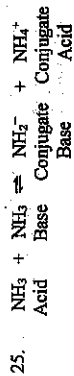
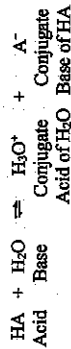


24. A Lewis acid must have an empty orbital to accept an electron pair, and a Lewis base must have an unshared pair of electrons.



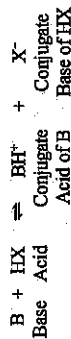
One of the  $\text{NH}_3$  molecules acts as a base and accepts a proton to form  $\text{NH}_4^+$ . The other  $\text{NH}_3$  molecule acts as an acid and donates a proton to form  $\text{NH}_2^-$ .  $\text{NH}_4^+$  is the conjugate acid of the  $\text{NH}_3$  base. In the reverse reaction,  $\text{NH}_4^+$  donates a proton.  $\text{NH}_2^-$  is the conjugate base of the  $\text{NH}_3$  acid. In the reverse reaction,  $\text{NH}_2^-$  accepts a proton. Conjugate acid-base pairs only differ by a  $\text{H}^+$  in the formula.

26. a. The first equation is for the reaction of some generic acid, HA, with  $\text{H}_2\text{O}$ .



HA is the proton donor (the acid) and  $\text{H}_2\text{O}$  is the proton acceptor (the base). In the reverse reaction,  $\text{H}_3\text{O}^+$  is the proton donor (the acid) and  $\text{A}^-$  is the proton acceptor (the base).

The second equation is for some generic base, B, with some generic acid, HX. Note that B has three hydrogens bonded to it.



B is the proton acceptor (the base) and HX is the proton donor (the acid). When B accepts a proton, the central atom goes from having 3 bonded hydrogens to 4 bonded hydrogens. In the reverse reaction,  $\text{BH}^+$  is the proton donor (the acid) and  $\text{X}^-$  is the proton acceptor (the base).

- b. Arrhenius acids produce  $\text{H}^+$  in solution. So HA in the first equation is an Arrhenius acid. However, in the second equation,  $\text{H}^+$  is not a product, so HX is not an Arrhenius acid. Both HA in the first equation and HX in the second equation are proton donors, so both are considered Brønsted-Lowry acids. All Brønsted-Lowry acids are Lewis acids, that is, all Brønsted-Lowry acids are electron pair acceptors. So both HA and HX are Lewis acids. It is the proton ( $\text{H}^+$ ) that accepts the lone pair.

For the bases in the two equations,  $\text{H}_2\text{O}$  and B, none of them produce  $\text{OH}^-$  in their equations, so none of them are Arrhenius bases. Both  $\text{H}_2\text{O}$  and B accept protons, so both are Brønsted-Lowry bases. As with Brønsted-Lowry acids, all Brønsted-Lowry bases are also electron-pair donors, so both  $\text{H}_2\text{O}$  and B are Lewis bases. The oxygen in  $\text{H}_2\text{O}$  and the central atom in B will always have a lone pair to donate to the Lewis acid (the proton).

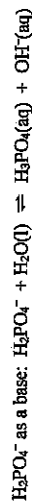
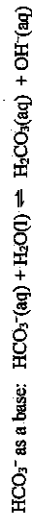
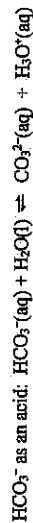
27. a. These are solutions of strong acids like HCl, HBr, HI,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ . So

## CHAPTER 14

## ACIDS AND BASES

## Questions

19. Acids are proton ( $\text{H}^+$ ) donors, and bases are proton acceptors.



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

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

22. When a strong acid (HX) is added to water, the reaction  $\text{HX} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{X}^-$  essentially goes to completion. All strong acids in water are completely converted into  $\text{H}_3\text{O}^+$  and  $\text{X}^-$ . Thus no acid stronger than  $\text{H}_3\text{O}^+$  will remain undissociated in water. Similarly, when a strong base (B) is added to water, the reaction  $\text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^-$  essentially goes to completion. All bases stronger than  $\text{OH}^-$  are completely converted into  $\text{OH}^-$  and  $\text{BH}^+$ . Even though there are acids and bases stronger than  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , in water these acids and bases are completely converted into  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ .

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  $[\text{H}^+]$  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  $[\text{H}^+]$ . In all three pH values, the  $[\text{H}^+]$  should be expressed only to two significant figures because these pH values have only two decimal places.

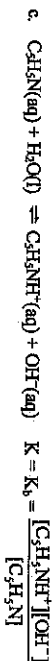
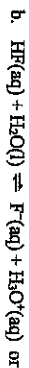
0.10 M solutions of any of the acids would be examples of a strong electrolyte solution that is very acidic.

- b. These are solutions containing salts of the conjugate acids of the bases in Table 14.3. These conjugate acids are all weak acids, and they are cations with a 1+ charge.  $\text{NH}_4\text{Cl}$ ,  $\text{CH}_3\text{NH}_3\text{NO}_3$ , and  $\text{C}_6\text{H}_5\text{NH}_3\text{Br}$  are three examples of this type of slightly acidic salts. 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  $\text{HSO}_4^-$ , which has weak acid properties).
- c. These are solutions of strong bases like  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{Sr(OH)}_2$ , and  $\text{Ba(OH)}_2$ . All of these strong bases are strong electrolytes.
- d. These are solutions containing salts of the conjugate bases of the neutrally charged weak acids in Table 14.2. These conjugate bases are all weak bases, and they are anions with a 1- charge. Three examples of this type of slightly basic salts are  $\text{NaClO}_2$ ,  $\text{KCH}_3\text{O}_2$ , and  $\text{CaF}_2$ . The cations used to form these salts are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$  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 solutions. The easiest way is to combine a conjugate base of a strong acid (except for  $\text{HSO}_4^-$ ) 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  $\text{NaCl}$ ,  $\text{KNO}_3$ , and  $\text{Sr}_2$ . 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 ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ). For this salt,  $K_a$  for  $\text{NH}_4^+ = K_b$  for  $\text{C}_2\text{H}_3\text{O}_2^- = 5.6 \times 10^{-10}$ . This salt at any concentration produces a neutral solution.

$$28. \quad K_a \times K_b = K_w, \quad -\log(K_a \times K_b) = -\log K_w$$

$$-\log K_a - \log K_b = -\log K_w, \quad \text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00 \quad (K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C})$$

$$29. \quad \text{a.} \quad \text{H}_2\text{CO}_3 + \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_3\text{CO}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad \text{or}$$



30. 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  $[\text{H}^+] > 1.0 \text{ M}$ . 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  $\text{Ba(OH)}_2$  solution will have an  $[\text{OH}^-]$  twice of the same concentration of  $\text{KOH}$ , but this does not correspond to a pOH value twice that of the same concentration of  $\text{KOH}$  (prove it to yourself).

31. a. This expression holds true for solutions of strong acids having a concentration greater than  $1.0 \times 10^{-4} \text{ M}$ .  $0.10 \text{ M HCl}$ ,  $7.8 \text{ M HNO}_3$ , and  $3.6 \times 10^{-4} \text{ M HClO}_4$  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  $\text{H}^+$  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  $1 \times 10^{-4}$  as long as there is a significant amount of weak acid present. Three example solutions are  $1.5 \text{ M HClCH}_2\text{O}_2$ ,  $0.10 \text{ M HOCl}$ , and  $0.72 \text{ M HCN}$ .

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

- d. This expression holds true for solutions of weak bases where the two normal assumptions hold. The assumptions are that the  $\text{OH}^-$  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  $0.10 \text{ M}$ . Three examples are  $0.10 \text{ M NH}_3$ ,  $0.54 \text{ M C}_6\text{H}_5\text{NH}_2$ , and  $1.1 \text{ M C}_6\text{H}_5\text{N}$ .

32.  $\text{H}_2\text{CO}_3$  is a weak acid with  $K_{a_1} = 4.3 \times 10^{-7}$  and  $K_{a_2} = 5.6 \times 10^{-11}$ . The  $[\text{H}^+]$  concentration in solution will be determined from the  $K_{a_1}$  reaction because  $K_{a_1} \gg K_{a_2}$ . Because  $K_{a_1} \ll 1$ , the  $[\text{H}^+] < 0.10 \text{ M}$ ; only a small percentage of the  $0.10 \text{ M H}_2\text{CO}_3$  will dissociate into  $\text{HCO}_3^-$  and  $\text{H}^+$ . So statement a best describes the  $0.10 \text{ M H}_2\text{CO}_3$  solution.  $\text{H}_2\text{SO}_4$  is a strong acid as well as a very good weak acid ( $K_{a_1} \gg 1$ ,  $K_{a_2} = 1.2 \times 10^{-2}$ ). All the  $0.10 \text{ M H}_2\text{SO}_4$  solution will dissociate into  $0.10 \text{ M H}^+$  and  $0.10 \text{ M HSO}_4^-$ . However, because  $\text{HSO}_4^-$  is a good weak acid due to the relatively large  $K_a$  value, some of the  $0.10 \text{ M HSO}_4^-$  will dissociate into some more  $\text{H}^+$  and  $\text{SO}_4^{2-}$ . Therefore, the  $[\text{H}^+]$  will be greater than  $0.10 \text{ M}$  but will not reach  $0.20 \text{ M}$  because only some of  $0.10 \text{ M HSO}_4^-$  will dissociate. Statement c is best for a  $0.10 \text{ M H}_2\text{SO}_4$  solution.

33. One reason  $\text{HF}$  is a weak acid is that the  $\text{H-F}$  bond is unusually strong and is difficult to break. This contributes significantly to the reluctance of the  $\text{HF}$  molecules to dissociate in water.

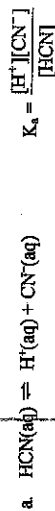
34. a. Sulfur reacts with oxygen to produce  $\text{SO}_2$  and  $\text{SO}_3$ . These sulfur oxides both react with water to produce  $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ , respectively. Acid rain can result when sulfur emissions are not controlled. Note that, in general, nonmetal oxides react with water to produce acidic solutions.

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

## Exercises

## Nature of Acids and Bases

35. a.  $\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$ . Only the forward reaction is indicated because  $\text{HClO}_4$  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  $\text{HClO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$ . 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:
- $$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{CH}_2\text{CO}_2^-(\text{aq}) \quad \text{or}$$
- $$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{CH}_2\text{CO}_2^-(\text{aq})$$
- c.  $\text{NH}_4^+$  is a weak acid. Similar to propanoic acid, the dissociation reaction is:
- $$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \quad \text{or} \quad \text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$$
36. 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  $\text{H}^+$  and the conjugate base of the acid that is dissociated.



37. An acid is a proton ( $\text{H}^+$ ) donor, and a base is a proton acceptor. A conjugate acid-base pair differs by only a proton ( $\text{H}^+$ ).

Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a. $\text{HCO}_3^-$	$\text{H}_2\text{O}$	$\text{HCO}_3^-$	$\text{H}_3\text{O}^+$

b. $\text{C}_5\text{H}_5\text{NH}^+$	$\text{H}_2\text{O}$	$\text{C}_5\text{H}_5\text{N}$	$\text{H}_3\text{O}^+$
c. $\text{C}_3\text{H}_7\text{NH}^+$	$\text{HCO}_3^-$	$\text{C}_3\text{H}_7\text{N}$	$\text{H}_2\text{CO}_3$
	Acid	Base	Conjugate Acid of Base
a. $\text{Al}(\text{H}_2\text{O})_6^{3+}$	$\text{H}_2\text{O}$	$\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	$\text{H}_3\text{O}^+$
b. $\text{HONH}_3^+$	$\text{H}_2\text{O}$	$\text{HONH}_2$	$\text{H}_3\text{O}^+$
c. $\text{HOCl}$	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{OCl}^-$	$\text{C}_6\text{H}_5\text{NH}_3^+$
	Conjugate Base of Acid	Conjugate Base of Acid	Conjugate Acid of Base

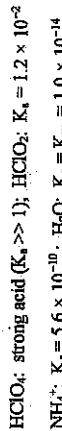
- 38.
39. Strong acids have  $K_a \gg 1$ , and weak acids have  $K_a < 1$ . Table 14.2 in the text lists some  $K_a$  values for weak acids.  $K_a$  values for strong acids are hard to determine, so they are not listed in the text. However, there are only a few common strong acids so, if you memorize the strong acids, then all other acids will be weak acids. The strong acids to memorize are  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$ .

- a.  $\text{HClO}_4$  is a strong acid.  
 b.  $\text{HOCl}$  is a weak acid ( $K_a = 3.5 \times 10^{-8}$ ).  
 c.  $\text{H}_2\text{SO}_4$  is a strong acid.  
 d.  $\text{H}_2\text{SO}_3$  is a weak diprotic acid because the  $K_{a1}$  and  $K_{a2}$  values are much less than 1.

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

- a.  $\text{HNO}_2$ : weak acid beaker  
 b.  $\text{HNO}_3$ : strong acid beaker  
 c.  $\text{HCl}$ : strong acid beaker  
 d.  $\text{HF}$ : weak acid beaker  
 e.  $\text{HC}_2\text{H}_3\text{O}_2$ : weak acid beaker

41. 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:



From the  $K_a$  values, the ordering is  $\text{HClO}_4 > \text{HClO}_2 > \text{NH}_4^+ > \text{H}_2\text{O}$ .

42. 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.  $\text{ClO}_2^-$  is the conjugate base of a strong acid; it is a terrible base (worse than water). The ordering is  $\text{NH}_3 > \text{ClO}_2^- > \text{H}_2\text{O} > \text{ClO}_4^-$ .

43. 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.  $HOOC_2H_3$ ,  $K_a = 1.6 \times 10^{-10}$ ;  $HCN$ ,  $K_a = 6.2 \times 10^{-10}$ ;  $HCN$  is a slightly stronger acid than  $HOOC_2H_3$  because  $K_a$  for  $HCN > K_a$  for  $HOOC_2H_3$ .
44. a.  $H_2O$ , the conjugate bases of strong acids are extremely weak 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  $HOOC_2H_3$  ( $K_a$  for  $HCN > K_a$  for  $HOOC_2H_3$ ),  $OC_6H_5^-$  will be a stronger base than  $CN^-$ .

#### Autoionization of Water and the pH Scale

45. At 25°C, the relationship  $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$  always holds for aqueous solutions. When  $[H^+]$  is greater than  $1.0 \times 10^{-7} M$ , the solution is acidic; when  $[H^+]$  is less than  $1.0 \times 10^{-7} M$ , the solution is basic; when  $[H^+] = 1.0 \times 10^{-7} M$ , the solution is neutral. In terms of  $[OH^-]$ , an acidic solution has  $[OH^-] < 1.0 \times 10^{-7} M$ , a basic solution has  $[OH^-] > 1.0 \times 10^{-7} M$ , and a neutral solution has  $[OH^-] = 1.0 \times 10^{-7} M$ .
- a.  $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} M$ , 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.
46. a.  $[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.5} = 6.7 \times 10^{-15} M$ , basic
- b.  $[H^+] = \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-13}} = 2.8 M$ , 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
47. a. Because the value of the equilibrium constant increases as the temperature increases, the reaction is endothermic. In endothermic reactions, heat is a reactant, so an increase in temperature (heat) shifts the reaction to produce more products and increases  $K$  in the process.
- b.  $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$   $K_w = 5.47 \times 10^{-14} = [H^+][OH^-]$  at 50.°C
- In pure water  $[H^+] = [OH^-]$ , so  $5.47 \times 10^{-14} = [H^+]^2$ ,  $[H^+] = 2.34 \times 10^{-7} M = [OH^-]$
48. a.  $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$   $K_w = 2.92 \times 10^{-14} = [H^+][OH^-]$
- 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.  $[H^+] = K_w/[OH^-] = (2.92 \times 10^{-14})/(0.10) = 2.9 \times 10^{-13} M$ ,  $pH = -\log(2.9 \times 10^{-13}) = 12.54$
49.  $pH = -\log[H^+]$ ,  $pOH = -\log[OH^-]$ , at 25°C,  $pH + pOH = 14.00$ , for Exercise 45:
- 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.  $pH = -\log(2) = -1.08$ ;  $pOH = 14.00 - (-1.08) = 15.08$
- 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 46:
- 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  $[\text{OH}^-]$  is greater than  $1.0\text{ M}$  (an extremely basic solution).

