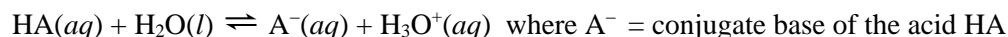


## Chapter 13 Review Questions and Text Homework Solutions

### Review Questions

2. a. The  $K_a$  reaction always refers to an acid reacting with water to produce the conjugate base of the acid and the hydronium ion ( $\text{H}_3\text{O}^+$ ). For a general weak acid HA, the  $K_a$  reaction is:

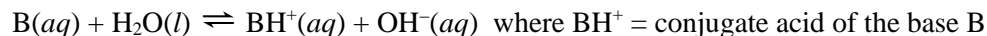


This reaction is often abbreviated as:  $\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$

- b. The  $K_a$  equilibrium constant is the equilibrium constant for the  $K_a$  reaction of some substance. For the general  $K_a$  reaction, the  $K_a$  expression is:

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]} \text{ or } K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \text{ (for the abbreviated } K_a \text{ reaction)}$$

- c. The  $K_b$  reaction always refers to a base reacting with water to produce the conjugate acid of the base and the hydroxide ion ( $\text{OH}^-$ ). For a general base, B, the  $K_b$  reaction is:

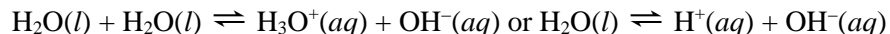


- d. The  $K_b$  equilibrium constant for the general  $K_b$  reaction is:  $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$

- e. A conjugate acid-base pair consists of two substances related to each other by the donating and accepting of a single proton ( $\text{H}^+$ ). The conjugate bases of the acids HCl,  $\text{HNO}_2$ ,  $\text{HC}_2\text{H}_3\text{O}_2$ , and  $\text{H}_2\text{SO}_4$  are  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ , and  $\text{HSO}_4^-$ , respectively. The conjugate acids of the bases  $\text{NH}_3$ ,  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{HONH}_2$  are  $\text{NH}_4^+$ ,  $\text{C}_5\text{H}_5\text{NH}^+$ , and  $\text{HONH}_3^+$ , respectively. Conjugate acid-base pairs only differ by  $\text{H}^+$  in their respective formulas.

3. a. Amphoteric: A substance that can behave either as an acid or as a base.

- b. The  $K_w$  reaction is also called the autoionization of water reaction. The reaction always occurs when water is present as the solvent. The reaction is:



- c. The  $K_w$  equilibrium constant is also called the ion-product constant or the dissociation constant of water. It is the equilibrium constant for the autoionization reaction of water:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \text{ or } K_w = [\text{H}^+][\text{OH}^-]$$

At typical solution temperatures of  $25^\circ\text{C}$ ,  $K_w = 1.0 \times 10^{-14}$ .

- d. pH is a mathematical term which is equal to the  $-\log$  of the  $\text{H}^+$  concentration of a solution ( $\text{pH} = -\log[\text{H}^+]$ ).

- e. pOH is a mathematical term which is equal to the  $-\log$  of the  $\text{OH}^-$  concentration of a solution ( $\text{pOH} = -\log[\text{OH}^-]$ ).
- f. The p of any quantity is the  $-\log$  of that quantity. So:  $\text{p}K_w = -\log K_w$ . At  $25^\circ\text{C}$ ,  $\text{p}K_w = -\log(1.0 \times 10^{-14}) = 14.00$ .

Neutral solution at  $25^\circ\text{C}$ :  $K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$  and  $\text{pH} + \text{pOH} = 14.00$

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}; \text{pH} = \text{pOH} = -\log(1.0 \times 10^{-7}) = 7.00$$

Acidic solution at  $25^\circ\text{C}$ :

$$[\text{H}^+] > [\text{OH}^-]; [\text{H}^+] > 1.0 \times 10^{-7} \text{ M}; [\text{OH}^-] < 1.0 \times 10^{-7} \text{ M}; \text{pH} < 7.00; \text{pOH} > 7.00$$

Basic solution at  $25^\circ\text{C}$ :

$$[\text{OH}^-] > [\text{H}^+]; [\text{OH}^-] > 1.0 \times 10^{-7} \text{ M}; [\text{H}^+] < 1.0 \times 10^{-7} \text{ M}; \text{pOH} < 7.00; \text{pH} > 7.00$$

As a solution becomes more acidic,  $[\text{H}^+]$  increases, so  $[\text{OH}^-]$  decreases, pH decreases, and pOH increases. As a solution becomes more basic,  $[\text{OH}^-]$  increases, so  $[\text{H}^+]$  decreases, pH increases, and pOH decreases.

4. The  $K_a$  value refers to the reaction of an acid reacting with water to produce the conjugate base and  $\text{H}_3\text{O}^+$ . The stronger the acid, the more conjugate base and  $\text{H}_3\text{O}^+$  produced, and the larger the  $K_a$  value.

Strong acids are basically 100% dissociated in water. Therefore, the strong acids have a  $K_a \gg 1$  because the equilibrium position lies far to the right. The conjugate bases of strong acids are terrible bases; much worse than water, so we can ignore their basic properties in water.

Weak acids are only partially dissociated in water. We say that the equilibrium lies far to the left, thus giving values for  $K_a < 1$  (weak acids have mostly reactants at equilibrium and few products present). The conjugate bases of weak acids are better bases than water. When we have a solution composed of just the conjugate base of a weak acid in water, the resulting pH is indeed basic ( $\text{pH} > 7.0$ ). In general, as the acid strength increases, the conjugate base strength decreases, or as acid strength decreases, the conjugate base strength increases. They are inversely related.

Base strength is directly related to the  $K_b$  value. The larger the  $K_b$  value, the more  $\text{OH}^-$  produced from the  $K_b$  reaction, and the more basic the solution (the higher the pH). Weak bases have a  $K_b < 1$  and their conjugate acids behave as weak acids in solution. As the strength of the base increases, the strength of the conjugate acid gets weaker; the stronger the base, the weaker the conjugate acid, or the weaker the base, the stronger the conjugate acid.

