1.50\text{ g} \times \dfrac{1\text{ mol}}{125\text{ g}}}{0.100\text{ L}} = 0.120\ M;\ \text{pH} = 1.80,\ [\text{H}^+] = 10^{-1.80} = 1.6 \times 10^{-2}\ M$$

	HA	$\rightleftharpoons$	H^+	+	A^-	
Initial	$0.120\ M$		~ 0		0	
Equil.	$0.120 - x$		x		x	where $x = [H^+] = 1.6 \times 10^{-2}\ M$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(1.6 \times 10^{-2})^2}{0.120 - 0.016} = 2.5 \times 10^{-3}$$

Marathon Problems

182. To determine the pH of solution A, the K_a value for HX must be determined. Use solution B to determine K_b for X^-, which can then be used to calculate K_a for HX ($K_a = K_w/K_b$).

Solution B:

	X^-	+	H_2O	$\rightleftharpoons$	HX	+	OH^-
Initial	$0.0500\ M$				0		~ 0
Change	$-x$			$\rightarrow$	$+x$		$+x$
Equil.	$0.0500 - x$				x		x

$$K_b = \frac{[HX][OH^-]}{[X^-]}$$

$$K_b = \frac{x^2}{0.0500 - x};$$ from the problem, pH = 10.02, so pOH = 3.98 and $[OH^-] = x = 10^{-3.98}$

$$K_b = \frac{(10^{-3.98})^2}{0.0500 - 10^{-3.98}} = 2.2 \times 10^{-7}$$

Solution A:

$$K_{a,\,HX} = K_w/K_{b,\,X^-} = (1.0 \times 10^{-14})/(2.2 \times 10^{-7}) = 4.5 \times 10^{-8}$$

	HX	$\rightleftharpoons$	H^+	+	X^-
Initial	$0.100\ M$		~ 0		0
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.100 - x$		x		x

$$K_a = 4.5 \times 10^{-8} = \frac{[H^+][X^-]}{[HX]}$$

$$K_a = 4.5 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100},\ x = [H^+] = 6.7 \times 10^{-5}\ M$$

Assumptions good (x is 0.067% of 0.100); pH = 4.17

Solution C:

Major species: H_2O, HX ($K_a = 4.5 \times 10^{-8}$), Na^+, and OH^-; the OH^- from the strong base is exceptional at accepting protons. OH^- will react with the best acid present (HX), and we can assume that OH^- will react to completion with HX, that is, until one (or both) of the reactants runs out. Because we have added one volume of substance to another, we have diluted both solutions from their initial concentrations. What hasn't changed is the moles of each reactant. So let's work with moles of each reactant initially.

$$\text{Mol HX} = 0.0500 \text{ L} \times \frac{0.100 \text{ mol HX}}{\text{L}} = 5.00 \times 10^{-3} \text{ mol HX}$$

$$\text{Mol OH}^- = 0.0150 \text{ L} \times \frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^-}{\text{mol NaOH}} = 3.75 \times 10^{-3} \text{ mol OH}^-$$

Now let's determine what is remaining in solution after OH^- reacts completely with HX. Note that OH^- is the limiting reagent.

	HX	+	OH^-	→	X^-	+	H_2O
Before	5.00×10^{-3} mol		3.75×10^{-3} mol		0		
Change	-3.75×10^{-3}		-3.75×10^{-3}	→	$+3.75 \times 10^{-3}$		$+3.75 \times 10^{-3}$
After completion	1.25×10^{-3} mol		0		3.75×10^{-3} mol		

After reaction, the solution contains HX, X^-, Na^+, and H_2O. The Na^+ (like most 1+ metal ions) has no effect on the pH of water. However, HX is a weak acid, and its conjugate base, X^-, is a weak base. Since both K_a and K_b reactions refer to these species, we could use either reaction to solve for the pH; we will use the K_b reaction. To solve the equilibrium problem using the K_b reaction, we need to convert to concentration units since K_b is in concentration units of mol/L.

$$[HX] = \frac{1.25 \times 10^{-3} \text{ mol}}{(0.0500 + 0.0150) \text{ L}} = 0.0192 \, M; \quad [X^-] = \frac{3.75 \times 10^{-3} \text{ mol}}{0.0650 \text{ L}} = 0.0577 \, M$$

$[OH^-] = 0$ (We reacted all of it to completion.)