50. a.  $[\text{H}^+] = 10^{-9.81}$ ,  $[\text{H}^+] = 10^{-7.40} = 4.0 \times 10^{-8}\text{ M}$   
 $\text{pOH} = 14.00 - \text{pH} = 14.00 - 7.40 = 6.60$ ;  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-6.60} = 2.5 \times 10^{-7}\text{ M}$   
 or  $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-8}} = 2.5 \times 10^{-7}\text{ M}$ ; this solution is basic since  $\text{pH} > 7.00$ .
- b.  $[\text{H}^+] = 10^{-15.3} = 5 \times 10^{-16}\text{ M}$ ;  $\text{pOH} = 14.00 - 15.3 = -1.3$ ;  $[\text{OH}^-] = 10^{-(-1.3)} = 20\text{ M}$ ; basic
- c.  $[\text{H}^+] = 10^{-(-1.0)} = 10\text{ M}$ ;  $\text{pOH} = 14.00 - (-1.0) = 15.0$ ;  $[\text{OH}^-] = 10^{-15.0} = 1 \times 10^{-15}\text{ M}$ ; acidic
- d.  $[\text{H}^+] = 10^{-3.20} = 6.3 \times 10^{-4}\text{ M}$ ;  $\text{pOH} = 14.00 - 3.20 = 10.80$ ;  $[\text{OH}^-] = 10^{-10.80} = 1.6 \times 10^{-11}\text{ M}$ ; acidic
- e.  $[\text{OH}^-] = 10^{-5.0} = 1 \times 10^{-5}\text{ M}$ ;  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.0 = 9.0$ ;  $[\text{H}^+] = 10^{-9.0} = 1 \times 10^{-9}\text{ M}$ ; basic
- f.  $[\text{OH}^-] = 10^{-9.60} = 2.5 \times 10^{-10}\text{ M}$ ;  $\text{pH} = 14.00 - 9.60 = 4.40$ ;  $[\text{H}^+] = 10^{-4.40} = 4.0 \times 10^{-5}\text{ M}$ ; acidic
51. a.  $\text{pOH} = 14.00 - 6.88 = 7.12$ ;  $[\text{H}^+] = 10^{-6.88} = 1.3 \times 10^{-7}\text{ M}$   
 $[\text{OH}^-] = 10^{-7.12} = 7.6 \times 10^{-8}\text{ M}$ ; acidic
- b.  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{8.4 \times 10^{-14}} = 0.12\text{ M}$ ;  $\text{pH} = -\log(0.12) = 0.92$   
 $\text{pOH} = 14.00 - 0.92 = 13.08$ ; acidic
- c.  $\text{pH} = 14.00 - 3.11 = 10.89$ ;  $[\text{H}^+] = 10^{-10.89} = 1.3 \times 10^{-11}\text{ M}$   
 $[\text{OH}^-] = 10^{-3.11} = 7.8 \times 10^{-4}\text{ M}$ ; basic
- d.  $\text{pH} = -\log(1.0 \times 10^{-7}) = 7.00$ ;  $\text{pOH} = 14.00 - 7.00 = 7.00$   
 $[\text{OH}^-] = 10^{-7.00} = 1.0 \times 10^{-7}\text{ M}$ ; neutral
52. a.  $\text{pOH} = 14.00 - 9.63 = 4.37$ ;  $[\text{H}^+] = 10^{-9.63} = 2.3 \times 10^{-10}\text{ M}$   
 $[\text{OH}^-] = 10^{-4.37} = 4.3 \times 10^{-5}\text{ M}$ ; basic

- b.  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{3.9 \times 10^{-6}} = 2.6 \times 10^{-9}\text{ M}$ ;  $\text{pH} = -\log(2.6 \times 10^{-9}) = 8.59$   
 $\text{pOH} = 14.00 - 8.59 = 5.41$ ; basic
- c.  $\text{pH} = -\log(0.027) = 1.57$ ;  $\text{pOH} = 14.00 - 1.57 = 12.43$   
 $[\text{OH}^-] = 10^{-12.43} = 3.7 \times 10^{-13}\text{ M}$ ; acidic
- d.  $\text{pH} = 14.00 - 1.22 = 12.78$ ;  $[\text{H}^+] = 10^{-12.78} = 1.7 \times 10^{-13}\text{ M}$   
 $[\text{OH}^-] = 10^{-1.22} = 0.060\text{ M}$ ; basic
53.  $\text{pOH} = 14.00 - \text{pH} = 14.00 - 2.1 = 11.9$ ;  $[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.1} = 8 \times 10^{-3}\text{ M}$  (1 sig. fig.)  
 $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{8 \times 10^{-3}} = 1 \times 10^{-12}\text{ M}$  or  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.9} = 1 \times 10^{-12}\text{ M}$   
 The sample of gastric juice is acidic because the pH is less than 7.00 at 25°C.
54.  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.74 = 8.26$ ;  $[\text{H}^+] = 10^{-\text{pH}} = 10^{-8.26} = 5.5 \times 10^{-9}\text{ M}$   
 $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{5.5 \times 10^{-9}} = 1.8 \times 10^{-6}\text{ M}$  or  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.74} = 1.8 \times 10^{-6}\text{ M}$   
 The solution of baking soda is basic because the pH is greater than 7.00 at 25°C.

### Solutions of Acids

55. 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  $\text{HA}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$ , where  $\text{A}^-$  is the conjugate base of the strong acid HA. For  $0.250\text{ M}$  solutions of these strong acids,  $0.250\text{ M H}^+$  and  $0.250\text{ M A}^-$  are present when the acids completely dissociate. The amount of  $\text{H}^+$  donated from water will be insignificant in this problem since  $\text{H}_2\text{O}$  is a very weak acid.
- a. Major species present after dissociation =  $\text{H}^+$ ,  $\text{ClO}_4^-$ , and  $\text{H}_2\text{O}$ ;  
 $\text{pH} = -\log[\text{H}^+] = -\log(0.250) = 0.602$
- b. Major species =  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{H}_2\text{O}$ ;  $\text{pH} = 0.602$
56. Both are strong acids, which are assumed to completely dissociate in water.  
 $0.0500\text{ L} \times 0.050\text{ mol/L} = 2.5 \times 10^{-3}\text{ mol HBr} = 2.5 \times 10^{-3}\text{ mol H}^+ + 2.5 \times 10^{-3}\text{ mol Br}^-$   
 $0.1500\text{ L} \times 0.10\text{ mol/L} = 1.5 \times 10^{-2}\text{ mol HI} = 1.5 \times 10^{-2}\text{ mol H}^+ + 1.5 \times 10^{-2}\text{ mol I}^-$

$$[\text{H}^+] = \frac{(2.5 \times 10^{-3} + 1.5 \times 10^{-2}) \text{ mol}}{0.2000 \text{ L}} = 0.088 \text{ M}, \quad \text{pH} = -\log(0.088) = 1.06$$

57. Strong acids are assumed to completely dissociate in water; for example;  $\text{HCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  or  $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ .

a. A 0.10 M HCl solution gives 0.10 M  $\text{H}^+$  and 0.10 M  $\text{Cl}^-$  because HCl completely dissociates. The amount of  $\text{H}^+$  from  $\text{H}_2\text{O}$  will be insignificant.

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

b. 5.0 M  $\text{H}^+$  is produced when 5.0 M HClO<sub>4</sub> completely dissociates. The amount of  $\text{H}^+$  from  $\text{H}_2\text{O}$  will be insignificant.  $\text{pH} = -\log(5.0) = -0.70$  (Negative pH values just indicate very concentrated acid solutions.)

c.  $1.0 \times 10^{-11}$  M  $\text{H}^+$  is produced when  $1.0 \times 10^{-11}$  M HI completely dissociates. If you take the negative log of  $1.0 \times 10^{-11}$ , this gives  $\text{pH} = 11.00$ . 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  $1.0 \times 10^{-7}$  M  $\text{H}^+$ . We can normally ignore the small amount of  $\text{H}^+$  from  $\text{H}_2\text{O}$  except when we have a very dilute solution of an acid (as in the case here). Therefore, the pH is that of neutral water ( $\text{pH} = 7.00$ ) because the amount of HI present is insignificant.

58.  $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$ .  $\text{HNO}_3$  is a strong acid, which means it is assumed to completely dissociate in water. The initial concentration of  $\text{HNO}_3$  will equal the  $[\text{H}^+]$  donated by the strong acid.

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

b.  $\text{pH} = -\log(4.0) = -0.60$

c. Because the concentration of  $\text{HNO}_3$  is so dilute, the pH will be that of neutral water ( $\text{pH} = 7.00$ ). In this problem, water is the major  $\text{H}^+$  producer present. Whenever the strong acid has a concentration less than  $1.0 \times 10^{-7}$  M, the  $[\text{H}^+]$  contribution from water must be considered.

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

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

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

$$M_1 V_1 = M_2 V_2, \quad V_1 = \frac{M_2 V_2}{M_1} = \frac{3.16 \times 10^{-2} \text{ mol/L} \times 1.6 \text{ L}}{12 \text{ mol/L}} = 4.2 \times 10^{-3} \text{ L}$$

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

62. 50.0 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 mL conc.  $\text{HNO}_3$  soln  $\times \frac{1.42 \text{ g}}{\text{mL}} \times \frac{70 \text{ g HNO}_3}{100 \text{ g soln}} \times \frac{1 \text{ mol HNO}_3}{63.0 \text{ g HNO}_3} = 0.32 \text{ mol HNO}_3$

$\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$  and  $\text{HNO}_3(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$  (Both are strong acids.)

So we will have 0.62 + 0.32 = 0.94 mol of  $\text{H}^+$  in the final solution.

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

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

63. a.  $\text{HNO}_2$  ( $K_a = 4.0 \times 10^{-4}$ ) and  $\text{H}_2\text{O}$  ( $K_a = K_w = 1.0 \times 10^{-14}$ ) are the major species.  $\text{HNO}_2$  is a much stronger acid than  $\text{H}_2\text{O}$ , so it is the major source of  $\text{H}^+$ . However,  $\text{HNO}_2$  is a weak acid ( $K_a < 1$ ), so it only partially dissociates in water. We must solve an equilibrium problem to determine  $[\text{H}^+]$ . In the Solutions Guide, we will summarize the initial, change, and equilibrium concentrations into one table called the ICE table. Solving the weak acid problem:

	$\text{HNO}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{NO}_2^-$
Initial	0.250 M		~0		0
	x mol/L $\text{HNO}_2$ dissociates to reach equilibrium		-x		+x
Change	-x		+x		+x
Equil.	0.250 - x		x		x

$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.0 \times 10^{-4} = \frac{x^2}{0.250 - x}; \quad \text{if we assume } x \ll 0.250, \text{ then:}$$

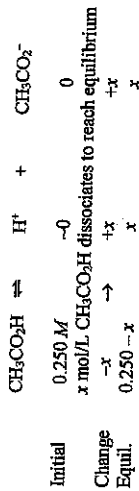
$$4.0 \times 10^{-4} \approx \frac{x^2}{0.250}, \quad x = \sqrt{4.0 \times 10^{-4} (0.250)} = 0.010 \text{ M}$$

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

All the assumptions are good. The  $\text{H}^+$  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:

$$x = 0.010 \text{ M} = [\text{H}^+], \quad \text{pH} = -\log(0.010) = 2.00$$

b.  $\text{CH}_3\text{CO}_2\text{H}$  ( $K_a = 1.8 \times 10^{-5}$ ) and  $\text{H}_2\text{O}$  ( $K_a = K_w = 1.0 \times 10^{-14}$ ) are the major species.  $\text{CH}_3\text{CO}_2\text{H}$  is the major source of  $\text{H}^+$ . Solving the weak acid problem:

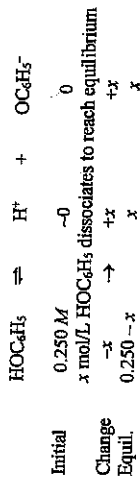


$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = 1.8 \times 10^{-5} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad (\text{assuming } x \ll 0.250)$$

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

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

64. a.  $\text{HOCl}_2\text{H}_3$  ( $K_a = 1.6 \times 10^{-10}$ ) and  $\text{H}_2\text{O}$  ( $K_a = K_w = 1.0 \times 10^{-14}$ ) are the major species. The major equilibrium is the dissociation of  $\text{HOCl}_2\text{H}_3$ . Solving the weak acid problem:

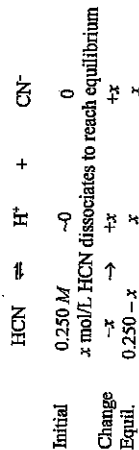


$$K_a = 1.6 \times 10^{-10} = \frac{[\text{H}^+][\text{OCl}_2\text{H}_2^-]}{[\text{HOCl}_2\text{H}_3]} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad (\text{assuming } x \ll 0.250)$$

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

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

- b.  $\text{HCN}$  ( $K_a = 6.2 \times 10^{-10}$ ) and  $\text{H}_2\text{O}$  are the major species.  $\text{HCN}$  is the major source of  $\text{H}^+$ .

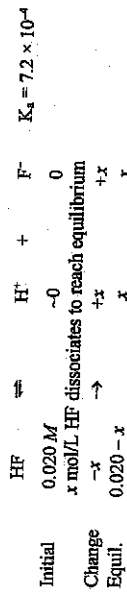


$$K_a = 6.2 \times 10^{-10} = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad (\text{assuming } x \ll 0.250)$$

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

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

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



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

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

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

19%

The assumption  $x \ll 0.020$  is not good ( $x$  is more than 5% of 0.020). We must solve  $x^2/(0.020 - x) = 7.2 \times 10^{-4}$  exactly by using either the quadratic formula or the method of successive approximations (see Appendix 1 of the text). Using successive approximations, we let 0.016 M be a new approximation for  $[\text{HF}]$ . 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.

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

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

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

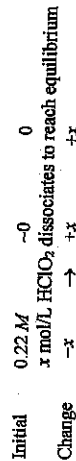
We repeat until we get a self-consistent answer. This would be the same answer we would get solving exactly using the quadratic equation. In this case it is,  $x = 3.5 \times 10^{-3}$ . Thus:

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

$$[\text{HF}] = 0.020 - x = 0.020 - 0.0035 = 0.017 \text{ M}; \quad \text{pH} = 2.46$$

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).

66.  $\text{HClO}_2 \rightleftharpoons \text{H}^+ + \text{ClO}_2^- \quad K_a = 1.2 \times 10^{-2}$



$x$  mol/L  $\text{HClO}_2$  dissociates to reach equilibrium

$$\text{Equil. } 0.22 - x \quad x \quad x$$

$$K_a = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{ClO}_2^-]}{[\text{HClO}_2]} = \frac{x^2}{0.22 - x} \approx \frac{x^2}{0.22}, x = 5.1 \times 10^{-2}$$

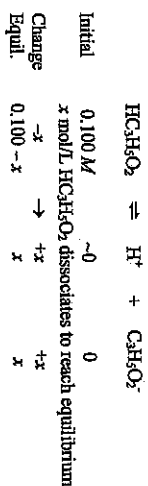
The assumption that  $x$  is small is not good ( $x$  is 23% of 0.22). Using the method of successive approximations and carrying extra significant figures:

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

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

$$[\text{H}^+] = [\text{ClO}_2^-] = x = 4.6 \times 10^{-2} M, \text{ percent dissociation} = \frac{4.6 \times 10^{-2}}{0.22} \times 100 = 21\%$$

67.  $\text{HC}_2\text{H}_3\text{O}_2$  ( $K_a = 1.3 \times 10^{-5}$ ) and  $\text{H}_2\text{O}$  ( $K_a = K_w = 1.0 \times 10^{-14}$ ) are the major species present.  $\text{HC}_2\text{H}_3\text{O}_2$  will be the dominant producer of  $\text{H}^+$  because  $\text{HC}_2\text{H}_3\text{O}_2$  is a stronger acid than  $\text{H}_2\text{O}$ . Solving the weak acid problem:



$$K_a = 1.3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

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

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

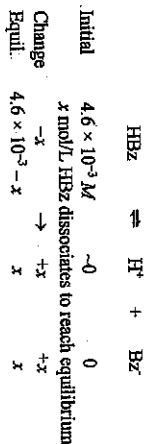
$$[\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 1.1 \times 10^{-3} M, [\text{OH}^-] = K_w/[\text{H}^+] = 9.1 \times 10^{-12} M$$

$$[\text{HC}_2\text{H}_3\text{O}_2] = 0.100 - 1.1 \times 10^{-3} = 0.099 M$$

$$\text{Percent dissociation} = \frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]_0} \times 100 = \frac{1.1 \times 10^{-3}}{0.100} \times 100 = 1.1\%$$

68. This is a weak acid in water. We must solve a weak acid problem. Let  $\text{HBz} = \text{C}_6\text{H}_5\text{CO}_2\text{H}$ .