5. Strong acids are assumed 100% dissociated in water, and we assume that the amount of  $\text{H}^+$  donated by water is negligible. Hence, the equilibrium  $[\text{H}^+]$  of a strong acid is generally equal to the initial acid concentration ( $[\text{HA}]_0$ ). Note that solutions of  $\text{H}_2\text{SO}_4$  can be different from this because  $\text{H}_2\text{SO}_4$  is a diprotic acid. Also, when you have very dilute solutions of a strong acid, the  $\text{H}^+$  contribution from water by itself must be considered. The strong acids to memorize are HCl, HBr, HI,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$ .

$K_a$  values for weak acids are listed in Table 13.2 and in Appendix 5 of the text. Because weak acids only partially dissociate in water, we must solve an equilibrium problem to determine how much  $H^+$  is added to water by the weak acid. We write down the  $K_a$  reaction, set-up the ICE table, then solve the equilibrium problem. The two assumptions generally made are that acids are less than 5% dissociated in water and that the  $H^+$  contribution from water is negligible.

The 5% rule comes from the assumptions that weak acids are less than 5% dissociated. When this is true, the mathematics of the problem are made much easier. The equilibrium expression we get for weak acids in water generally has the form (assuming an initial acid concentration of 0.10 M):

$$K_a = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

The 5% rule refers to assuming  $0.10 - x \approx 0.10$ . The assumption is valid if  $x$  is less than 5% of the number the assumption was made against ( $[HA]_0$ ). When the 5% rule is valid, solving for  $x$  is very straight forward. When the 5% rule fails, we must solve the mathematical expression exactly using the quadratic equation (or your graphing calculator). Even if you do have a graphing calculator, reference Appendix 1 to review the quadratic equation. Appendix 1 also discusses the method of successive approximations which can also be used to solve quadratic (and cubic) equations.

6. Strong bases are soluble ionic compounds containing the  $OH^-$  anion. Strong bases increase the  $OH^-$  concentration in water by just dissolving. Thus, for strong bases like LiOH, NaOH, KOH, RbOH, and CsOH, the initial concentration of the strong base equals the equilibrium  $[OH^-]$  of water.

The other strong bases to memorize have +2 charged metal cations. The soluble ones to know are  $Ca(OH)_2$ ,  $Sr(OH)_2$ , and  $Ba(OH)_2$ . These are slightly more difficult to solve because they donate 2 moles  $OH^-$  for every mole of salt dissolved. Here, the  $[OH^-]$  is equal to two times the initial concentration of the soluble alkaline earth hydroxide salt dissolved.

Neutrally charged organic compounds containing at least one nitrogen atom generally behave as weak bases. The nitrogen atom has an unshared pair of electrons around it. This lone pair of electrons is used to form a bond to  $H^+$ .

Weak bases only partially react with water to produce  $OH^-$ . To determine the amount of  $OH^-$  produced by the weak base (and, in turn, the pH of the solution), we set-up the ICE table using the  $K_b$  reaction of the weak base. The typical weak base equilibrium expression is:

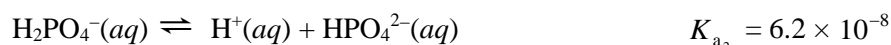
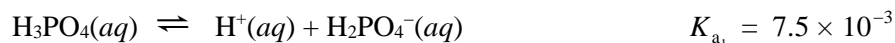
$$K_b = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25} \quad (\text{assuming } [B]_0 = 0.25 \text{ M})$$

Solving for  $x$  gives us the  $[OH^-]$  in solution. We generally assume that weak bases are less than 5% reacted with water and that the  $OH^-$  contribution from water is negligible. The 5% assumption makes the math easier. By assuming an expression like  $0.25 \text{ M} - x \approx 0.25 \text{ M}$ , the calculation is very straight forward. The 5% rule applied here is that if  $(x/0.25) \times 100$  is less than 5%, the assumption is valid. When the assumption is not valid, then we solve the equilibrium expression exactly using the quadratic equation (or by the method of successive approximations).

7. Monoprotic acid: An acid with one acidic proton; the general formula for monoprotic acids is HA.  
 Diprotic acid: An acid with two acidic protons ( $H_2A$ ).  
 Triprotic acid: An acid with three acidic protons ( $H_3A$ ).



When  $\text{H}_2\text{SO}_4$  is dissolved in water, the first proton is assumed 100% dissociated because  $\text{H}_2\text{SO}_4$  is a strong acid. After  $\text{H}_2\text{SO}_4$  dissociates, we have  $\text{H}^+$  and  $\text{HSO}_4^-$  present.  $\text{HSO}_4^-$  is a weak acid and can donate some more protons to water. To determine the amount of  $\text{H}^+$  donated by  $\text{HSO}_4^-$ , one must solve an equilibrium problem using the  $K_{a_2}$  reaction for  $\text{HSO}_4^-$ .

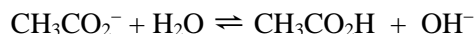


When  $\text{H}_3\text{PO}_4$  is added to water, the three acids that are present are  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ , and  $\text{HPO}_4^{2-}$ .  $\text{H}_3\text{PO}_4$ , with the largest  $K_a$  value, is the strongest of these weak acids. The conjugate bases of the three acids are  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . Because  $\text{HPO}_4^{2-}$  is the weakest acid (smallest  $K_a$  value), its conjugate base ( $\text{PO}_4^{3-}$ ) will have the largest  $K_b$  value and is the strongest base.

See Examples 13.15-13.17 of the text on the strategies used to solve for the pH of polyprotic acids. The strategy to solve most polyprotic acid solutions is covered in Example 13.15. For typical polyprotic acids,  $K_{a_1} \gg K_{a_2}$  (and  $K_{a_3}$  if a triprotic acid). Because of this, the dominant producer of  $\text{H}^+$  in solution is just the  $K_{a_1}$  reaction. We set-up the equilibrium problem using the  $K_{a_1}$  reaction and solve for  $\text{H}^+$ . We then assume that the  $\text{H}^+$  donated by the  $K_{a_2}$  (and  $K_{a_3}$  if triprotic) reaction is negligible, that is, the  $\text{H}^+$  donated by the  $K_{a_1}$  reaction is assumed to be the  $\text{H}^+$  donated by the entire acid system. This assumption is great when  $K_{a_1} \gg K_{a_2}$  (roughly a 1000 fold difference in magnitude).