	X^-	+	H_2O	⇌	HX	+	OH^-	$K_b = 2.2 \times 10^{-7}$
Initial	$0.0577 \, M$				$0.0192 \, M$		0	
	x mol/L of X^- reacts to reach equilibrium							
Change	$-x$			→	$+x$		$+x$	
Equil.	$0.0577 - x$				$0.0192 + x$		x	

$$K_b = 2.2 \times 10^{-7} = \frac{(0.0192 + x)x}{0.0577 - x} \approx \frac{(0.0192)x}{0.0577} \quad \text{(assuming } x \text{ is} << 0.0192\text{)}$$

$$x = [OH^-] = \frac{(2.2 \times 10^{-7})(0.0577)}{0.0192} = 6.6 \times 10^{-7} \, M;$$ assumptions great (x is 0.0034% of 0.0192).

$[OH^-] = 6.6 \times 10^{-7} \, M$, pOH = 6.18, pH = 14.00 = 6.18 = 7.82 = pH of solution C

The combination is 4-17-7-82.

183. a. Strongest acid from group I = HCl; weakest base (smallest K_b) from group II = $NaNO_2$

$0.20\ M$ HCl + $0.20\ M$ $NaNO_2$; major species = H^+, Cl^-, Na^+, NO_2^-, and H_2O; let the H^+ react to completion with the NO_2^-; then solve the back equilibrium problem.

	H^+	+ NO_2^-	$\rightarrow$ HNO_2	
Before	$0.10\ M$	$0.10\ M$	0	(Molarities are halved due to dilution.)
After	0	0	$0.10\ M$	

	HNO_2	$\rightleftharpoons$	H^+	+ NO_2^-	$K_a = 4.0 \times 10^{-4}$
Initial	$0.10\ M$		0	0	
Change	$-x$	$\rightarrow$	$+x$	$+x$	
Equil.	$0.10 - x$		x	x	

$$\frac{x^2}{0.10 - x} = 4.0 \times 10^{-4}; \quad \text{solving: } x = [H^+] = 6.1 \times 10^{-3}\ M; \quad pH = 2.21$$

b. Weakest acid from group I = $(C_2H_5)_3NHCl$; best base from group II = KOI; the dominant equilibrium will be the best base reacting with the best acid.

	OI^-	+ $(C_2H_5)_3NH^+$	$\rightleftharpoons$ HOI	+ $(C_2H_5)_3N$
Initial	$0.10\ M$	$0.10\ M$	0	0
Equil.	$0.10 - x$	$0.10 - x$	x	x

$$K = \frac{K_{a,\ (C_2H_5)_3NH^+}}{K_{a,\ HOI}} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} \times \frac{1}{2.0 \times 10^{-11}} = 1.25 \text{ (carrying extra sig. fig.)}$$

$$\frac{x^2}{(0.10 - x)^2} = 1.25, \quad \frac{x}{0.10 - x} = 1.12, \quad x = 0.053\ M$$

So [HOI] = $0.053\ M$ and $[OI^-] = 0.10 - x = 0.047\ M$; using the K_a equilibrium constant for HOI to solve for $[H^+]$:

$$2.0 \times 10^{-11} = \frac{[H^+](0.047)}{(0.053)}, \quad [H^+] = 2.3 \times 10^{-11}\ M; \quad pH = 10.64$$

c. K_a for $(C_2H_5)_3NH^+ = \dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$

K_b for $NO_2^- = \dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$

Because $K_a = K_b$, mixing $(C_2H_5)_3NHCl$ with $NaNO_2$ will result in a solution with pH = 7.00.