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



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

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

Assumption is not good ( $x$  is 12% of  $4.6 \times 10^{-3}$ ). 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:

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

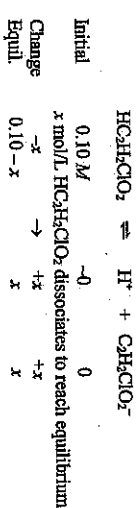
$$\frac{x^2}{(4.6 \times 10^{-3}) - (5.1 \times 10^{-4})} = 6.4 \times 10^{-5}, x = 5.1 \times 10^{-4}$$

$$\text{Thus: } x = [\text{H}^+] = [\text{Bz}^-] = [\text{C}_6\text{H}_5\text{CO}_2^-] = 5.1 \times 10^{-4} M$$

$$[\text{HBz}] = [\text{C}_6\text{H}_5\text{CO}_2\text{H}] = 4.6 \times 10^{-3} - x = 4.1 \times 10^{-3} M$$

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

69. Major species:  $\text{HC}_2\text{H}_2\text{ClO}_2$  ( $K_a = 1.35 \times 10^{-3}$ ) and  $\text{H}_2\text{O}$ , major source of  $\text{H}^+$ :  $\text{HC}_2\text{H}_2\text{ClO}_2$



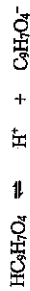
$$K_a = 1.35 \times 10^{-3} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, x = 1.2 \times 10^{-2} M$$

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  $x = [\text{H}^+] = 1.1 \times 10^{-2} M$ .

$$\text{pH} = -\log[\text{H}^+] = -\log(1.1 \times 10^{-2}) = 1.96$$



$$70. [\text{HC}_6\text{H}_7\text{O}_4] = \frac{2 \text{ tablets} \times \frac{0.325 \text{ g HC}_6\text{H}_7\text{O}_4}{\text{tablet}} \times \frac{1 \text{ mol HC}_6\text{H}_7\text{O}_4}{180.15 \text{ g}}}{0.237 \text{ L}} = 0.0152 \text{ M}$$



Initial	0.0152 M	~0	0
Change	$x$ mol/L	$-x$	$+x$
Equil.	$0.0152 - x$	$x$	$x$

$x$  mol/L  $\text{HC}_6\text{H}_7\text{O}_4$  dissociates to reach equilibrium

$$K_a = 3.3 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_6\text{H}_7\text{O}_4^-]}{[\text{HC}_6\text{H}_7\text{O}_4]} = \frac{x^2}{0.0152 - x} \approx \frac{x^2}{0.0152}, x = 2.2 \times 10^{-3} \text{ M}$$

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  $x = 2.1 \times 10^{-3} \text{ M}$ .

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

71. HF and  $\text{HOC}_6\text{H}_5$  are both weak acids with  $K_a$  values of  $7.2 \times 10^{-4}$  and  $1.6 \times 10^{-10}$ , respectively. Since the  $K_a$  value for HF is much greater than the  $K_a$  value for  $\text{HOC}_6\text{H}_5$ , HF will be the dominant producer of  $\text{H}^+$  (we can ignore the amount of  $\text{H}^+$  produced from  $\text{HOC}_6\text{H}_5$  because it will be insignificant).

HF	$\rightleftharpoons$	$\text{H}^+$	+	$\text{F}^-$
Initial	1.0 M	~0	0	0
Change	$x$ mol/L	$-x$	$+x$	$+x$
Equil.	$1.0 - x$	$x$	$x$	$x$

$x$  mol/L HF dissociates to reach equilibrium

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

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

Solving for  $[\text{OC}_6\text{H}_5^-]$  using  $\text{HOC}_6\text{H}_5 \rightleftharpoons \text{H}^+ + \text{OC}_6\text{H}_5^-$  equilibrium:

$$K_a = 1.6 \times 10^{-10} = \frac{[\text{H}^+][\text{OC}_6\text{H}_5^-]}{[\text{HOC}_6\text{H}_5]} = \frac{(2.7 \times 10^{-2})[\text{OC}_6\text{H}_5^-]}{1.0}, [\text{OC}_6\text{H}_5^-] = 5.9 \times 10^{-9} \text{ M}$$

Note that this answer indicates that only  $5.9 \times 10^{-9} \text{ M}$   $\text{HOC}_6\text{H}_5$  dissociates, which confirms that HF is truly the only significant producer of  $\text{H}^+$  in this solution.

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

	$\text{HC}_2\text{H}_3\text{O}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	0.100 M		$5.00 \times 10^{-4} \text{ M}$		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:

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

$$x = 1.1 \times 10^{-2} \text{ M}; [\text{H}^+] = 5.00 \times 10^{-4} + x = 1.6 \times 10^{-3} \text{ M}, \text{pH} = 2.80$$

$$\text{b. } x = [\text{C}_2\text{H}_3\text{O}_2^-] = 1.1 \times 10^{-2} \text{ M}$$

73. In all parts of this problem, acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) is the best weak acid present. We must solve a weak acid problem.

	$\text{HC}_2\text{H}_3\text{O}_2$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$
Initial	0.50 M		~0		0
Change	$x$ mol/L		$-x$		$+x$
Equil.	$0.50 - x$		$x$		$x$

$x$  mol/L  $\text{HC}_2\text{H}_3\text{O}_2$  dissociates to reach equilibrium

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50}$$

$$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 3.0 \times 10^{-3} \text{ M}; \text{assumptions good.}$$

$$\text{Percent dissociation} = \frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]_0} \times 100 = \frac{3.0 \times 10^{-3}}{0.50} \times 100 = 0.60\%$$

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  $\text{HC}_2\text{H}_3\text{O}_2$  is different.

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

$$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 9.5 \times 10^{-4} \text{ M}; \text{assumptions good.}$$

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

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

$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 3.0 \times 10^{-4} \text{ M}$ , 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):

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

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:

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

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

- e.  $[\text{H}^+]$  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  $[\text{H}^+]$  decreases.

74. a.  $\text{HNO}_3$  is a strong acid; it is assumed 100% dissociated in solution.

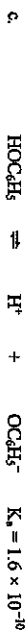


Initial	0.20 M	~0	0
	$x$ mol/L $\text{HNO}_2$ dissociates to reach equilibrium		
Change	$-x$	$+x$	$+x$
Equil.	$0.20 - x$	$x$	$x$

$$K_a = 4.0 \times 10^{-4} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$x = [\text{H}^+] = [\text{NO}_2^-] = 8.9 \times 10^{-3} \text{ M}$ , assumptions good.

$$\text{Percent dissociation} = \frac{[\text{H}^+]}{[\text{HNO}_2]_0} \times 100 = \frac{8.9 \times 10^{-3}}{0.20} \times 100 = 4.5\%$$



Initial	0.20 M	~0	0
	$x$ mol/L $\text{HOCC}_6\text{H}_5$ dissociates to reach equilibrium		
Change	$-x$	$+x$	$+x$

$$\text{Equil.} \quad 0.20 - x \quad x \quad x$$

$$K_a = 1.6 \times 10^{-10} = \frac{[\text{H}^+][\text{OC}_6\text{H}_5^-]}{[\text{HOCC}_6\text{H}_5]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$$x = [\text{H}^+] = [\text{OC}_6\text{H}_5^-] = 5.7 \times 10^{-6} \text{ M}, \text{ assumptions good.}$$

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

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

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

	HA	$\rightleftharpoons$	H <sup>+</sup>	+	A <sup>-</sup>
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  $x = [\text{H}^+] = 3.0\%$  of  $0.15$ :  $x = 0.030 \times (0.15 \text{ M}) = 4.5 \times 10^{-3} \text{ M}$ . Now that we know the value of  $x$ , we can solve for  $K_a$ .

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

76.  $\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$

Initial	1	~0	0
	$x$ mol/L HX dissociates to reach equilibrium		
Change	$-x$	$\rightarrow$	$+x$
Equil.	$1 - x$		$x$

where  $1 = [\text{HX}]_0$

From the problem,  $x = 0.25(1)$  and  $1 - x = 0.30 \text{ M}$ .

$$1 - 0.25(1) = 0.30 \text{ M}, \quad 1 = 0.40 \text{ M} \text{ and } x = 0.25(0.40 \text{ M}) = 0.10 \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]} = \frac{x^2}{1 - x} = \frac{(0.10)^2}{0.30} = 0.033$$

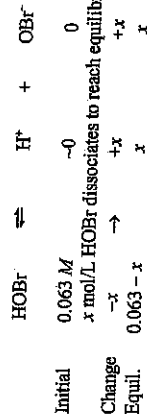
77.  $\text{HClO}_4$  is a strong acid with  $[\text{H}^+] = 0.040 \text{ M}$ . This equals the  $[\text{H}^+]$  in the trichloroacetic acid solution. Set up the problem using the  $K_a$  equilibrium reaction for  $\text{CCl}_3\text{CO}_2\text{H}$ .

	$\text{CCl}_3\text{CO}_2\text{H} \rightleftharpoons \text{H}^+ + \text{CCl}_3\text{CO}_2^-$		
Initial	0.050 M	~0	0
Equil.	$0.050 - x$	$x$	$x$

$$K_a = \frac{[H^+][ClCO_2^-]}{[ClCO_2H]} = \frac{x^2}{0.050 - x}; \text{ from the problem, } x = [H^+] = 4.0 \times 10^{-2} M$$

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

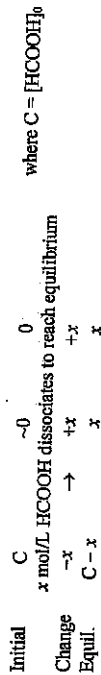
78. Set up the problem using the  $K_a$  equilibrium reaction for HOBr.



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

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

79. Major species: HCOOH and H<sub>2</sub>O; major source of H<sup>+</sup>: HCOOH



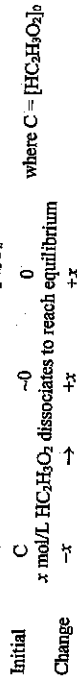
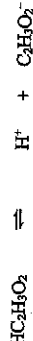
$$K_a = 1.8 \times 10^{-4} = \frac{[H^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{C - x}, \text{ where } x = [H^+]$$

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

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

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

80. Major species: HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (acetic acid) and H<sub>2</sub>O; major source of H<sup>+</sup>: HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>



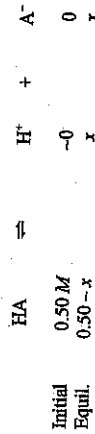
$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{C - x}, \text{ where } x = [H^+]$$

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

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

A 6 × 10<sup>-2</sup> M acetic acid solution will have pH = 3.0.

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

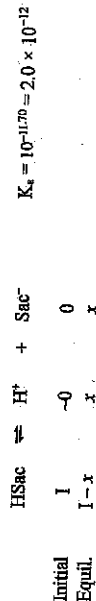


$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.50 - x}; \text{ in this problem, } [\text{HA}] = 0.45 M \text{ so:}$$

$$[\text{HA}] = 0.45 M = 0.50 M - x; x = 0.05 M$$

$$K_a = \frac{(0.05)^2}{0.45} = 6 \times 10^{-3}$$

82. Let HSac = saccharin and I = [HSac]<sub>0</sub>.



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

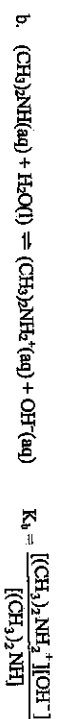
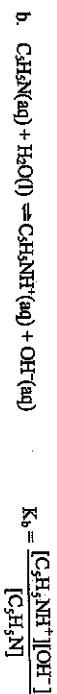
$$2.0 \times 10^{-12} = \frac{(1.8 \times 10^{-6})^2}{I - (1.8 \times 10^{-6})}; I = 1.6 M = [\text{HSac}]_0$$

$$100.0 \text{ g HC}_2\text{H}_3\text{O}_2 \times \frac{1 \text{ mol}}{183.19 \text{ g}} \times \frac{1 \text{ L}}{1.6 \text{ mol}} \times \frac{1000 \text{ mL}}{\text{L}} = 340 \text{ mL}$$

### Solutions of Bases

83. All  $K_b$  reactions refer to the base reacting with water to produce the conjugate acid of the

base and OH<sup>-</sup>.



85.  $\text{NO}_2^-$ : Because  $\text{HNO}_3$  is a strong acid,  $\text{NO}_2^-$  is a terrible base ( $K_b \ll K_w$ ). All conjugate bases of strong acids have no base strength.



Base strength =  $\text{NH}_3 > \text{C}_6\text{H}_5\text{N} > \text{H}_2\text{O} > \text{NO}_2^-$  (As  $K_b$  increases, base strength increases.)

86. 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  $\text{NH}_4^+$  and  $\text{C}_6\text{H}_5\text{NH}_3^+$  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  $\text{NH}_4^+$  and  $\text{C}_6\text{H}_5\text{NH}_3^+$  ( $K_a = K_w/K_b$ ).

Acid strength =  $\text{HNO}_3 > \text{C}_6\text{H}_5\text{NH}_3^+ > \text{NH}_4^+ > \text{H}_2\text{O}$

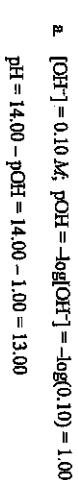


The base with the largest  $K_b$  value is the strongest base ( $K_b, \text{C}_6\text{H}_5\text{NH}_2 = 3.8 \times 10^{-10}$ ;  $K_b, \text{CH}_3\text{NH}_2 = 4.4 \times 10^{-4}$ ).  $\text{OH}^-$  is the strongest base possible in water.



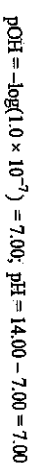
The acid with the largest  $K_a$  value is the strongest acid. To calculate  $K_a$  values for  $\text{C}_6\text{H}_5\text{NH}_3^+$  and  $\text{CH}_3\text{NH}_3^+$ , use  $K_a = K_w/K_b$ , where  $K_b$  refers to the bases  $\text{C}_6\text{H}_5\text{NH}_2$  or  $\text{CH}_3\text{NH}_2$ .

89.  $\text{NaOH}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq})$ :  $\text{NaOH}$  is a strong base that completely dissociates into  $\text{Na}^+$  and  $\text{OH}^-$ . The initial concentration of  $\text{NaOH}$  will equal the concentration of  $\text{OH}^-$  donated by  $\text{NaOH}$ .



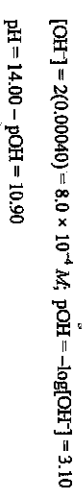
Note that  $\text{H}_2\text{O}$  is also present, but the amount of  $\text{OH}^-$  produced by  $\text{H}_2\text{O}$  will be insignificant compared to the  $0.10 \text{ M}$   $\text{OH}^-$  produced from the  $\text{NaOH}$ .

b. The  $[\text{OH}^-]$  concentration donated by the  $\text{NaOH}$  is  $1.0 \times 10^{-10} \text{ M}$ . Water by itself donates  $1.0 \times 10^{-7} \text{ M}$ . In this exercise, water is the major  $\text{OH}^-$  contributor, and  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ .

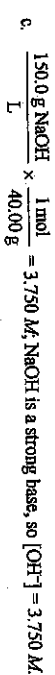


c.  $[\text{OH}^-] = 2.0 \text{ M}$ ,  $\text{pOH} = -\log(2.0) = -0.30$ ,  $\text{pH} = 14.00 - (-0.30) = 14.30$

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



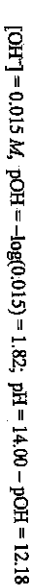
$\text{KOH}$  is a strong base, so  $[\text{OH}^-] = 0.45 \text{ M}$ ,  $\text{pOH} = -\log(0.45) = 0.35$ ;  $\text{pH} = 13.65$



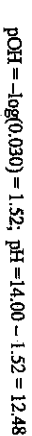
$\text{pOH} = -\log(3.750) = -0.5740$  and  $\text{pH} = 14.0000 - (-0.5740) = 14.5740$

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

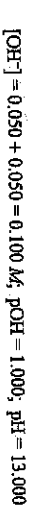
91. a. Major species:  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$  ( $\text{KOH}$  is a strong base.)



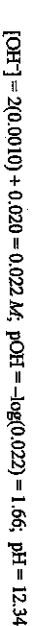
b. Major species:  $\text{Ba}^{2+}$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{Ba}(\text{OH})_2(\text{aq}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq})$ , because each mole of the strong base  $\text{Ba}(\text{OH})_2$  dissolves in water to produce two mol  $\text{OH}^-$ ,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



92. a. Major species:  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$  ( $\text{NaOH}$  and  $\text{LiOH}$  are both strong bases.)