Examples 13.16 and 13.17 cover strategies for the other type of polyprotic acid problems. This other type is solutions of  $\text{H}_2\text{SO}_4$ . As discussed previously,  $\text{H}_2\text{SO}_4$  problems are both a strong acid and a weak acid problem in one. To solve for the  $[\text{H}^+]$ , we sometimes must worry about the  $\text{H}^+$  contribution from  $\text{HSO}_4^-$ . Example 13.16 is an example of an  $\text{H}_2\text{SO}_4$  solution where the  $\text{HSO}_4^-$  contribution of  $\text{H}^+$  can be ignored. Example 13.17 illustrates an  $\text{H}_2\text{SO}_4$  problem where we can't ignore the  $\text{H}^+$  contribution from  $\text{HSO}_4^-$ .

8.
  - a.  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{CO}_2^-$
  - b. An acid-base reaction can be thought of as a competition between two opposing bases. Since this equilibrium lies far to the left ( $K_a < 1$ ),  $\text{CH}_3\text{CO}_2^-$  is a stronger base than  $\text{H}_2\text{O}$ .
  - c. The acetate ion is a better base than water and produces basic solutions in water. When we put acetate ion into solution as the only major basic species, the reaction is:



Now the competition is between  $\text{CH}_3\text{CO}_2^-$  and  $\text{OH}^-$  for the proton. Hydroxide ion is the strongest base possible in water. The equilibrium above lies far to the left, resulting in a  $K_b$  value less than one. Those species we specifically call weak bases ( $10^{-14} < K_b < 1$ ) lie between  $\text{H}_2\text{O}$  and  $\text{OH}^-$  in base strength. Weak bases are stronger bases than water but are weaker bases than  $\text{OH}^-$ .

The  $\text{NH}_4^+$  ion is a weak acid because it lies between  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  ( $\text{H}^+$ ) in terms of acid strength. Weak acids are better acids than water, thus their aqueous solutions are acidic. They are weak acids because they are not as strong as  $\text{H}_3\text{O}^+$  ( $\text{H}^+$ ). Weak acids only partially dissociate in water and have  $K_a$  values between  $10^{-14}$  and 1.

For a strong acid  $\text{HX}$  having  $K_a = 1 \times 10^6$ , the conjugate base,  $\text{X}^-$ , has  $K_b = K_w/K_a = 1.0 \times 10^{-14}/1 \times 10^6 = 1 \times 10^{-20}$  (a very small value).

The conjugate bases of strong acids have extremely small values for  $K_b$ ; so small that they are worse bases than water ( $K_b \ll K_w$ ). Therefore, conjugate bases of strong acids have no basic properties in water. They are present, but they only balance charge in solution and nothing else. The conjugate bases of the six strong acids are  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ , and  $\text{HSO}_4^-$ .

Summarizing the acid-base properties of conjugates:

- The conjugate base of a weak acid is a weak base ( $10^{-14} < K_b < 1$ )
- The conjugate acid of a weak base is a weak acid ( $10^{-14} < K_a < 1$ )
- The conjugate base of a strong acid is a worthless base ( $K_b \ll 10^{-14}$ )
- The conjugate acid of a strong base is a worthless acid ( $K_a \ll 10^{-14}$ )

Identifying/recognizing the acid-base properties of conjugates is crucial in order to understand the acid-base properties of salts. The salts we will give you will be salts containing the conjugates discussed above. Your job is to recognize the type of conjugate present, and then use that information to solve an equilibrium problem (if necessary).

- A salt is an ionic compound composed of a cation and an anion.

**Weak base anions:** These are the conjugate bases of the weak acids having the  $\text{HA}$  general formula. Table 13.2 of the text lists several  $\text{HA}$  type acids. Some weak base anions derived from the acids in Table 13.2 are  $\text{ClO}_2^-$ ,  $\text{F}^-$ ,  $\text{NO}_2^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ ,  $\text{OCl}^-$ , and  $\text{CN}^-$ .

**Garbage anions** (those anions with no basic or acidic properties): These are the conjugate bases of the strong acids having the  $\text{HA}$  general formula. These are  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{ClO}_4^-$ .

**Weak acid cations:** These are the conjugate acids of the weak bases which contain nitrogen. Table 13.3 of the text lists several nitrogen-containing bases. Some weak acid cations derived from the weak bases in Table 13.3 are  $\text{NH}_4^+$ ,  $\text{CH}_3\text{NH}_3^+$ ,  $\text{C}_2\text{H}_5\text{NH}_3^+$ ,  $\text{C}_6\text{H}_5\text{NH}_3^+$ , and  $\text{C}_5\text{H}_5\text{NH}^+$ .

Garbage cations (those cations with no acidic properties or basic properties): The most common ones used are the cations in the strong bases. These are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ .

We mix and match the cations and anions to get what type of salt we want. For a weak base salt, we combine a weak base anion with a garbage cation. Some weak base salts are  $\text{NaF}$ ,  $\text{KNO}_2$ ,  $\text{Ca}(\text{CN})_2$ , and  $\text{RbC}_2\text{H}_3\text{O}_2$ . To determine the pH of a weak base salt, we write out the  $K_b$  reaction for the weak base anion and determine  $K_b (= K_w/K_a)$ . We set up the ICE table under the  $K_b$  reaction, and then solve the equilibrium problem to calculate  $[\text{OH}^-]$  and, in turn, pH.

For a weak acid salt, we combine a weak acid cation with a garbage anion. Some weak acid salts are  $\text{NH}_4\text{Cl}$ ,  $\text{C}_5\text{H}_5\text{NHNO}_3$ ,  $\text{CH}_3\text{NH}_3\text{I}$ , and  $\text{C}_2\text{H}_5\text{NH}_3\text{ClO}_4$ . To determine the pH, we write out the  $K_a$  reaction for the weak acid cation and determine  $K_a (= K_w/K_b)$ . We set up the ICE table under the  $K_a$  reaction, and then solve the equilibrium problem to calculate  $[\text{H}^+]$  and, in turn, pH.

For a neutral (pH = 7.0) salt, we combine a garbage cation with a garbage anion. Some examples are  $\text{NaCl}$ ,  $\text{KNO}_3$ ,  $\text{BaBr}_2$ , and  $\text{Sr}(\text{ClO}_4)_2$ .

For salts that contain a weak acid cation and a weak base anion, we compare the  $K_a$  value of the weak acid cation to the  $K_b$  value for the weak base anion. When  $K_a > K_b$ , the salt produces an acidic solution (pH < 7.0). When  $K_b > K_a$ , the salt produces a basic solution. And when  $K_a = K_b$ , the salt produces a neutral solution (pH = 7.0).

## Text Homework

20. Acidic solutions (at  $25^\circ\text{C}$ ) have an  $[\text{H}^+] > 1.0 \times 10^{-7} \text{ M}$ , which gives a 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 pH > 7.0 (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 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 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 pH < 7.0 (pH =  $14.00 - 11.21 = 2.79$ ) and is therefore not basic (solution is acidic).
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.
27. a. These are solutions of strong acids like  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ . So 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 13-3. 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  $\text{C}_2\text{H}_5\text{NH}_3\text{Br}$  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 (except for  $\text{HSO}_4^-$ , which has weak acid properties).

- c. These are solutions of strong bases like  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{RbOH}$ ,  $\text{CsOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Sr}(\text{OH})_2$ , and  $\text{Ba}(\text{OH})_2$ . All these strong bases are strong electrolytes.
  - d. These are solutions containing salts of the conjugate bases of the neutrally charged weak acids in Table 13-2. 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  $\text{NaClO}_2$ ,  $\text{KC}_2\text{H}_3\text{O}_2$ , 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 solution. 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  $\text{SrI}_2$ . Another type of strong electrolyte that can produce neutral solutions are salts that contain an ion with weak acid properties combined with an ion of opposite charge having weak base properties. If the  $K_a$  for the weak acid ion is equal to the  $K_b$  for the weak base ion, then the salt will produce a neutral solution. The most common example of this type of salt is ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ). 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.
29. a.  $\text{H}_2\text{O}(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$  or
- $$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K = K_w = [\text{H}^+][\text{OH}^-]$$
- b.  $\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{F}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$  or
- $$\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq}) \quad K = K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$
- c.  $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K = K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}$
30. Only statement a is true (assuming the species is not amphoteric). You cannot add a base to water and get an acidic pH ( $\text{pH} < 7.0$ ). 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  $\text{Ba}(\text{OH})_2$  solution will have an  $[\text{OH}^-]$  twice of the same concentration of  $\text{KOH}$ , but this does not correspond to a  $\text{pOH}$  value twice that of the same concentration of  $\text{KOH}$  (prove it to yourselves).
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  $0.10 \text{ M}$   $\text{H}_2\text{CO}_3$  will dissociate into  $\text{HCO}_3^-$  and  $\text{H}^+$ . So statement a best describes the  $0.10 \text{ M}$   $\text{H}_2\text{CO}_3$  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  $0.10 \text{ M}$   $\text{H}_2\text{SO}_4$  solution will dissociate into  $0.10 \text{ M}$   $\text{H}^+$  and  $0.10 \text{ M}$   $\text{HSO}_4^-$ . 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.

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  $\text{Ca(OH)}_2$ , 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  $\text{Ca(OH)}_2$ . Note that, in general, metal oxides react with water to produce basic solutions.
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:
- $$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NH}_3(\text{aq}) \quad \text{or} \quad \text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$$
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 ( $\text{H}^+$ ).

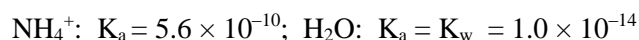
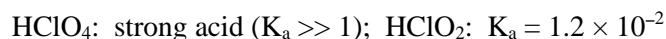
	Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a.	$\text{H}_2\text{CO}_3$	$\text{H}_2\text{O}$	$\text{HCO}_3^-$	$\text{H}_3\text{O}^+$
b.	$\text{C}_5\text{H}_5\text{NH}^+$	$\text{H}_2\text{O}$	$\text{C}_5\text{H}_5\text{N}$	$\text{H}_3\text{O}^+$
c.	$\text{C}_5\text{H}_5\text{NH}^+$	$\text{HCO}_3^-$	$\text{C}_5\text{H}_5\text{N}$	$\text{H}_2\text{CO}_3$

39. Strong acids have a  $K_a \gg 1$ , and weak acids have  $K_a < 1$ . Table 13-2 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 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 HB dissociates into ions, so the acid exists mostly as undissociated 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  $\text{HClO}_4 > \text{HClO}_2 > \text{NH}_4^+ > \text{H}_2\text{O}$ .

43. a.  $\text{HCl}$  is a strong acid, and water is a very weak acid with  $K_a = K_w = 1.0 \times 10^{-14}$ .  $\text{HCl}$  is a much stronger acid than  $\text{H}_2\text{O}$ .
- b.  $\text{H}_2\text{O}$ ,  $K_a = K_w = 1.0 \times 10^{-14}$ ;  $\text{HNO}_2$ ,  $K_a = 4.0 \times 10^{-4}$ ;  $\text{HNO}_2$  is a stronger acid than  $\text{H}_2\text{O}$  because  $K_a$  for  $\text{HNO}_2 > K_w$  for  $\text{H}_2\text{O}$ .
- c.  $\text{HOC}_6\text{H}_5$ ,  $K_a = 1.6 \times 10^{-10}$ ;  $\text{HCN}$ ,  $K_a = 6.2 \times 10^{-10}$ ;  $\text{HCN}$  is a slightly stronger acid than  $\text{HOC}_6\text{H}_5$  because  $K_a$  for  $\text{HCN} > K_a$  for  $\text{HOC}_6\text{H}_5$ .
45. At  $25^\circ\text{C}$ , the relationship  $[\text{H}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$  always holds for aqueous solutions. When  $[\text{H}^+]$  is greater than  $1.0 \times 10^{-7} \text{ M}$ , the solution is acidic; when  $[\text{H}^+]$  is less than  $1.0 \times 10^{-7} \text{ M}$ , the solution is basic; when  $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$ , the solution is neutral. In terms of  $[\text{OH}^-]$ , an acidic solution has  $[\text{OH}^-] < 1.0 \times 10^{-7} \text{ M}$ , a basic solution has  $[\text{OH}^-] > 1.0 \times 10^{-7} \text{ M}$ , and a neutral solution has  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ .