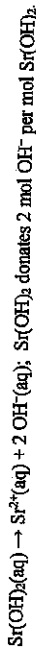
b. Major species:  $\text{Ca}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ . Both  $\text{Ca}(\text{OH})_2$  and  $\text{RbOH}$  are strong bases, and  $\text{Ca}(\text{OH})_2$  donates 2 mol  $\text{OH}^-$  per mol  $\text{Ca}(\text{OH})_2$ .



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

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

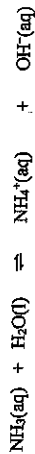
94.  $\text{pH} = 10.50$ ;  $\text{pOH} = 14.00 - 10.50 = 3.50$ ;  $[\text{OH}^-] = 10^{-3.50} = 3.2 \times 10^{-4} M$



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

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

95.  $\text{NH}_3$  is a weak base with  $K_b = 1.8 \times 10^{-5}$ . The major species present will be  $\text{NH}_3$  and  $\text{H}_2\text{O}$  ( $K_b = K_w = 1.0 \times 10^{-14}$ ). Because  $\text{NH}_3$  has a much larger  $K_b$  value than  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  is the stronger base present and will be the major producer of  $\text{OH}^-$ . To determine the amount of  $\text{OH}^-$  produced from  $\text{NH}_3$ , we must perform an equilibrium calculation using the  $K_b$  reaction for  $\text{NH}_3$ .



Initial	0.150 M	0	0
Change	$-x$	$+x$	$+x$
Equil.	$0.150 - x$	$x$	$x$

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.150 - x} \approx \frac{x^2}{0.150} \quad (\text{assuming } x \ll 0.150)$$

$x = [\text{OH}^-] = 1.6 \times 10^{-3} M$ , 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  $\text{OH}^-$  from water will be insignificant (which will usually be the case). Finishing the problem:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(1.6 \times 10^{-3} M) = 2.80$$
;  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.80 = 11.20$ .

96. Major species:  $\text{H}_2\text{NNH}_2$  ( $K_b = 3.0 \times 10^{-6}$ ) and  $\text{H}_2\text{O}$  ( $K_b = K_w = 1.0 \times 10^{-14}$ ); the weak base  $\text{H}_2\text{NNH}_2$  will dominate  $\text{OH}^-$  production. We must perform a weak base equilibrium calculation.



Initial	2.0 M	0	0
Change	$-x$	$+x$	$+x$
Equil.	$2.0 - x$	$x$	$x$

$$K_b = 3.0 \times 10^{-6} = \frac{[\text{H}_2\text{NNH}_3^+][\text{OH}^-]}{[\text{H}_2\text{NNH}_2]} = \frac{x^2}{2.0 - x} \approx \frac{x^2}{2.0} \quad (\text{assuming } x \ll 2.0)$$

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

$$[\text{H}_2\text{NNH}_3^+] = 2.4 \times 10^{-3} M$$
;  $[\text{H}_2\text{NNH}_2] = 2.0 M$ ;  $[\text{H}^+] = 10^{-11.38} = 4.2 \times 10^{-12} M$

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



Initial	0.20 M	0	0
Change	$-x$	$+x$	$+x$
Equil.	$0.20 - x$	$x$	$x$

$x$  mol/L of  $(\text{C}_2\text{H}_5)_3\text{N}$  reacts with  $\text{H}_2\text{O}$  to reach equilibrium

$$K_b = 4.0 \times 10^{-4} = \frac{[(\text{C}_2\text{H}_5)_3\text{NH}^+][\text{OH}^-]}{[(\text{C}_2\text{H}_5)_3\text{N}]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}, \quad x = [\text{OH}^-] = 8.9 \times 10^{-3} M$$

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

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



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

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

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

98. These are solutions of weak bases in water.



Initial	0.40 M	0	0
Change	$-x$	$+x$	$+x$
Equil.	$0.40 - x$	$x$	$x$

$x$  mol/L of  $\text{C}_6\text{H}_5\text{NH}_2$  reacts with  $\text{H}_2\text{O}$  to reach equilibrium

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

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



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

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

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

99. This is a solution of a weak base in water. We must solve the weak base equilibrium problem.



Initial	0.20 M	0	-0
Change	-x	+x	+x
Equil.	0.20 - x	x	x

$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20} \quad (\text{assuming } x \ll 0.20)$$

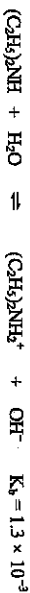
$$x = 1.1 \times 10^{-2}, \text{ checking assumption: } \frac{1.1 \times 10^{-2}}{0.20} \times 100 = 5.5\%$$

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:

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

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

100.



Initial	0.050 M	0	-0
Change	-x	+x	+x
Equil.	0.050 - x	x	x

$$K_b = 1.3 \times 10^{-3} = \frac{[(\text{C}_2\text{H}_5)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{C}_2\text{H}_5)_2\text{NH}]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x = 8.1 \times 10^{-3}, \text{ assumption is bad (} x \text{ is } 16\% \text{ of } 0.050).$$

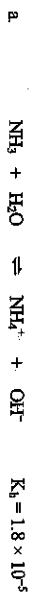
Using successive approximations:

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

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

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

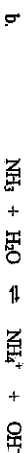
101. To solve for percent ionization, we first solve the weak base equilibrium problem.



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

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

$$\text{Percent ionization} = \frac{x}{[\text{NH}_3]_0} \times 100 = \frac{1.3 \times 10^{-3} M}{0.10 M} \times 100 = 1.3\%$$



Initial	0.010 M	0	-0
Equil.	0.010 - x	x	x

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

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

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



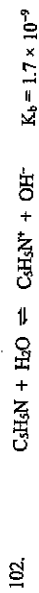
Initial	0.10 M	0	-0
Equil.	0.10 - x	x	x

$$4.38 \times 10^{-4} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, \quad x = 6.6 \times 10^{-3}, \text{ assumption fails the 5\% rule (} x \text{ is } 6.6\% \text{ of } 0.10).$$

Using successive approximations and carrying extra significant figures:

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

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

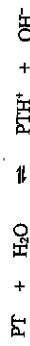


Initial	0.10 M	0	-0
Equil.	0.10 - x	x	x

$$K_b = 1.7 \times 10^{-9} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, x = [C_3H_5NH^+] = 1.3 \times 10^{-5} M, \text{ assumptions good.}$$

$$\text{Percent } C_3H_5N \text{ ionized} = \frac{1.3 \times 10^{-5} M}{0.10 M} \times 100 = 1.3 \times 10^{-2}\%$$

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

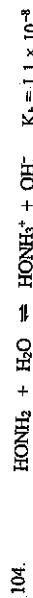


Initial	0.016 M	0	-0
Change	x mol/L of PT reacts with $H_2O$ to reach equilibrium	-x	+x
Equil.	0.016 - x	+x	x

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

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

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



Initial	I	0	-0
Equil.	I - x	x	x

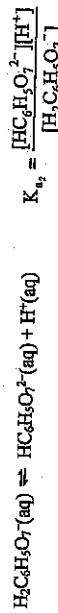
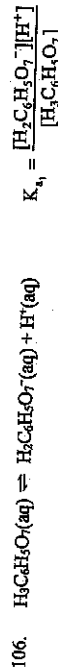
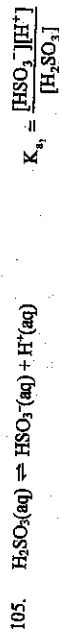
$$K_b = 1.1 \times 10^{-8} = \frac{x^2}{I - x}$$

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

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

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

## Polyprotic Acids



107. For  $H_2C_6H_4O_7$ ,  $K_{a_1} = 7.9 \times 10^{-5}$  and  $K_{a_2} = 1.6 \times 10^{-12}$ . Because  $K_{a_1} \gg K_{a_2}$ , the amount of  $H^+$  produced by the  $K_{a_2}$  reaction will be negligible.

$$[H_2C_6H_4O_7]_0 = \frac{0.500 \text{ g} \times \frac{1 \text{ mol } H_2C_6H_4O_7}{176.12 \text{ g}}}{0.2000 \text{ L}} = 0.0142 M$$



Initial	0.0142 M	0	-0
Equil.	0.0142 - x	x	x

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

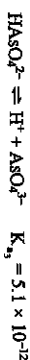
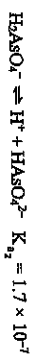
Solving by the method of successive approximations:

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

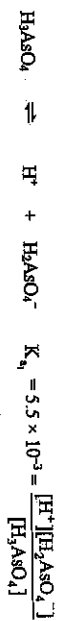
Because  $H^+$  produced by the  $K_{a_2}$  reaction will be negligible,  $[H^+] = 1.0 \times 10^{-3}$  and  $pH = 3.00$ .

108. The reactions are:





We will deal with the reactions in order of importance, beginning with the largest  $K_{a_1}$ ,  $K_{a_2}$ .



$$5.5 \times 10^{-3} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}, \quad x = 3.3 \times 10^{-2} M, \text{ assumption fails the 5\% rule.}$$

Solving by the method of successive approximations:

$$5.5 \times 10^{-3} = x^2/(0.20 - 0.033), \quad x = 3.03 \times 10^{-2} \text{ (carrying an extra significant figure)}$$

$$5.5 \times 10^{-3} = x^2/(0.20 - 0.0303), \quad x = 3.06 \times 10^{-2}$$

$$5.5 \times 10^{-3} = x^2/(0.20 - 0.0306), \quad x = 3.05 \times 10^{-2} \text{ (consistent answer)}$$

$$[\text{H}^+] = [\text{HASO}_4^{2-}] = 3.05 \times 10^{-2} = 3.1 \times 10^{-2} M, \quad [\text{H}_2\text{AsO}_4^-] = 0.20 - 0.031 = 0.17 M$$

Because  $K_{a_2} = \frac{[\text{H}^+][\text{HASO}_4^{2-}]}{[\text{H}_2\text{AsO}_4^-]} = 1.7 \times 10^{-7}$  is much smaller than the  $K_{a_1}$  value, very little

of  $\text{H}_2\text{AsO}_4^-$  (and  $\text{HASO}_4^{2-}$ ) dissociates as compared to  $\text{H}_3\text{AsO}_4$ . Therefore,  $[\text{H}^+]$  and  $[\text{HASO}_4^{2-}]$  will not change significantly by the  $K_{a_2}$  reaction. Using the previously calculated concentrations of  $\text{H}^+$  and  $\text{H}_2\text{AsO}_4^-$  to calculate the concentration of  $\text{HASO}_4^{2-}$ :

$$1.7 \times 10^{-7} = \frac{(3.1 \times 10^{-2})([\text{HASO}_4^{2-}])}{3.1 \times 10^{-2}}, \quad [\text{HASO}_4^{2-}] = 1.7 \times 10^{-7} M$$

The assumption that the  $K_{a_2}$  reaction does not change  $[\text{H}^+]$  and  $[\text{HASO}_4^{2-}]$  is good. We repeat the process using  $K_{a_3}$  to get  $[\text{AsO}_4^{3-}]$ .

$$K_{a_3} = 5.1 \times 10^{-12} = \frac{[\text{H}^+][\text{AsO}_4^{3-}]}{[\text{HASO}_4^{2-}]} = \frac{(3.1 \times 10^{-2})([\text{AsO}_4^{3-}])}{1.7 \times 10^{-7}}$$

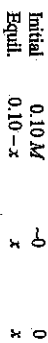
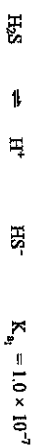
$$[\text{AsO}_4^{3-}] = 2.8 \times 10^{-12}, \text{ assumption good}$$

So in 0.20 M analytical concentration of  $\text{H}_3\text{AsO}_4$ :

$$[\text{H}_3\text{AsO}_4] = 0.17 M, \quad [\text{H}^+] = [\text{HASO}_4^{2-}] = 3.1 \times 10^{-2} M; \quad [\text{HASO}_4^{2-}] = 1.7 \times 10^{-7} M$$

$$[\text{AsO}_4^{3-}] = 2.8 \times 10^{-12} M, \quad [\text{OH}^-] = K_w/[\text{H}^+] = 3.2 \times 10^{-13} M$$

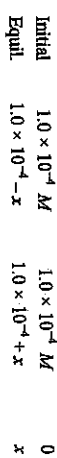
109. Because  $K_{a_2}$  for  $\text{H}_2\text{S}$  is so small, we can ignore the  $\text{H}^+$  contribution from the  $K_{a_2}$  reaction.



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

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

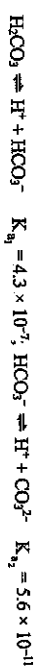
Use the  $K_{a_2}$  reaction to determine  $[\text{S}^{2-}]$ .



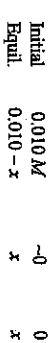
$$K_{a_2} = 1.0 \times 10^{-19} = \frac{(1.0 \times 10^{-4} + x)x}{(1.0 \times 10^{-4} - x)} \approx \frac{(1.0 \times 10^{-4})x}{1.0 \times 10^{-4}}$$

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

110. The relevant reactions are:



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



$$K_{a_1} = 4.3 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010}$$

$$x = 6.6 \times 10^{-5} M = [\text{H}^+] = [\text{HCO}_3^-], \text{ assumptions good}$$



$$\text{If } y \text{ is small, then } [\text{H}^+] = [\text{HCO}_3^-], \text{ and } K_{a_2} = 5.6 \times 10^{-11} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \approx y$$



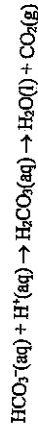
$y = [\text{CO}_3^{2-}] = 5.6 \times 10^{-11} \text{ M}$ ; assumptions good.

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

$$\frac{5.6 \times 10^{-11}}{6.6 \times 10^{-3}} \times 100 = 8.5 \times 10^{-6}\%$$

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

The reaction that occurs when acid is added to a solution of  $\text{HCO}_3^-$  is:



The bubbles are  $\text{CO}_2(\text{g})$  and are formed by the breakdown of unstable  $\text{H}_2\text{CO}_3$  molecules. We should write  $\text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$  for what we call carbonic acid. It is for convenience, however, that we write  $\text{H}_2\text{CO}_3(\text{aq})$ .

111. The dominant  $\text{H}^+$  producer is the strong acid  $\text{H}_2\text{SO}_4$ . A 2.0 M  $\text{H}_2\text{SO}_4$  solution produces 2.0 M  $\text{HSO}_4^-$  and 2.0 M  $\text{H}^+$ . However,  $\text{HSO}_4^-$  is a weak acid that could also add  $\text{H}^+$  to the solution.

	$\rightleftharpoons$	$\text{H}^+$	+	$\text{SO}_4^{2-}$
Initial		2.0 M		0
Change		$-x$	$+x$	$+x$
Equil.		$2.0 - x$	$2.0 + x$	$x$

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(2.0+x)x}{2.0-x} \approx \frac{2.0(x)}{2.0}, x = 1.2 \times 10^{-2} \text{ M}$$

Because  $x$  is 0.60% of 2.0, the assumption is valid by the 5% rule. The amount of additional  $\text{H}^+$  from  $\text{HSO}_4^-$  is  $1.2 \times 10^{-2} \text{ M}$ . The total amount of  $\text{H}^+$  present is:

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

Note: In this problem,  $\text{H}^+$  from  $\text{HSO}_4^-$  could have been ignored. However, this is not usually the case in more dilute solutions of  $\text{H}_2\text{SO}_4$ .

112. For  $\text{H}_2\text{SO}_4$ , the first dissociation occurs to completion. The hydrogen sulfate ion ( $\text{HSO}_4^-$ ) is a weak acid with  $K_{a_2} = 1.2 \times 10^{-2}$ . We will consider this equilibrium for additional  $\text{H}^+$  production:

	$\rightleftharpoons$	$\text{H}^+$	+	$\text{SO}_4^{2-}$
Initial		0.0050 M		0
Change		$-x$	$+x$	$+x$
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:

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

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

$$[\text{H}^+] = 0.0050 + x = 0.0050 + 0.0030 = 0.0080 \text{ M}, \text{pH} = 2.10$$

Note: We had to consider both  $\text{H}_2\text{SO}_4$  and  $\text{HSO}_4^-$  for  $\text{H}^+$  production in this problem.

### Acid-Base Properties of Salts

113. 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<sub>3</sub>, HClO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>
- b. Memorize the following strong bases: LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>
- 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<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>) and heavier alkaline earth metal ions (Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) have no acidic or basic properties in water.
- g. All conjugate bases of strong acids (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>) have no basic properties in water ( $K_b \ll K_w$ ), and only HSO<sub>4</sub><sup>-</sup> has any acidic properties in water.