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

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

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

- d.  $[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{5.4 \times 10^{-5}} = 1.9 \times 10^{-10} M$ ; the solution is acidic.
46. a.  $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.5} = 6.7 \times 10^{-15} M$ ; basic
- b.  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{3.6 \times 10^{-15}} = 2.8 M$ ; acidic
- c.  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} M$ ; neutral
- d.  $[\text{H}^+] = \frac{1.0 \times 10^{-14}}{7.3 \times 10^{-4}} = 1.4 \times 10^{-11} M$ ; basic
53.  $\text{pOH} = 14.0 - \text{pH} = 14.0 - 2.1 = 11.9$ ;  $[\text{H}^+] = 10^{-\text{pH}} = 10^{-2.1} = 8 \times 10^{-3} M$  (1 sig. fig.)
- $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{8 \times 10^{-3}} = 1 \times 10^{-12} M$  or  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.9} = 1 \times 10^{-12} M$
- The sample of gastric juice is acidic because the pH is less than 7.00 at 25°C.
54.  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.74 = 8.26$ ;  $[\text{H}^+] = 10^{-\text{pH}} = 10^{-8.26} = 5.5 \times 10^{-9} M$
- $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{5.5 \times 10^{-9}} = 1.8 \times 10^{-6} M$  or  $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.74} = 1.8 \times 10^{-6} M$
- The solution of baking soda is basic because the pH is greater than 7.00 at 25°C.
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 M solutions of these strong acids, 0.250 M  $\text{H}^+$  and 0.250 M  $\text{A}^-$  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  $\text{H}_2\text{O}$ ;  $\text{pH} = 0.602$
- $[\text{H}^+] = \frac{(2.5 \times 10^{-3} + 1.5 \times 10^{-2}) \text{ mol}}{0.2000 \text{ L}} = 0.088 M$ ;  $\text{pH} = -\log(0.088) = 1.06$
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.  $5.0 \text{ M H}^+$  is produced when  $5.0 \text{ M HClO}_4$  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.  $1.0 \times 10^{-11} \text{ M H}^+$  is produced when  $1.0 \times 10^{-11} \text{ M HI}$  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  $1.0 \times 10^{-7} \text{ M H}^+$ . 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.

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

64. a.  $\text{HOC}_6\text{H}_5$  ( $K_a = 1.6 \times 10^{-10}$ ) 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  $\text{HOC}_6\text{H}_5$ . Solving the weak acid problem:

	$\text{HOC}_6\text{H}_5$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{OC}_6\text{H}_5^-$
Initial	$0.250 \text{ M}$		$\sim 0$		$0$
	$x \text{ mol/L HOC}_6\text{H}_5$ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.250 - x$		$x$		$x$

$$K_a = 1.6 \times 10^{-10} = \frac{[\text{H}^+][\text{OC}_6\text{H}_5^-]}{[\text{HOC}_6\text{H}_5]} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad (\text{assuming } x \ll 0.250)$$

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

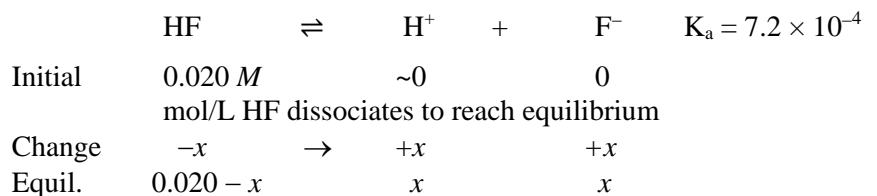
	$\text{HCN}$	$\rightleftharpoons$	$\text{H}^+$	+	$\text{CN}^-$
Initial	$0.250 \text{ M}$		$\sim 0$		$0$
	$x \text{ mol/L HCN}$ dissociates to reach equilibrium				
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.250 - x$		$x$		$x$

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

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

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:



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

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

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

The assumption  $x \ll 0.020$  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 [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 [HF], that is,  $0.020 - x = 0.020 - 0.0034 = 0.0166$  (carrying an extra sig. fig.).

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

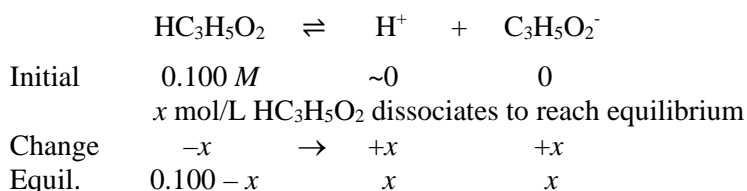
We repeat until we get a self-consistent answer. This would be the same answer we would get solving exactly using the quadratic equation. In this case it is,  $x = 3.5 \times 10^{-3}$ . Thus:

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

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

*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).