Let's apply these ideas 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<sub>3</sub>: Neutral; K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> have no acidic/basic properties (f and g).

KCN: CN<sup>-</sup> is a weak base,  $K_b = K_w/K_{a,\text{HCN}} = 1.0 \times 10^{-14}/6.2 \times 10^{-6} = 1.6 \times 10^{-5}$  (c and d). Ignore K<sup>+</sup> (f).

$\text{NH}_4\text{Cl}$ .  $\text{NH}_4^+$  is a weak acid,  $K_a = 5.6 \times 10^{-10}$  (c and e). Ignore  $\text{Cl}^-$  (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  $\text{KNO}_3$  solution will be neutral at  $\text{pH} = 7.00$ .

Most acidic  $\rightarrow$  most basic:  $\text{HCl} > \text{NH}_4\text{Cl} > \text{KNO}_3 > \text{KCN} > \text{KOH}$

114. See Exercise 113 for some generalizations on acid-base properties of salts. The letters in parenthesis is(are) the generalization(s) listed in Exercise 113 that identifies the species.

$\text{CaBr}_2$ : Neutral;  $\text{Ca}^{2+}$  and  $\text{Br}^-$  have no acidic/basic properties (f and g).

$\text{KNO}_2$ :  $\text{NO}_2^-$  is a weak base,  $K_b = K_w/K_a$ ,  $\text{HNO}_2 = (1.0 \times 10^{-14})/(4.0 \times 10^{-4}) = 2.5 \times 10^{-11}$  (c and d). Ignore  $\text{K}^+$  (f).

$\text{HClO}_4$ : Strong acid (a)

$\text{HNO}_2$ : Weak acid,  $K_a = 4.0 \times 10^{-4}$  (c)

$\text{HONH}_3\text{ClO}_4$ :  $\text{HONH}_3^+$  is a weak acid,  $K_a = K_w/K_b$ ,  $\text{HONH}_2 = (1.0 \times 10^{-14})/(1.1 \times 10^{-8}) = 9.1 \times 10^{-7}$  (c and e). Ignore  $\text{ClO}_4^-$  (g). Note that  $\text{HNO}_2$  has a larger  $K_a$  value than  $\text{HONH}_3^+$ , so  $\text{HNO}_2$  is a stronger weak acid than  $\text{HONH}_3^+$ .

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

Most acidic  $\rightarrow$  most basic:  $\text{HClO}_4 > \text{HNO}_2 > \text{HONH}_3\text{ClO}_4 > \text{CaBr}_2 > \text{KNO}_2$

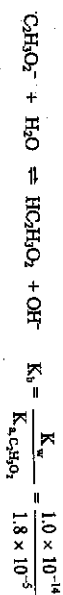
115. From the  $K_a$  values, acetic acid is a stronger acid than hypochlorous acid. Conversely, the conjugate base of acetic acid,  $\text{C}_2\text{H}_3\text{O}_2^-$ , will be a weaker base than the conjugate base of hypochlorous acid,  $\text{OCl}^-$ . Thus the hypochlorite ion,  $\text{OCl}^-$ , is a stronger base than the acetate ion,  $\text{C}_2\text{H}_3\text{O}_2^-$ . 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.

116. Because  $\text{NH}_3$  is a weaker base (smaller  $K_b$  value) than  $\text{CH}_3\text{NH}_2$ , the conjugate acid of  $\text{NH}_3$  will be a stronger acid than the conjugate acid of  $\text{CH}_3\text{NH}_2$ . Thus  $\text{NH}_4^+$  is a stronger acid than  $\text{CH}_3\text{NH}_3^+$ .

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

b.  $\text{K}_2\text{H}_3\text{O}_7$  is also a soluble ionic compound that dissolves in water to produce  $\text{K}^+$ (aq) and  $\text{C}_2\text{H}_3\text{O}_7^{2-}$ (aq). The difference between the  $\text{KCl}$  solution and the  $\text{K}_2\text{H}_3\text{O}_7$  solution is that  $\text{C}_2\text{H}_3\text{O}_7^{2-}$  does have basic properties in water, unlike  $\text{Cl}^-$ .  $\text{C}_2\text{H}_3\text{O}_7^{2-}$  is the conjugate base of the weak acid  $\text{HC}_2\text{H}_3\text{O}_7$ , and as is true for all conjugate bases of weak acids,  $\text{C}_2\text{H}_3\text{O}_7^{2-}$  is a

weak base in water. We must solve an equilibrium problem in order to determine the amount of  $\text{OH}^-$  this weak base produces in water.



Initial	1.0 M	0	-0	$K_b = 5.6 \times 10^{-10}$
x mol/L of $\text{C}_2\text{H}_3\text{O}_7^{2-}$ reacts with $\text{H}_2\text{O}$ to reach equilibrium	-x	$\rightarrow$	+x	
Change	-x		+x	
Equil.	1.0 - x		x	x

$$K_b = 5.6 \times 10^{-10} = \frac{[\text{HC}_2\text{H}_3\text{O}_7][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_7^{2-}]}, \quad 5.6 \times 10^{-10} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$$x = [\text{OH}^-] = 2.4 \times 10^{-5}\text{ M}; \text{ assumptions}$$

good

$$\text{pOH} = 4.62; \text{ pH} = 14.00 - 4.62 = 9.38; \text{ [H}^+] = 10^{-9.38} = 4.2 \times 10^{-10}\text{ M}$$

118.  $\text{C}_2\text{H}_5\text{NH}_3\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{Cl}^-$ ;  $\text{C}_2\text{H}_5\text{NH}_3^+$  is the conjugate acid of the weak base  $\text{C}_2\text{H}_5\text{NH}_2$  ( $K_b = 5.6 \times 10^{-4}$ ). As is true for all conjugate acids of weak bases,  $\text{C}_2\text{H}_5\text{NH}_3^+$  is a weak acid.  $\text{Cl}^-$  has no basic (or acidic) properties. Ignore  $\text{Cl}^-$ . Solving the weak acid problem:

Initial	0.25 M	0	-0
x mol/L $\text{C}_2\text{H}_5\text{NH}_3^+$ dissociates to reach equilibrium	-x	$\rightarrow$	+x
Change	-x		+x
Equil.	0.25 - x		x

$$K_a = 1.8 \times 10^{-11} = \frac{[\text{C}_2\text{H}_5\text{NH}_2][\text{H}^+]}{[\text{C}_2\text{H}_5\text{NH}_3^+]}, \quad 0.25 - x \approx 0.25 \quad (\text{assuming } x \ll 0.25)$$

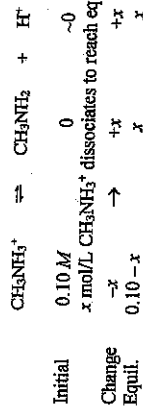
$$x = [\text{H}^+] = 2.1 \times 10^{-6}\text{ M}; \text{ pH} = 5.68; \text{ assumptions good.}$$

$$[\text{C}_2\text{H}_5\text{NH}_2] = [\text{H}^+] = 2.1 \times 10^{-6}\text{ M}; \text{ [C}_2\text{H}_5\text{NH}_3^+] = 0.25\text{ M}; \text{ [Cl}^-] = 0.25\text{ M}$$

$$[\text{OH}^-] = K_w/[\text{H}^+] = 4.8 \times 10^{-9}\text{ M}$$

119. a.  $\text{CH}_3\text{NH}_3\text{Cl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$ ;  $\text{CH}_3\text{NH}_3^+$  is a weak acid.  $\text{Cl}^-$  is the conjugate base of a strong acid.  $\text{Cl}^-$  has no basic (or acidic) properties.

$$\text{CH}_3\text{NH}_3^+ \rightleftharpoons \text{CH}_3\text{NH}_2 + \text{H}^+ \quad K_a = \frac{[\text{CH}_3\text{NH}_2][\text{H}^+]}{[\text{CH}_3\text{NH}_3^+]} = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{4.38 \times 10^{-4}} = 2.28 \times 10^{-11}$$



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

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

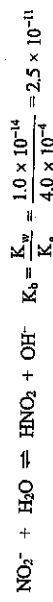
b.  $\text{NaCN} \rightarrow \text{Na}^+ + \text{CN}^-$ :  $\text{CN}^-$  is a weak base.  $\text{Na}^+$  has no acidic (or basic) properties.



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

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

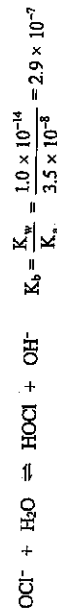
120. a.  $\text{KNO}_2 \rightarrow \text{K}^+ + \text{NO}_2^-$ :  $\text{NO}_2^-$  is a weak base. Ignore  $\text{K}^+$ .



$$K_b = 2.5 \times 10^{-11} = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = \frac{x^2}{0.12 - x} \approx \frac{x^2}{0.12}$$

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

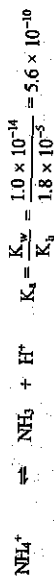
b.  $\text{NaOCl} \rightarrow \text{Na}^+ + \text{OCl}^-$ :  $\text{OCl}^-$  is a weak base. Ignore  $\text{Na}^+$ .



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

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

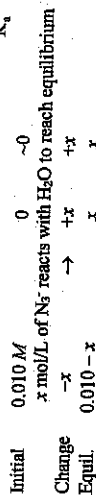
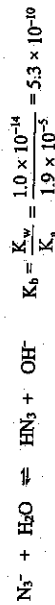
c.  $\text{NH}_4\text{ClO}_4 \rightarrow \text{NH}_4^+ + \text{ClO}_4^-$ :  $\text{NH}_4^+$  is a weak acid.  $\text{ClO}_4^-$  is the conjugate base of a strong acid.  $\text{ClO}_4^-$  has no basic (or acidic) properties.



$$K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.40 - x} \approx \frac{x^2}{0.40}$$

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

121.  $\text{NaN}_3 \rightarrow \text{Na}^+ + \text{N}_3^-$ ; azide ( $\text{N}_3^-$ ) 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  $\text{Na}^+$ .

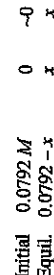
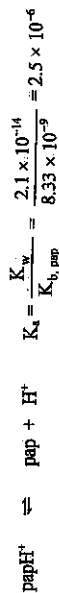


$$K_b = \frac{[\text{HN}_3][\text{OH}^-]}{[\text{N}_3^-]} = 5.3 \times 10^{-10} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} \quad (\text{assuming } x \ll 0.010)$$

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

$$[\text{HN}_3] = [\text{OH}^-] = 2.3 \times 10^{-6} \text{ M}; \text{ [Na}^+] = 0.010 \text{ M}; \text{ [N}_3^-] = 0.010 - 2.3 \times 10^{-6} = 0.010 \text{ M}$$

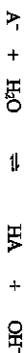
$$122. \frac{30.0 \text{ mg papH}^+\text{Cl}^-}{\text{mL soln}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol papH}^+\text{Cl}^-}{378.85 \text{ g}} \times \frac{1 \text{ mol papH}^+}{1 \text{ mol papH}^+\text{Cl}^-} = 0.0792 \text{ M}$$



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

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

123. All these salts contain  $\text{Na}^+$ , which has no acidic/basic properties, and a conjugate base of a weak acid (except for  $\text{NaCl}$ , where  $\text{Cl}^-$  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  $K_a$  value for the weak conjugate base. From the  $K_a$  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  $\text{A}^-$  as an abbreviation for the weak conjugate base:



Initial	0.100 mol/1.00 L	0	-0
	$x$ mol/L $\text{A}^-$ reacts with $\text{H}_2\text{O}$ to reach equilibrium		
Change	$-x$	$+x$	$+x$
Equil.	$0.100 - x$	$x$	$x$

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

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

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

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

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

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



Initial	0.10 M	0	-0
	$x$ mol/L $\text{BH}^+$ dissociates to reach equilibrium		
Change	$-x$	$+x$	$+x$
Equil.	$0.10 - x$	$x$	$x$

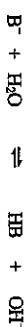
$$K_a = \frac{[\text{B}][\text{H}^+]}{[\text{BH}^+]} = \frac{x^2}{0.10 - x}; \text{ from the problem, } \text{pH} = 5.82.$$

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

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

125. From Table 14.3 of the text, this  $K_b$  value is closest to  $\text{CH}_3\text{NH}_2$ , so the unknown salt is  $\text{CH}_3\text{NH}_3\text{Cl}$ .

$\text{B}^-$  is a weak base. Use the weak base data to determine  $K_b$  for  $\text{B}^-$ .



Initial	0.050 M	0	-0
Equil.	$0.050 - x$	$x$	$x$

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

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

Because  $\text{B}^-$  is a weak base,  $\text{HB}$  will be a weak acid. Solve the weak acid problem.



Initial	0.010 M	-0	0
Equil.	$0.010 - x$	$x$	$x$

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

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

126. From the pH,  $\text{C}_2\text{H}_3\text{ClO}_2^-$  is a weak base. Use the weak base data to determine  $K_b$  for  $\text{C}_2\text{H}_3\text{ClO}_2^-$  (which we will abbreviate as  $\text{CB}^-$ ).



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

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

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

Because  $\text{CB}^-$  is a weak base,  $\text{HCB}$ , chloroacetic acid, is a weak acid. Solving the weak acid problem:

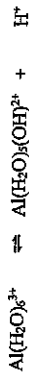


Initial	0.20 M	-0	0
Equil.	$0.20 - x$	$x$	$x$

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

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

127. Major species present:  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  ( $K_a = 1.4 \times 10^{-5}$ ),  $\text{NO}_2^-$  (neutral), and  $\text{H}_2\text{O}$  ( $K_w = 1.0 \times 10^{-14}$ );  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  is a stronger acid than water, so it will be the dominant  $\text{H}^+$  producer.



Initial	0.050 M	0	0
Change	-x	+x	-0
Equil.	0.050 - x	x	x

$$K_a = 1.4 \times 10^{-5} = \frac{[\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

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

128. Major species:  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ( $K_a = 1.0 \times 10^{-5}$ ),  $\text{Cl}^-$  (neutral), and  $\text{H}_2\text{O}$  ( $K_w = 1.0 \times 10^{-14}$ );  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  will determine the pH because it is a stronger acid than water. Solving the weak acid problem in the usual manner:

	$\text{Co}(\text{H}_2\text{O})_6^{2+}$	$\rightleftharpoons$	$\text{Co}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	+	$\text{H}^+$	$K_a = 1.0 \times 10^{-5}$
Initial	0.10 M		0		0	
Equil.	0.10 - x		x		x	

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

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

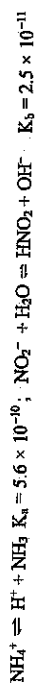
129. Reference Table 14.6 of the text and the solution to Exercise 113 for some generalizations on acid-base properties of salts.

- a.  $\text{NaNO}_3 \rightarrow \text{Na}^+ + \text{NO}_3^-$  neutral; neither species has any acidic/basic properties.  
 b.  $\text{NaNO}_2 \rightarrow \text{Na}^+ + \text{NO}_2^-$  basic;  $\text{NO}_2^-$  is a weak base, and  $\text{Na}^+$  has no effect on pH.  

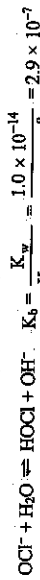
$$\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^- \quad K_b = \frac{K_w}{K_a, \text{HNO}_2} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$$
  
 c.  $\text{C}_6\text{H}_5\text{NHClO}_4 \rightarrow \text{C}_6\text{H}_5\text{NH}^+ + \text{ClO}_4^-$  acidic;  $\text{C}_6\text{H}_5\text{NH}^+$  is a weak acid, and  $\text{ClO}_4^-$  has no effect on pH.  

$$\text{C}_6\text{H}_5\text{NH}^+ \rightleftharpoons \text{H}^+ + \text{C}_6\text{H}_5\text{N} \quad K_a = \frac{K_w}{K_b, \text{C}_6\text{H}_5\text{N}} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

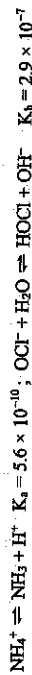
- d.  $\text{NH}_4\text{NO}_2 \rightarrow \text{NH}_4^+ + \text{NO}_2^-$  acidic;  $\text{NH}_4^+$  is a weak acid ( $K_a = 5.6 \times 10^{-10}$ ), and  $\text{NO}_2^-$  is a weak base ( $K_b = 2.5 \times 10^{-11}$ ). Because  $K_a, \text{NH}_4^+ > K_b, \text{NO}_2^-$ , the solution is acidic.



- e.  $\text{KOCI} \rightarrow \text{K}^+ + \text{OCI}^-$  basic;  $\text{OCI}^-$  is a weak base, and  $\text{K}^+$  has no effect on pH.

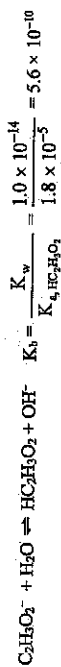
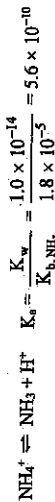


- f.  $\text{NH}_4\text{OCl} \rightarrow \text{NH}_4^+ + \text{OCl}^-$  basic;  $\text{NH}_4^+$  is a weak acid, and  $\text{OCl}^-$  is a weak base. Because  $K_b, \text{OCl}^- > K_a, \text{NH}_4^+$ , the solution is basic.

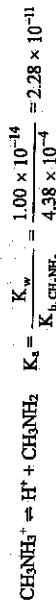


130. a.  $\text{Sr}(\text{NO}_3)_2 \rightarrow \text{Sr}^{2+} + 2\text{NO}_3^-$  neutral;  $\text{Sr}^{2+}$  and  $\text{NO}_3^-$  have no effect on pH.

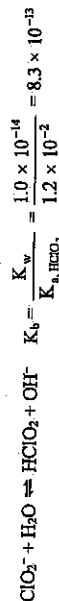
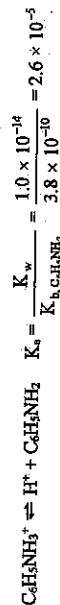
- b.  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2 \rightarrow \text{NH}_4^+ + \text{C}_2\text{H}_3\text{O}_2^-$  neutral;  $\text{NH}_4^+$  is a weak acid, and  $\text{C}_2\text{H}_3\text{O}_2^-$  is a weak base. Because  $K_a, \text{NH}_4^+ = K_b, \text{C}_2\text{H}_3\text{O}_2^-$ , the solution will be neutral ( $\text{pH} = 7.00$ ).



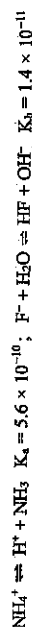
- c.  $\text{CH}_3\text{NH}_2\text{Cl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$  acidic;  $\text{CH}_3\text{NH}_3^+$  is a weak acid, and  $\text{Cl}^-$  has no effect on pH. Because only a weak acid is present, the solution will be acidic.



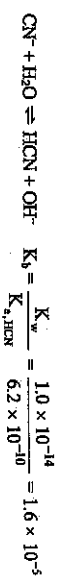
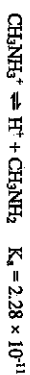
- d.  $\text{CaH}_2\text{NH}_2\text{ClO}_4 \rightarrow \text{CaH}_2\text{NH}_3^+ + \text{ClO}_4^-$  acidic;  $\text{CaH}_2\text{NH}_3^+$  is a weak acid, and  $\text{ClO}_4^-$  is a very weak base. Because  $K_a, \text{CaH}_2\text{NH}_3^+ > K_b, \text{ClO}_4^-$ , the solution is acidic.



- e.  $\text{NH}_4\text{F} \rightarrow \text{NH}_4^+ + \text{F}^-$  acidic;  $\text{NH}_4^+$  is a weak acid, and  $\text{F}^-$  is a weak base. Because  $K_a, \text{NH}_4^+ > K_b, \text{F}^-$ , the solution is acidic.



12.  $\text{CH}_3\text{NH}_2\text{CN} \rightarrow \text{CH}_3\text{NH}_2^+ + \text{CN}^-$  basic;  $\text{CH}_3\text{NH}_2^+$  is a weak acid, and  $\text{CN}^-$  is a weak base. Because  $K_{\text{b, CN}^-} > K_{\text{a, CH}_3\text{NH}_2^+}$ , the solution is basic.



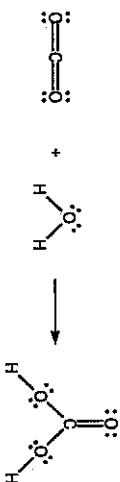
### Relationships Between Structure and Strengths of Acids and Bases

131. a.  $\text{HIO}_3 < \text{HBrO}_3$ , as the electronegativity of the central atom increases, acid strength increases.  
 b.  $\text{HNO}_2 < \text{HNO}_3$ , as the number of oxygen atoms attached to the central nitrogen atom increases, acid strength increases.  
 c.  $\text{HOI} < \text{HOCl}$ ; same reasoning as in a.  
 d.  $\text{H}_3\text{PO}_3 < \text{H}_3\text{PO}_4$ ; same reasoning as in b.
132. a.  $\text{BrO}_2^- < \text{IO}_2^-$ , these are the conjugate bases of the acids in Exercise 131a. Since  $\text{HBrO}_2$  is the stronger acid, the conjugate base of  $\text{HBrO}_2$  ( $\text{BrO}_2^-$ ) will be the weaker base.  $\text{IO}_2^-$  will be the stronger base because  $\text{HIO}_2$  is the weaker acid.  
 b.  $\text{NO}_2^- < \text{NO}_3^-$ , these are the conjugate bases of the acids in Exercise 131b. Conjugate base strength is inversely related to acid strength.  
 c.  $\text{OCl}^- < \text{OI}^-$ , these are the conjugate bases of the acids in Exercise 131c.  
 133. a.  $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$ ; as the strength of the H-X bond decreases, acid strength increases.  
 b.  $\text{CH}_3\text{CO}_2\text{H} < \text{FCH}_2\text{CO}_2\text{H} < \text{F}_2\text{CHCO}_2\text{H} < \text{F}_3\text{CCO}_2\text{H}$ ; as the electronegativity of neighboring atoms increases, acid strength increases.  
 c.  $\text{NH}_4^+ < \text{HONH}_3^+$ ; same reason as in b.  
 d.  $\text{NH}_4^+ < \text{PH}_4^+$ ; same reason as in a.
134. In general, the stronger the acid, the weaker is the conjugate base.  
 a.  $\text{SeH} < \text{SH} < \text{OH}$ ; these are the conjugate bases of the acids in Exercise 133a. The ordering of the base strength is the opposite of the acids.  
 b.  $\text{PH}_3 < \text{NH}_3$  (See Exercise 133d.)  
 c.  $\text{HONH}_2 < \text{NH}_3$  (See Exercise 133c.)
135. In general, metal oxides form basic solutions when dissolved in water, and nonmetal oxides form acidic solutions in water.
- a. Basic;  $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$ ;  $\text{Ca}(\text{OH})_2$  is a strong base.  
 b. Acidic;  $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$ ;  $\text{H}_2\text{SO}_3$  is a weak diprotic acid.

- c. Acidic;  $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{HOCl}(\text{aq})$ ;  $\text{HOCl}$  is a weak acid.  
 136. a. Basic;  $\text{Li}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{LiOH}(\text{aq})$ ;  $\text{LiOH}$  is a strong base.  
 b. Acidic;  $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$ ;  $\text{H}_2\text{CO}_3$  is a weak diprotic acid.  
 c. Basic;  $\text{SiO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Si}(\text{OH})_2(\text{aq})$ ;  $\text{Si}(\text{OH})_2$  is a strong base.

### Lewis Acids and Bases

137. A Lewis base is an electron pair donor, and a Lewis acid is an electron pair acceptor.  
 a.  $\text{B}(\text{OH})_3$ , acid;  $\text{H}_2\text{O}$ , base  
 b.  $\text{Ag}^+$ , acid;  $\text{NH}_3$ , base  
 c.  $\text{BF}_3$ , acid;  $\text{F}^-$ , base
138. a.  $\text{Fe}^{2+}$ , acid;  $\text{H}_2\text{O}$ , base  
 b.  $\text{H}_2\text{O}$ , acid;  $\text{CN}^-$ , base  
 c.  $\text{HgI}_2$ , acid;  $\text{I}^-$ , base
139.  $\text{Al}(\text{OH})_3(\text{s}) + 3 \text{H}^+(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$  (Bronsted-Lowry base,  $\text{H}^+$  acceptor)  
 $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq})$  (Lewis acid, electron pair acceptor)
140.  $\text{Zn}(\text{OH})_2(\text{s}) + 2 \text{H}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$  (Bronsted-Lowry base)  
 $\text{Zn}(\text{OH})_2(\text{s}) + 2 \text{OH}^-(\text{aq}) \rightarrow \text{Zn}(\text{OH})_4^{2-}(\text{aq})$  (Lewis acid)
141.  $\text{Fe}^{3+}$  should be the stronger Lewis acid.  $\text{Fe}^{2+}$  is smaller and has a greater positive charge. Because of this,  $\text{Fe}^{2+}$  will be more strongly attracted to lone pairs of electrons as compared to  $\text{Fe}^{3+}$ .
142. The Lewis structures for the reactants and products are:



In this reaction,  $\text{H}_2\text{O}$  donates a pair of electrons to carbon in  $\text{CO}_2$ , which is followed by a proton shift to form  $\text{H}_2\text{CO}_3$ .  $\text{H}_2\text{O}$  is the Lewis base, and  $\text{CO}_2$  is the Lewis acid.

### Additional Exercises

143. At pH = 2.000,  $[\text{H}^+] = 10^{-2.000} = 1.00 \times 10^{-3} \text{ M}$   
 At pH = 4.000,  $[\text{H}^+] = 10^{-4.000} = 1.00 \times 10^{-4} \text{ M}$

M

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

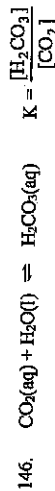
Let V = total volume of solution at pH = 4.000:

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

L

Volume of water added =  $1.00 \text{ L} - 0.0100 \text{ L} = 0.99 \text{ L} = 990 \text{ mL}$

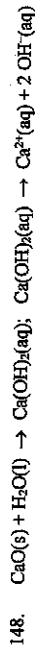
144. Conjugate acid-base pairs differ by an  $\text{H}^+$  in the formula. Pairs in parts a, c, and d are conjugate acid-base pairs. For part b,  $\text{HSO}_4^-$  is the conjugate base of  $\text{H}_2\text{SO}_4$ . In addition,  $\text{HSO}_4^-$  is the conjugate acid of  $\text{SO}_4^{2-}$ .
145. The 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  $\text{NH}_4\text{Cl}$  are strong electrolytes. Of these three substances, only  $\text{NH}_4\text{Cl}$  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).  $\text{NH}_4\text{Cl}$  dissociates into  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions when dissolved in water.  $\text{Cl}^-$  is the conjugate base of a strong acid, so it has no basic (or acidic properties) in water.  $\text{NH}_4^+$ , however, is the conjugate acid of the weak base  $\text{NH}_3$ , so  $\text{NH}_4^+$  is a weak acid and would produce a solution with a pH = 4.6 when the concentration is  $\sim 1.0 \text{ M}$ .  $\text{NH}_4\text{Cl}$  is the solute.



During exercise:  $[\text{H}_2\text{CO}_3] = 26.3 \text{ mM}$  and  $[\text{CO}_2] = 1.63 \text{ mM}$ , so:  $K = \frac{26.3 \text{ mM}}{1.63 \text{ mM}} = 16.1$

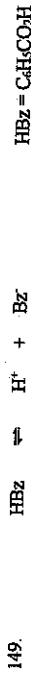
At rest:  $K = 16.1 = \frac{24.9 \text{ mM}}{[\text{CO}_2]}$ ,  $[\text{CO}_2] = 1.55 \text{ mM}$

147. a. In the lungs there is a lot of  $\text{O}_2$ , and the equilibrium favors  $\text{Hb}(\text{O}_2)_4$ . In the cells there is a lower concentration of  $\text{O}_2$ , and the equilibrium favors  $\text{HbH}_4^{4+}$ .
- b.  $\text{CO}_2$  is a weak acid,  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ . Removing  $\text{CO}_2$  essentially decreases  $\text{H}^+$ , which causes the hemoglobin reaction to shift right.  $\text{Hb}(\text{O}_2)_4$  is then favored, and  $\text{O}_2$  is not released by hemoglobin in the cells. Breathing into a paper bag increases  $\text{CO}_2$  in the blood, thus increasing  $[\text{H}^+]$ , which shifts the hemoglobin reaction left.
- c.  $\text{CO}_2$  builds up in the blood, and it becomes too acidic, driving the hemoglobin equilibrium to the left. Hemoglobin can't bind  $\text{O}_2$  as strongly in the lungs. Bicarbonate ion acts as a base in water and neutralizes the excess acidity.



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

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



Initial  $\text{C} = 0$   $\text{C} = [\text{HBz}]_0 = \text{concentration of HBz that dissolves to give saturated solution.}$

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

Equil.  $\text{C} - x$   $x$   $x$

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

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

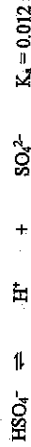
$$\text{C} - (1.6 \times 10^{-3}) = \frac{(1.6 \times 10^{-3})^2}{6.4 \times 10^{-5}} = 4.0 \times 10^{-2}$$

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

The molar solubility of  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  is  $4.2 \times 10^{-2} \text{ mol/L}$ .

150.  $[\text{H}^+]_0 = (1.0 \times 10^{-2}) + (1.0 \times 10^{-2}) = 2.0 \times 10^{-2} \text{ M}$  from strong acids HCl and  $\text{H}_2\text{SO}_4$ .

$\text{HSO}_4^-$  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  $\text{H}^+$  contribution from  $\text{HSO}_4^-$ :



Initial  $0.010 \text{ M}$   $0.020 \text{ M}$   $0$

Equil.  $0.010 - x$   $0.020 + x$   $x$

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

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

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

151. For this problem we will abbreviate  $\text{CH}_2=\text{CHCO}_2\text{H}$  as Haer and  $\text{CH}_2=\text{CHCO}_2^-$  as aer $^-$ .

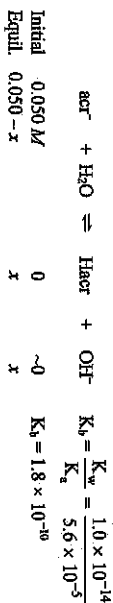
a. Solving the weak acid problem:

	Haer	$\rightleftharpoons$	$\text{H}^+$	+	aer $^-$	
Initial	0.10 M		~0		0	$K_a = 5.6 \times 10^{-5}$
Equil.	0.10 - x		x		x	

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

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

c. acr<sup>-</sup> is a weak base and the major source of OH<sup>-</sup> in this solution.



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

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

152. 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<sub>3</sub>, HClO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>. Common strong bases = LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>.

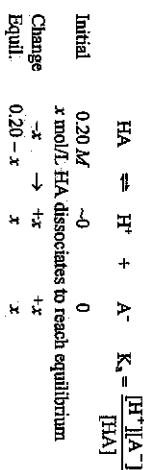
(2) All other acids and bases are weak and will have  $K_a$  and  $K_b$  values of less than 1 but greater than  $K_w$  ( $1.0 \times 10^{-14}$ ). Reference Table 14.2 for  $K_a$  values for some weak acids and Table 14.3 for  $K_b$  values for some weak bases. There are too many weak acids and weak 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 ( $K_a = 7.2 \times 10^{-9}$ ) |
| g. weak acid ( $K_a = 1.8 \times 10^{-4}$ )  | h. strong base                              |
| i. strong acid                               |   |

153. a. HA is a weak acid. Most of the acid is present as HA molecules; only one set of H<sup>+</sup> and A<sup>-</sup> ions is present. In a strong acid, all of the acid would be dissociated into H<sup>+</sup> and A<sup>-</sup> ions.

b. This picture is the result of 1 out of 10 HA molecules dissociating.

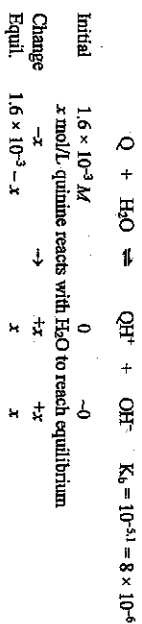
$$\text{Percent dissociation} = \frac{1}{10} \times 100 = 10\% \text{ (an exact number)}$$



$$[\text{H}^+] = [\text{A}^-] = x = 0.10 \times 0.20 M = 0.020 M, \quad [\text{HA}] = 0.20 - 0.020 = 0.18 M$$

$$K_a = \frac{(0.020)^2}{0.18} = 2.2 \times 10^{-3}$$

154.  $\frac{1.0 \text{ g quinine}}{1.9000 \text{ L}} \times \frac{1 \text{ mol quinine}}{324.4 \text{ g quinine}} = 1.6 \times 10^{-3} M$  quinine; let Q = quinine = C<sub>9</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>.