67.  $\text{HC}_3\text{H}_5\text{O}_2$  ( $K_a = 1.3 \times 10^{-5}$ ) and  $\text{H}_2\text{O}$  ( $K_a = K_w = 1.0 \times 10^{-14}$ ) are the major species present.  $\text{HC}_3\text{H}_5\text{O}_2$  will be the dominant producer of  $\text{H}^+$  because  $\text{HC}_3\text{H}_5\text{O}_2$  is a stronger acid than  $\text{H}_2\text{O}$ . Solving the weak acid problem:



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

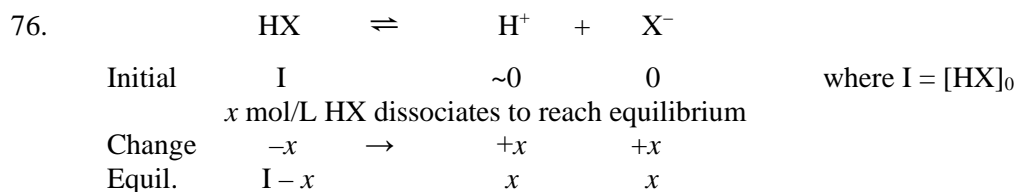
$$x = [H^+] = 1.1 \times 10^{-3} M; \text{ pH} = -\log(1.1 \times 10^{-3}) = 2.96$$

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

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

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

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

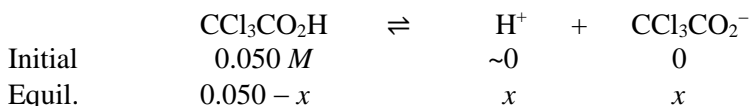


From the problem,  $x = 0.25(I)$  and  $I - x = 0.30 M$ .

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

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

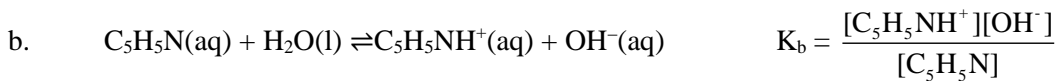
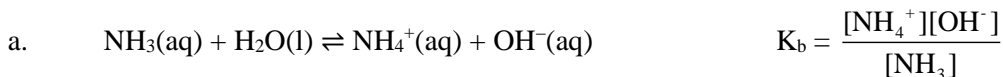
77. HClO<sub>4</sub> is a strong acid with  $[H^+] = 0.040 M$ . This equals the  $[H^+]$  in the trichloroacetic acid. Set up the problem using the  $K_a$  equilibrium reaction for CCl<sub>3</sub>CO<sub>2</sub>H.



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

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

83. All  $K_b$  reactions refer to the base reacting with water to produce the conjugate acid of the base and OH<sup>-</sup>.



87. a.  $\text{C}_6\text{H}_5\text{NH}_2$       b.  $\text{C}_6\text{H}_5\text{NH}_2$       c.  $\text{OH}^-$       d.  $\text{CH}_3\text{NH}_2$

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.

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

a.  $[\text{OH}^-] = 0.10 \text{ M}$ ;  $\text{pOH} = -\log[\text{OH}^-] = -\log(0.10) = 1.00$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.00 = 13.00$$

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 NaOH.

- b. The  $[\text{OH}^-]$  concentration donated by the 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  $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ .

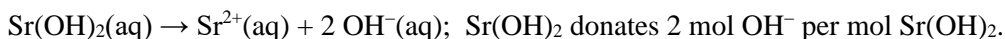
$$\text{pOH} = -\log(1.0 \times 10^{-7}) = 7.00; \text{pH} = 14.00 - 7.00 = 7.00$$

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

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

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

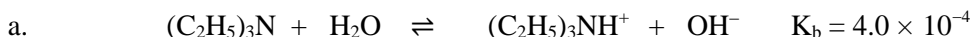
94.  $\text{pH} = 10.50$ ;  $\text{pOH} = 14.00 - 10.50 = 3.50$ ;  $[\text{OH}^-] = 10^{-3.50} = 3.2 \times 10^{-4} \text{ M}$



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

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

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



Initial       $0.20 \text{ M}$                               0               $\sim 0$   
 $x \text{ mol/L of } (\text{C}_2\text{H}_5)_3\text{N} \text{ reacts with } \text{H}_2\text{O} \text{ to reach equilibrium}$

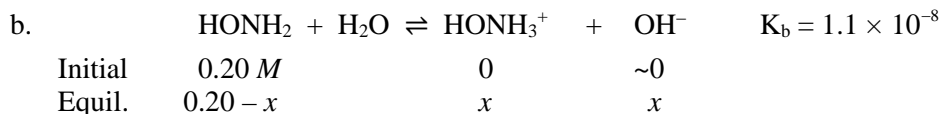
Change       $-x$                                $+x$                $+x$

Equil.       $0.20 - x$                                $x$                $x$

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

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

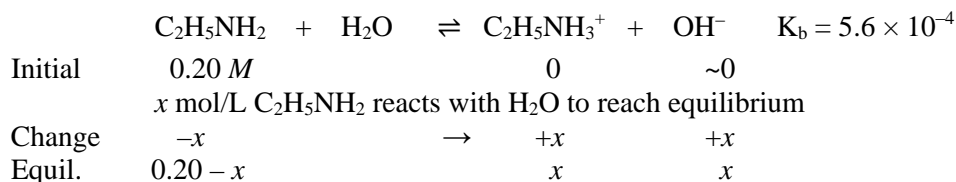
$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{8.9 \times 10^{-3}} = 1.1 \times 10^{-12} \text{ M}; \text{ pH} = 11.96$$



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

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

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



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

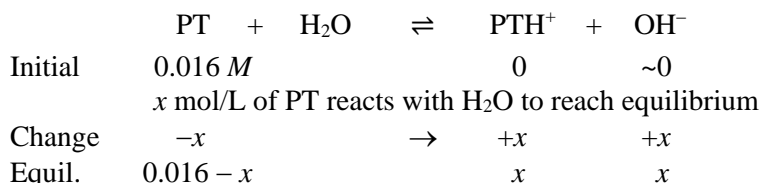
$$x = 1.1 \times 10^{-2}; \text{ checking assumption: } \frac{1.1 \times 10^{-2}}{0.20} \times 100 = 5.5\%$$

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:

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

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

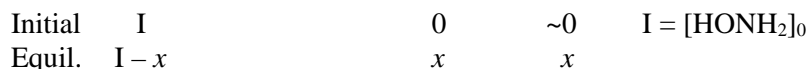
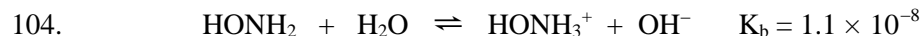
103. Using the  $K_b$  reaction to solve where PT = p-toluidine ( $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2$ ):