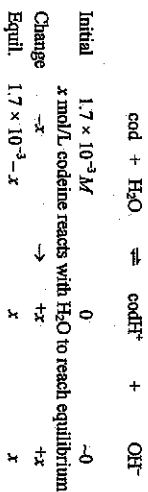
$$K_b = 8 \times 10^{-6} = \frac{[\text{QH}^+][\text{OH}^-]}{[\text{Q}]} = \frac{x^2}{(1.6 \times 10^{-3} - x)} \approx \frac{x^2}{1.6 \times 10^{-3}}$$

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

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

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

155. Let cod = codine, C<sub>9</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>; using the  $K_b$  reaction to solve:



$$K_b = \frac{x^2}{1.7 \times 10^{-3} - x}; \quad \text{pH} = 9.39; \quad \text{pOH} = 14.00 - 9.39 = 4.41$$

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



156. Codeine =  $C_{18}H_{21}NO_5$ ; codeine sulfate =  $C_{36}H_{42}N_2O_{10}S$

The formula for codeine sulfate works out to  $(\text{codeineH}^+)_2\text{SO}_4^{2-}$ , where  $\text{codeineH}^+ = \text{HC}_{18}\text{H}_{21}\text{NO}_5^+$ . Two codeine molecules are protonated by  $\text{H}_2\text{SO}_4$ , forming the conjugate acid of codeine. The  $\text{SO}_4^{2-}$  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.



$$\begin{array}{l} \text{Initial} \quad 0.10 \text{ M} \\ \text{Equil.} \quad 0.10 - x \end{array} \qquad \begin{array}{l} 0 \\ x \end{array} \qquad \begin{array}{l} \sim 0 \\ x \end{array}$$

$$K_a = \frac{[\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}][\text{H}_3\text{O}^+]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]}, \quad 6.0 \times 10^{-3} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

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

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

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

$$x = [\text{H}^+] = 0.022 \text{ M}; \quad \text{pH} = 1.66$$

b. Because of the lower charge,  $\text{Fe}^{2+}(\text{aq})$  will not be as strong an acid as  $\text{Fe}^{3+}(\text{aq})$ . 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,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$   
 b. Memorize the following strong bases: LiOH, NaOH, KOH, RbOH, CsOH,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$

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

g. Conjugate bases of strong acids ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{HSO}_4^-$ ) have no basic properties in water ( $K_b \ll K_w$ ), and only  $\text{HSO}_4^-$  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<sup>-</sup> is the conjugate base of the weak acid HF, so F<sup>-</sup> is a weak base. The  $K_b$  value for F<sup>-</sup> =  $K_w/K_{a,\text{HF}} = 1.4 \times 10^{-11}$ . Na<sup>+</sup> has no acidic or basic properties.

NaI: Neutral ( $\text{pH} = 7.0$ ); Na<sup>+</sup> and I<sup>-</sup> 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:  $\text{HI} < \text{HF} < \text{NaI} < \text{NaF}$ .

b.  $\text{NH}_4\text{Br}$ :  $\text{NH}_4^+$  is a weak acid ( $K_a = 5.6 \times 10^{-10}$ ), and Br<sup>-</sup> is a neutral species.

HBr: Strong acid

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

NH<sub>3</sub>: Weak base,  $K_b = 1.8 \times 10^{-5}$

Increasing pH:  $\text{HBr} < \text{NH}_4\text{Br} < \text{KBr} < \text{NH}_3$   
 Most acidic

c.  $\text{C}_6\text{H}_5\text{NH}_2$ :  $\text{C}_6\text{H}_5\text{NH}_3^+$  is a weak acid ( $K_a = K_w/K_b = K_w/K_{b,\text{C}_6\text{H}_5\text{NH}_2} = 1.0 \times 10^{-14}/3.8 \times 10^{-10} = 2.6 \times 10^{-5}$ ), and  $\text{NO}_3^-$  is a neutral species.

NaNO<sub>3</sub>: Neutral; Na<sup>+</sup> and NO<sub>3</sub><sup>-</sup> have no acidic/basic properties.

NaOH: Strong base

HOC<sub>6</sub>H<sub>5</sub>: Weak acid ( $K_a = 1.6 \times 10^{-10}$ )

KOC<sub>6</sub>H<sub>5</sub>: OC<sub>6</sub>H<sub>5</sub><sup>-</sup> is a weak base ( $K_b = K_w/K_{a,\text{HOC}_6\text{H}_5} = 6.3 \times 10^{-5}$ ), and K<sup>+</sup> is a neutral species.

C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup>: Weak base ( $K_b = 3.8 \times 10^{-10}$ )

HNO<sub>3</sub>: 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<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> is a stronger weak acid than HOC<sub>6</sub>H<sub>5</sub> since the  $K_a$  value for C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub><sup>+</sup> is larger than the  $K_a$  value for

$\text{HOCC}_6\text{H}_5$ . Between the two weak bases, because the  $K_b$  value for  $\text{OCC}_6\text{H}_5^-$  is larger than the  $K_b$  value for  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{OCC}_6\text{H}_5^-$  is a stronger weak base than  $\text{C}_6\text{H}_5\text{NH}_2$ .

Increasing pH:  $\text{HNO}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{HOCC}_6\text{H}_5 < \text{NaNNO}_2 < \text{C}_6\text{H}_5\text{NH}_2 < \text{KOC}_6\text{H}_5 < \text{NaOH}$   
Most acidic Most basic

159. The solution is acidic from  $\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$ . Solving the weak acid problem:

$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$K_a = 1.2 \times 10^{-2}$
Initial	0.10 M    ~0    0
Equal	0.10 - x    x    x

$$1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, \quad x = 0.035$$

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

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

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

$$x = [\text{H}^+] = 0.029 \text{ M}, \quad \text{pH} = 1.54$$

160. a.  $\text{NH}_3 + \text{H}_3\text{O}^+ \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$

$$K_{\text{eq}} = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}^+]} = \frac{1}{K_a \text{ for } \text{NH}_4^+} = \frac{K_b \text{ for } \text{NH}_3}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^9$$

b.  $\text{NO}_2^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$   $K_{\text{eq}} = \frac{[\text{HNO}_2]}{[\text{NO}_2^-][\text{H}^+]} = \frac{1}{K_a \text{ for } \text{HNO}_2} = \frac{1}{4.0 \times 10^{-4}} = 2.5 \times 10^3$

c.  $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$   $K_{\text{eq}} = \frac{1}{K_b \text{ for } \text{NH}_3} = \frac{1}{1.8 \times 10^{-5}} = 5.6 \times 10^4$

- d.  $\text{HNO}_2 + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^-$

$$K_{\text{eq}} = \frac{[\text{NO}_2^-]}{[\text{HNO}_2][\text{OH}^-]} \times \frac{[\text{H}^+]}{[\text{H}^+]} = \frac{K_a \text{ for } \text{HNO}_2}{K_w} = \frac{4.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 4.0 \times 10^{10}$$

161. a.  $\text{H}_2\text{SO}_4$     b.  $\text{HClO}_3$     c.  $\text{H}_3\text{PO}_3$

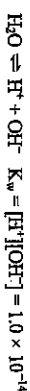
$\text{NaOH}$  and  $\text{KOH}$  are soluble ionic compounds composed of  $\text{Na}^+$  and  $\text{K}^+$  cations and  $\text{OH}^-$  anions. All soluble ionic compounds dissolve to form the ions from which they are formed. In oxyacids, the compounds are all covalent compounds in which electrons are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

### ChemWork Problems

The answers to the problems 162-169 (or a variation to these problems) are found in OWL. These problems are also assignable in OWL.

### Challenge Problems

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



$\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$   $K_a$  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  $[\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$

From  $K_w$ ,  $[\text{OH}^-] = K_w/[\text{H}^+]$ , and from  $1.0 \times 10^{-3} \text{ M HCl}$ ,  $[\text{Cl}^-] = 1.0 \times 10^{-3} \text{ M}$ . Substituting into the charge balance equation:

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{[\text{H}^+]} + 1.0 \times 10^{-3}, \quad [\text{H}^+]^2 - (1.0 \times 10^{-3})[\text{H}^+] - 1.0 \times 10^{-14} = 0$$

Using the quadratic formula to solve:

$$[\text{H}^+] = \frac{-(-1.0 \times 10^{-3}) \pm [(-1.0 \times 10^{-3})^2 - 4(1)(-1.0 \times 10^{-14})]^{1/2}}{2(1)}, \quad [\text{H}^+] = 1.1 \times 10^{-7} \text{ M}$$

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

171. Because this is a very dilute solution of  $\text{NaOH}$ , we must worry about the amount of  $\text{OH}^-$  donated from the autoionization of water.



$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

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

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

Substituting into the charge balance equation:

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

Using the quadratic formula to solve:

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

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



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

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

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

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



Initial  $\text{C} \quad -0 \quad 0 \quad \text{C} = [\text{HA}]_0, \text{ for pH} = 4.000,$

Equil.  $\text{C} - 1.00 \times 10^{-4} \quad 1.00 \times 10^{-4} \quad 1.00 \times 10^{-4} \quad x = [\text{H}^+] = 1.00 \times 10^{-4} \text{ M}$

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

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



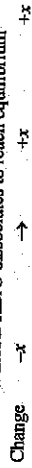
Initial  $5.05 \times 10^{-4} \text{ mol/V} \quad -0 \quad 0$

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

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

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

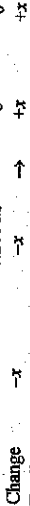
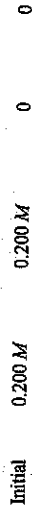
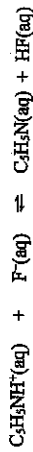
$V = 4.59 \text{ L}$ ;  $50.0 \text{ mL}$  are present initially, so we need to add  $4540 \text{ mL}$  of water.



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

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.

175. Major species present are  $\text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_5\text{NH}^+$  [ $K_a = K_w/K_{b, \text{C}_3\text{H}_5\text{N}} = (1.0 \times 10^{-14})/(1.7 \times 10^{-9}) = 5.9 \times 10^{-6}$ ], and  $\text{F}^-$  [ $K_b = K_w/K_{a, \text{HF}} = (1.0 \times 10^{-14})/(7.2 \times 10^{-4}) = 1.4 \times 10^{-11}$ ]. The reaction to consider is the best acid present ( $\text{C}_3\text{H}_5\text{NH}^+$ ) reacting with the best base present ( $\text{F}^-$ ). Let's solve by first setting up an ICE table.



$$K = K_{a, \text{C}_3\text{H}_5\text{NH}^+} \times \frac{1}{K_{b, \text{F}^-}} = 5.9 \times 10^{-6} \times \frac{1}{7.2 \times 10^{-4}} = 8.2 \times 10^{-3}$$

$$K = \frac{[\text{C}_3\text{H}_5\text{N}][\text{HF}]}{[\text{C}_3\text{H}_5\text{NH}^+][\text{F}^-]}, \quad 8.2 \times 10^{-3} = \frac{x^2}{(0.200 - x)^2}; \text{ taking the square root of both sides:}$$

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

From the setup to the problem,  $x = [\text{C}_3\text{H}_5\text{N}] = [\text{HF}] = 0.016 \text{ M}$ , and  $0.200 - x = 0.200 - 0.016 = 0.184 \text{ M} = [\text{C}_3\text{H}_5\text{NH}^+] = [\text{F}^-]$ . To solve for the  $[\text{H}^+]$ , we can use either the  $K_a$  equilibrium for  $\text{C}_3\text{H}_5\text{NH}^+$  or the  $K_b$  equilibrium for  $\text{F}^-$ . Using  $\text{C}_3\text{H}_5\text{NH}^+$  data:

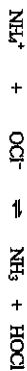
$$K_{a, \text{C}_3\text{H}_5\text{NH}^+} = 5.9 \times 10^{-6} = \frac{[\text{C}_3\text{H}_5\text{N}][\text{H}^+]}{[\text{C}_3\text{H}_5\text{NH}^+]}, \quad [\text{H}^+] = 6.8 \times 10^{-5} \text{ M}$$

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

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.

176. Major species:  $\text{NH}_4^+$ ,  $\text{OCl}^-$ , and  $\text{H}_2\text{O}$ ;  $K_a$  for  $\text{NH}_4^+ = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$  and  $K_b$  for  $\text{OCl}^- = (1.0 \times 10^{-14})/(3.5 \times 10^{-8}) = 2.9 \times 10^{-7}$ .

Because  $\text{OCl}^-$  is a better base than  $\text{NH}_4^+$  is an acid, the solution will be basic. The dominant equilibrium is the best acid ( $\text{NH}_4^+$ ) reacting with the best base ( $\text{OCl}^-$ ) present:



Initial	0.50 M	0.50 M	0	0
Change	-x	-x	+x	+x
Equil.	0.50-x	0.50-x	x	x

$$K = K_{a,\text{NH}_4^+} \times \frac{1}{K_{a,\text{HOCl}}} = (5.6 \times 10^{-10}) / (3.5 \times 10^{-8}) = 0.016$$

$$K = 0.016 = \frac{[\text{NH}_3][\text{HOCl}]}{[\text{NH}_4^+][\text{OCl}^-]} = \frac{x(x)}{(0.50-x)(0.50-x)}$$

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

To solve for the  $\text{H}^+$ , use any pertinent  $K_a$  or  $K_b$  value. Using  $K_a$  for  $\text{NH}_4^+$ :

$$K_{a,\text{NH}_4^+} = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} = \frac{(0.058)[\text{H}^+]}{0.50-0.058}, [\text{H}^+] = 4.3 \times 10^{-9} M, \text{pH} = 8.37$$

177. Because  $\text{NH}_3$  is so concentrated, we need to calculate the  $\text{OH}^-$  contribution from the weak base  $\text{NH}_3$ .



Initial	15.0 M	0	0.0100 M	(Assume no volume change.)
Equil.	15.0-x	x	0.0100+x	

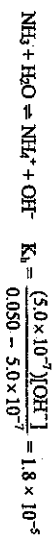
$$K_b = 1.8 \times 10^{-5} = \frac{x(0.0100+x)}{15.0-x} \approx \frac{x(0.0100)}{15.0}, x = 0.027; \text{ assumption is horrible (x is 270\% of 0.0100)}$$

Using the quadratic formula:

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

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

178. For 0.0010% dissociation:  $[\text{NH}_4^+] = 1.0 \times 10^{-5}$ ,  $(0.050) = 5.0 \times 10^{-2} M$



Solving:  $[\text{OH}^-] = 1.8 M$ , assuming no volume change.

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

179.  $1.000 \text{ L} \times \frac{1.00 \times 10^{-4} \text{ mol HA}}{\text{L}} = 1.00 \times 10^{-4} \text{ mol HA}$

25.0% dissociation gives:

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

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

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

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

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

The volume goes from 100.0 mL to 83.3 mL, so 917 mL of water evaporated.

180.  $\text{HC}_2\text{H}_3\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \quad K_a = 1.8 \times 10^{-5}$

Initial	1.00 M	~0	0
Equil.	1.00-x	x	x

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

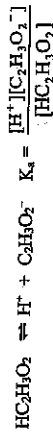
$$\text{pH} = -\log(4.24 \times 10^{-3}) = 2.37; \text{ assumptions good.}$$

We want to double the pH to 2(2.37) = 4.74 by addition of the strong base  $\text{NaOH}$ . 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  $\text{HC}_2\text{H}_3\text{O}_2$ . The initial reaction that occurs when the strong base is added is:



Note that this reaction has the net effect of converting  $\text{HC}_2\text{H}_3\text{O}_2$  into its conjugate base,  $\text{C}_2\text{H}_3\text{O}_2^-$ .

For a pH = 4.74, let's calculate the ratio of  $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$  necessary to achieve this pH.



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

$$K_a = 1.8 \times 10^{-5} = \frac{(1.8 \times 10^{-5})[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}, \quad \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.0$$

For a solution having  $\text{pH} = 4.74$ , we need to have equal concentrations (equal moles) of  $\text{C}_2\text{H}_3\text{O}_2^-$  and  $\text{HC}_2\text{H}_3\text{O}_2$ . Therefore, we need to add an amount of  $\text{NaOH}$  that will convert one-half of the  $\text{HC}_2\text{H}_3\text{O}_2$  into  $\text{C}_2\text{H}_3\text{O}_2^-$ . This amount is  $0.50 \text{ M NaOH}$ .



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  $\text{NaOH(s)}$  to produce a  $0.50 \text{ M OH}^-$  solution will convert one-half the  $\text{HC}_2\text{H}_3\text{O}_2$  into  $\text{C}_2\text{H}_3\text{O}_2^-$ ; this results in a solution with  $\text{pH} = 4.74$ .

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

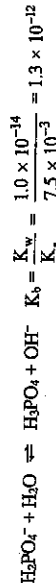
181.  $\text{PO}_4^{3-}$  is the conjugate base of  $\text{HPO}_4^{2-}$ . The  $K_a$  value for  $\text{HPO}_4^{2-}$  is  $K_a = 4.8 \times 10^{-13}$ .



$\text{HPO}_4^{2-}$  is the conjugate base of  $\text{H}_2\text{PO}_4^-$  ( $K_{a2} = 6.2 \times 10^{-8}$ ).

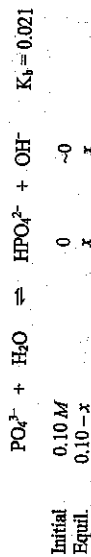


$\text{H}_2\text{PO}_4^-$  is the conjugate base of  $\text{H}_3\text{PO}_4$  ( $K_{a1} = 7.5 \times 10^{-3}$ ).



From the  $K_b$  values,  $\text{PO}_4^{3-}$  is the strongest base. This is expected because  $\text{PO}_4^{3-}$  is the conjugate base of the weakest acid ( $\text{HPO}_4^{2-}$ ).

182. Major species:  $\text{Na}^+$ ,  $\text{PO}_4^{3-}$  (a weak base),  $\text{H}_2\text{O}$ . From the  $K_b$  values calculated in Exercise 181, the dominant producer of  $\text{OH}^-$  is the  $K_b$  reaction for  $\text{PO}_4^{3-}$ . We can ignore the contribution of  $\text{OH}^-$  from the  $K_b$  reactions for  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$ . From Exercise 181,  $K_b$  for  $\text{PO}_4^{3-} = 0.021$ .



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

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

183. a.  $\text{NH}_4(\text{HCO}_3) \rightarrow \text{NH}_4^+ + \text{HCO}_3^-$

$$K_{a,\text{NH}_4^+} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-3}} = 5.6 \times 10^{-10}, \quad K_{b,\text{HCO}_3^-} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

The solution is basic because  $\text{HCO}_3^-$  is a stronger base than  $\text{NH}_4^+$  is as an acid. The acidic properties of  $\text{HCO}_3^-$  were ignored because  $K_{a2}$  is very small ( $4.8 \times 10^{-11}$ ).

b.  $\text{NaH}_2\text{PO}_4 \rightarrow \text{Na}^+ + \text{H}_2\text{PO}_4^-$ ; ignore  $\text{Na}^+$ .

$$K_{a2,\text{H}_2\text{PO}_4^-} = 6.2 \times 10^{-8}, \quad K_{b,\text{H}_2\text{PO}_4^-} = \frac{K_w}{K_{a1}} = \frac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}$$

Solution is acidic because  $K_{a2} > K_b$ .

c.  $\text{Na}_2\text{HPO}_4 \rightarrow 2 \text{Na}^+ + \text{HPO}_4^{2-}$ ; ignore  $\text{Na}^+$ .

$$K_{a3,\text{HPO}_4^{2-}} = 4.8 \times 10^{-13}, \quad K_{b,\text{HPO}_4^{2-}} = \frac{K_w}{K_{a2}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-8}} = 1.6 \times 10^{-7}$$

Solution is basic because  $K_b > K_{a3}$ .

d.  $\text{NH}_4(\text{H}_2\text{PO}_4) \rightarrow \text{NH}_4^+ + \text{H}_2\text{PO}_4^-$

$\text{NH}_4^+$  is a weak acid, and  $\text{H}_2\text{PO}_4^-$  is also acidic (see part b). Solution with both ions present will be acidic.

e.  $\text{NH}_4(\text{HCO}_3) \rightarrow \text{NH}_4^+ + \text{HCO}_3^-$ ; from Appendix 5,  $K_{a,\text{HCO}_3^-} = 1.8 \times 10^{-4}$ .

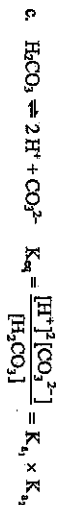
$$K_{a,\text{NH}_4^+} = 5.6 \times 10^{-10}, \quad K_{b,\text{HCO}_3^-} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

Solution is acidic because  $\text{NH}_4^+$  is a stronger acid than  $\text{HCO}_3^-$  is a base.

184. a.  $\text{HCO}_3^- + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3 + \text{CO}_3^{2-}$

$$K_{a1} = \frac{[\text{H}_2\text{CO}_3][\text{CO}_3^{2-}]}{[\text{HCO}_3^-][\text{HCO}_3^-]} \times \frac{[\text{H}^+]}{[\text{H}^+]} = \frac{K_{a2}}{K_{a1}} = \frac{5.6 \times 10^{-11}}{4.3 \times 10^{-7}} = 1.3 \times 10^{-4}$$

b.  $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]$  since the reaction in part a is the principal equilibrium reaction.



Because  $[\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]$  from part b,  $[\text{H}^+]^2 = K_{a1} \times K_{a2}$ .

$$[\text{H}^+] = (K_{a1} \times K_{a2})^{1/2}, \text{ or taking the } -\log \text{ of both sides: } \text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$$

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

$$185. \text{ Molarity} = m = \frac{0.100 \text{ g} \times \frac{1 \text{ mol}}{100.0 \text{ g}}}{0.5000 \text{ kg}} = 2.00 \times 10^{-3} \text{ mol/kg} \approx 2.00 \times 10^{-3} \text{ mol/L}$$

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



Because the weak acid is 50% dissociated:

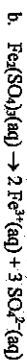
$$[\text{H}^+] = [\text{A}^-] = [\text{HA}]_0 \times 0.50 = 2.00 \times 10^{-3} \text{ M} \times 0.50 = 1.0 \times 10^{-3} \text{ M}$$

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

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

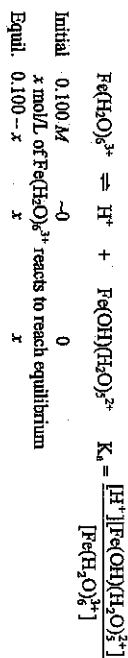
186. a. Assuming no ion association between  $\text{SO}_4^{2-}(\text{aq})$  and  $\text{Fe}^{2+}(\text{aq})$ , then  $i = 5$  for  $\text{Fe}_2(\text{SO}_4)_3$ .

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



Under ideal circumstances, 2/5 of  $\pi$  calculated above results from  $\text{Fe}^{2+}$  and 3/5 results from  $\text{SO}_4^{2-}$ . The contribution to  $\pi$  from  $\text{SO}_4^{2-}$  is  $3/5 \times 6.11 \text{ atm} = 3.67 \text{ atm}$ . Because  $\text{SO}_4^{2-}$  is assumed uncharged in solution, the  $\text{SO}_4^{2-}$  contribution in the actual solution will also be 3.67 atm. The contribution to the actual osmotic pressure from the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  dissociation reaction is  $6.73 - 3.67 = 3.06 \text{ atm}$ .

The initial concentration of  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  is  $2(0.0500) = 0.100 \text{ M}$ . The set up for the weak acid problem is:



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

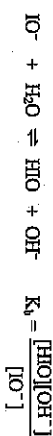
$$0.125 \text{ M} = 0.100 - x + x + x = 0.100 + x, \quad x = 0.025 \text{ M}$$

$$K_a = \frac{[\text{H}^+][\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]} = \frac{x^2}{0.100 - x} = \frac{(0.025)^2}{(0.100 - 0.025)} = 0.075$$

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

### Integrative Problems

$$187. [\text{IO}^-] = \frac{2.14 \text{ g NaIO} \times \frac{1 \text{ mol NaIO}}{165.89 \text{ g}} \times \frac{1 \text{ mol IO}^-}{1 \text{ mol NaIO}}}{1.25 \text{ L}} = 1.03 \times 10^{-2} \text{ M IO}^-$$



Initial	$1.03 \times 10^{-2} \text{ M}$	0	~0
Equil.	$1.03 \times 10^{-2} - x$	$x$	$x$

$$K_b = \frac{x^2}{1.03 \times 10^{-2} - x}; \text{ from the problem, } \text{pOH} = 14.00 - 11.32 = 2.68$$

$$[\text{OH}^-] = 10^{-2.68} = 2.1 \times 10^{-3} \text{ M} = x, \quad K_b = \frac{(2.1 \times 10^{-3})^2}{1.03 \times 10^{-2} - 2.1 \times 10^{-3}} = 5.4 \times 10^{-4}$$

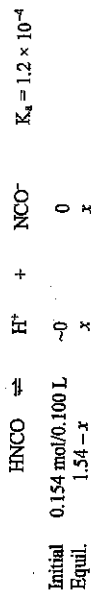
188. If NaOCl is limiting:

$$10.0 \text{ g NaOCl} \times \frac{1 \text{ mol NaOCl}}{65.01 \text{ g NaOCl}} \times \frac{2 \text{ mol HNCO}}{2 \text{ mol NaOCl}} = 0.154 \text{ mol HNCO}$$

If  $\text{H}_2\text{C}_2\text{O}_4$  is limiting:

$$10.0 \text{ g H}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mol H}_2\text{C}_2\text{O}_4}{90.04 \text{ g H}_2\text{C}_2\text{O}_4} \times \frac{2 \text{ mol HNCO}}{2 \text{ mol H}_2\text{C}_2\text{O}_4} = 0.222 \text{ mol HNCO}$$

Because NaOCN produces the smaller amount of product, NaOCN is limiting and 0.154 mol H<sub>2</sub>CO<sub>3</sub> can be produced.



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

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

$$189. \quad \text{Molar mass} = \frac{dRT}{P} = \frac{5.11 \text{ g/L} \times \frac{0.08206 \text{ L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \times 298 \text{ K}}{1.00 \text{ atm}} = 125 \text{ g/mol}$$

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



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

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

### Marathon Problems

190. Let's abbreviate HCO<sub>2</sub>H with HA and CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H with HB. From the problem, we have:  
0.0500 M HCO<sub>2</sub>H (HA),  $K_a = 1.77 \times 10^{-4}$ ; 0.150 M CH<sub>3</sub>CH<sub>2</sub>CO<sub>2</sub>H (HB),  $K_a = 1.34 \times 10^{-5}$

Because two comparable weak acids are present, each will contribute to the total pH. In order to solve for the pH, we need to determine some relationships that must hold true in this solution. Two equations that must hold true are the  $K_a$  expressions for the two acids:

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = 1.77 \times 10^{-4}, \quad \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]} = 1.34 \times 10^{-5}$$

Another relationship that must hold true recognizes that all of the HA originally dissolved (0.0500 M) must be present as either A<sup>-</sup> or HA at equilibrium. So:

$$0.0500 = [\text{HA}] + [\text{A}^-]$$

A similar relationship holds for HB:  $0.150 = [\text{HB}] + [\text{B}^-]$

The last relationship we need recognizes that in any solution, the net positive charge must equal the net negative charge. This is called the charge balance equation. This equation is:

$$[\text{H}^+] = [\text{A}^-] + [\text{B}^-] + [\text{OH}^-] = [\text{A}^-] + [\text{B}^-] + K_w/[\text{H}^+]$$

We now have five equations and five unknowns ([HA], [HB], [A<sup>-</sup>], [B<sup>-</sup>], and [H<sup>+</sup>]). We should be able to manipulate the equations to solve for [H<sup>+</sup>]. Solving:

$$[\text{H}^+] = [\text{A}^-] + [\text{B}^-] + K_w/[\text{H}^+]; \quad [\text{H}^+]^2 = [\text{H}^+][\text{A}^-] + [\text{H}^+][\text{B}^-] + K_w$$

$$[\text{H}^+][\text{A}^-] = (1.77 \times 10^{-4})[\text{HA}] = (1.77 \times 10^{-4})(0.0500 - [\text{A}^-])$$

$$\text{If } [\text{A}^-] \ll 0.0500, \text{ then } [\text{H}^+][\text{A}^-] \approx (1.77 \times 10^{-4})(0.0500) = 8.85 \times 10^{-6}$$

$$\text{Similarly, assume } [\text{H}^+][\text{B}^-] \approx (1.34 \times 10^{-5})(0.150) = 2.01 \times 10^{-6}$$

$$[\text{H}^+]^2 = 8.85 \times 10^{-6} + 2.01 \times 10^{-6} + 1.00 \times 10^{-14}; \quad [\text{H}^+] = 3.30 \times 10^{-3} \text{ mol/L}$$

$$\text{Checking assumptions: } [\text{H}^+][\text{A}^-] \approx 8.85 \times 10^{-6}, \quad [\text{A}^-] \approx \frac{8.85 \times 10^{-6}}{3.30 \times 10^{-3}} \approx 2.68 \times 10^{-3}$$

We assumed  $0.0500 - [\text{A}^-] \approx 0.0500$ . This assumption is borderline ( $2.68 \times 10^{-3}$  is 5.4% of 0.0500). The HB assumption is good (0.4% error).

Using successive approximations to refine the  $[\text{H}^+][\text{A}^-]$  value gives  $[\text{H}^+][\text{A}^-] = 8.39 \times 10^{-6}$ , which gives:

$$[\text{H}^+] = 3.22 \times 10^{-3} M, \quad \text{pH} = -\log(3.22 \times 10^{-3}) = 2.492$$

Note: If we treat each acid separately:

$$\text{H}^+ \text{ from HA} = 2.9 \times 10^{-3} M$$

$$\text{H}^+ \text{ from HB} = 1.4 \times 10^{-3} M$$

$$4.3 \times 10^{-3} M = [\text{H}^+]_{\text{total}}$$

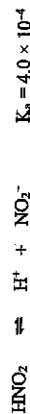
This assumes the acids did not suppress each other's ionization. They do, and we expect the [H<sup>+</sup>] to be less than  $4.3 \times 10^{-3} M$ . We get such an answer ( $[\text{H}^+] = 3.22 \times 10^{-3} M$ ).

191. a. Strongest acid from group I = HCl; weakest base (smallest  $K_a$ ) from group II = NaNO<sub>2</sub>

0.20 M HCl + 0.20 M NaNO<sub>2</sub>; major species = H<sup>+</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, NO<sub>2</sub><sup>-</sup>, and H<sub>2</sub>O; let the H<sup>+</sup> react to completion with the NO<sub>2</sub><sup>-</sup>; then solve the back equilibrium problem.

	H <sup>+</sup> +	NO <sub>2</sub> <sup>-</sup>	→	HNO <sub>2</sub>
Before	0.10 M	0.10 M	0	0
After	0	0	0.10 M	0.10 M

(Molarities are halved due to dilution.)



Initial	0.10 M	0	0
Change	-x	+x	+x
Equil.	0.10 - x	x	x

$$\frac{x^2}{0.10 - x} = 4.0 \times 10^{-4}; \text{ solving: } x = [\text{H}^+] = 6.1 \times 10^{-3} \text{ M}; \text{ pH} = 2.21$$

- b. Weakest acid from group I =  $(\text{C}_2\text{H}_5)_2\text{NHCl}$ , best base from group II =  $\text{KOH}$ ; the dominant equilibrium will be the best base reacting with the best acid.



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

$$K = \frac{K_a(\text{C}_2\text{H}_5)_2\text{NH}^+}{K_a(\text{HOI})} = \frac{1.0 \times 10^{-4}}{4.0 \times 10^{-4}} \times \frac{1}{2.0 \times 10^{-11}} = 1.25 \text{ (carrying extra sig. fig.)}$$

$$\frac{x^2}{(0.10 - x)^2} = 1.25; \frac{x}{0.10 - x} = 1.12; x = 0.053 \text{ M}$$

So  $[\text{HOI}] = 0.053 \text{ M}$  and  $[\text{OH}^-] = 0.10 - x = 0.047 \text{ M}$ , using the  $K_a$  equilibrium constant for HOI to solve for  $[\text{H}^+]$ :

$$2.0 \times 10^{-11} = \frac{[\text{H}^+](0.047)}{(0.053)}; [\text{H}^+] = 2.3 \times 10^{-11} \text{ M}; \text{ pH} = 10.64$$

c.  $K_a$  for  $(\text{C}_2\text{H}_5)_2\text{NH}^+ = \frac{1.0 \times 10^{-4}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$

$$K_b \text{ for } \text{NO}_2^- = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$$

Because  $K_a = K_b$ , mixing  $(\text{C}_2\text{H}_5)_2\text{NHCl}$  with  $\text{NaNO}_2$  will result in a solution with  $\text{pH} = 7.00$ .