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

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

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

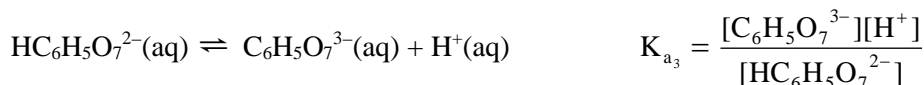
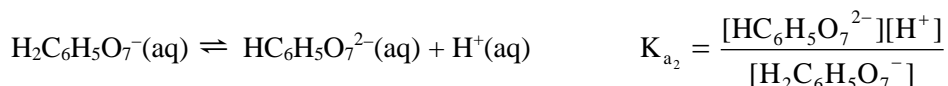
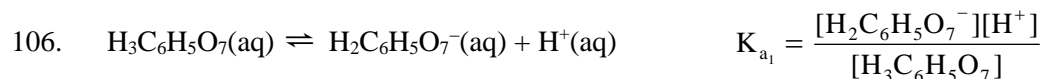


$$K_b = 1.1 \times 10^{-8} = \frac{x^2}{I - x}$$

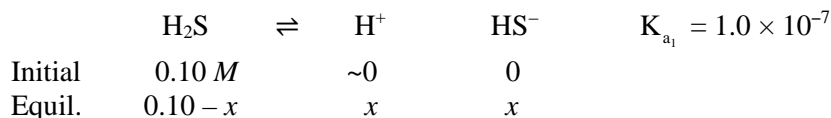
From problem, pH = 10.00, so pOH = 4.00 and  $x = [\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$ .

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

$$\text{Mass HONH}_2 = 0.2500 \text{ L} \times \frac{0.91 \text{ mol HONH}_2}{\text{L}} \times \frac{33.03 \text{ g HONH}_2}{\text{mol HONH}_2} = 7.5 \text{ g HONH}_2$$



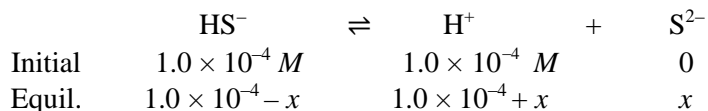
109. Because  $K_{a_2}$  for  $\text{H}_2\text{S}$  is so small, we can ignore the  $\text{H}^+$  contribution from the  $K_{a_2}$  reaction.



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

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

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



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

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

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.

- 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>
- 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>
- Weak acids have a K<sub>a</sub> value of less than 1 but greater than K<sub>w</sub>. Some weak acids are listed in Table 13.2 of the text. Weak bases have a K<sub>b</sub> value of less than 1 but greater than K<sub>w</sub>. Some weak bases are listed in Table 13.3 of the text.
- Conjugate bases of weak acids are weak bases; that is, all have a K<sub>b</sub> value of less than 1 but greater than K<sub>w</sub>. Some examples of these are the conjugate bases of the weak acids listed in Table 13.2 of the text.
- Conjugate acids of weak bases are weak acids; that is, all have a K<sub>a</sub> value of less than 1 but greater than K<sub>w</sub>. Some examples of these are the conjugate acids of the weak bases listed in Table 13.3 of the text.
- 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.
- 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<sub>b</sub> << K<sub>w</sub>), and only HSO<sub>4</sub><sup>-</sup> has any acidic properties in water.

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

KOH: Strong base (b)

KNO<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,  $K_b = K_w/K_{a,\text{HCN}} = 1.0 \times 10^{-14}/6.2 \times 10^{-10} = 1.6 \times 10^{-5}$  (c and d).

Ignore K<sup>+</sup> (f).

NH<sub>4</sub>Cl: NH<sub>4</sub><sup>+</sup> is a weak acid,  $K_a = 5.6 \times 10^{-10}$  (c and e). Ignore Cl<sup>-</sup> (g).

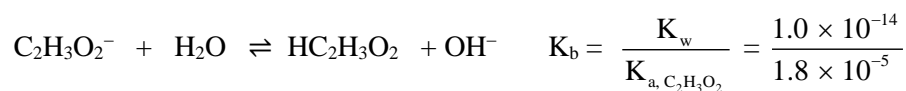
HCl: Strong acid (a)

The most acidic solution will be the strong acid solution, with the weak acid solution less acidic. The most basic solution will be the strong base solution, with the weak base solution less basic. The KNO<sub>3</sub> solution will be neutral at pH = 7.00.

Most acidic → most basic: HCl > NH<sub>4</sub>Cl > KNO<sub>3</sub> > KCN > KOH

- From the K<sub>a</sub> values, acetic acid is a stronger acid than hypochlorous acid. Conversely, the conjugate base of acetic acid, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>, will be a weaker base than the conjugate base of hypochlorous acid, OCl<sup>-</sup>. Thus the hypochlorite ion, OCl<sup>-</sup>, is a stronger base than the acetate ion, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>. 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.
- Because NH<sub>3</sub> is a weaker base (smaller K<sub>b</sub> value) than CH<sub>3</sub>NH<sub>2</sub>, the conjugate acid of NH<sub>3</sub> will be a stronger acid than the conjugate acid of CH<sub>3</sub>NH<sub>2</sub>. Thus NH<sub>4</sub><sup>+</sup> is a stronger acid than CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>.

117. a. KCl is a soluble ionic compound that dissolves in water to produce  $K^+(aq)$  and  $Cl^-(aq)$ .  $K^+$  (like the other alkali metal cations) has no acidic or basic properties.  $Cl^-$  is the conjugate base of the strong acid HCl.  $Cl^-$  has no basic (or acidic) properties. Therefore, a solution of KCl will be neutral because neither of the ions has any acidic or basic properties. The 1.0 M KCl solution has  $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$  and  $pH = pOH = 7.00$ .
- b.  $KC_2H_3O_2$  is also a soluble ionic compound that dissolves in water to produce  $K^+(aq)$  and  $C_2H_3O_2^-(aq)$ . The difference between the KCl solution and the  $KC_2H_3O_2$  solution is that  $C_2H_3O_2^-$  does have basic properties in water, unlike  $Cl^-$ .  $C_2H_3O_2^-$  is the conjugate base of the weak acid  $HC_2H_3O_2$ , and as is true for all conjugate bases of weak acids,  $C_2H_3O_2^-$  is a weak base in water. We must solve an equilibrium problem to determine the amount of  $OH^-$  this weak base produces in water.



$x$  mol/L of  $C_2H_3O_2^-$  reacts with  $H_2O$  to reach equilibrium

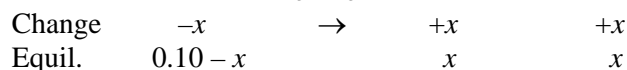
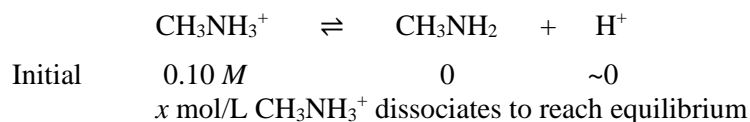
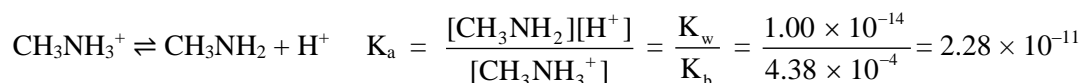


$$K_b = 5.6 \times 10^{-10} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}, \quad 5.6 \times 10^{-10} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

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

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

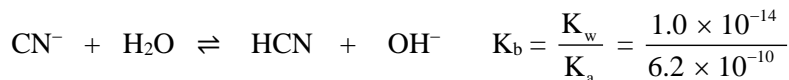
119. a.  $CH_3NH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$ :  $CH_3NH_3^+$  is a weak acid.  $Cl^-$  is the conjugate base of a strong acid.  $Cl^-$  has no basic (or acidic) properties.



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

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

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



Initial      0.050 *M*                      0              ~0               $K_b = 1.6 \times 10^{-5}$   
                  *x* mol/L  $\text{CN}^-$  reacts with  $\text{H}_2\text{O}$  to reach equilibrium

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

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

$x = [\text{OH}^-] = 8.9 \times 10^{-4} M$ ; pOH = 3.05; pH = 10.95; 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 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  $K_b$  value for the weak conjugate base. From the  $K_b$  value and data in Table 13.2 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*

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

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

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

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

From Table 13.2 of the text, this  $K_a$  value is closest to HF. Therefore, the unknown salt is NaF.

124.  $\text{BHCl} \rightarrow \text{BH}^+ + \text{Cl}^-$ ;  $\text{Cl}^-$  is the conjugate base of the strong acid 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*

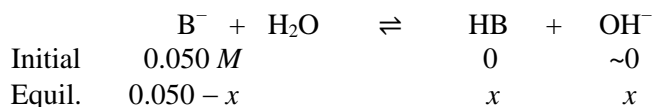
$$K_a = \frac{[B][H^+]}{[BH^+]} = \frac{x^2}{0.10 - x}; \text{ from the problem, pH} = 5.82:$$

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

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

From Table 13.3 of the text, this  $K_b$  value is closest to  $CH_3NH_2$ , so the unknown salt is  $CH_3NH_3Cl$ .

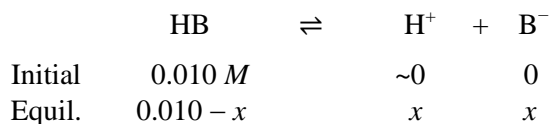
125.  $B^-$  is a weak base. Use the weak base data to determine  $K_b$  for  $B^-$ .



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

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

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



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

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

129. Reference Table 13.6 of the text and the solution to Exercise 113 for some generalizations on acid-base properties of salts.

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

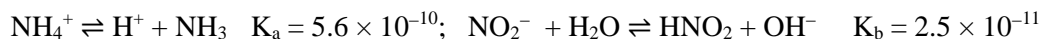
b.  $NaNO_2 \rightarrow Na^+ + NO_2^-$  basic;  $NO_2^-$  is a weak base, and  $Na^+$  has no effect on pH.

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

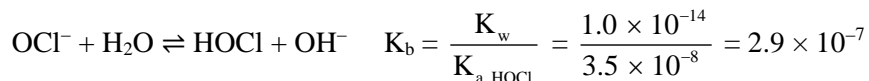
c.  $C_5H_5NHClO_4 \rightarrow C_5H_5NH^+ + ClO_4^-$  acidic;  $C_5H_5NH^+$  is a weak acid, and  $ClO_4^-$  has no effect on pH.

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

- d.  $\text{NH}_4\text{NO}_2 \rightarrow \text{NH}_4^+ + \text{NO}_2^-$  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.  $\text{KOC}\text{I} \rightarrow \text{K}^+ + \text{O}\text{C}\text{I}^-$  basic;  $\text{O}\text{C}\text{I}^-$  is a weak base, and  $\text{K}^+$  has no effect on pH.



- f.  $\text{NH}_4\text{O}\text{C}\text{I} \rightarrow \text{NH}_4^+ + \text{O}\text{C}\text{I}^-$  basic;  $\text{NH}_4^+$  is a weak acid, and  $\text{O}\text{C}\text{I}^-$  is a weak base. Because  $K_{b, \text{O}\text{C}\text{I}^-} > K_{a, \text{NH}_4^+}$ , the solution is basic.



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

- 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.
- 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.
- Acidic;  $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{HO}\text{C}\text{I}(\text{aq})$ ;  $\text{HO}\text{C}\text{I}$  is a weak acid.

136.
  - 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.
  - 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.
  - Basic;  $\text{SrO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Sr}(\text{OH})_2(\text{aq})$ ;  $\text{Sr}(\text{OH})_2$  is a strong base.

143. At pH = 2.000,  $[\text{H}^+] = 10^{-2.000} = 1.00 \times 10^{-2} \text{ M}$

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

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

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

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

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

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  $\text{SO}_4^{2-}$ .

155.
  - 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  $\text{HbH}_4^{4+}$ .
  - $\text{CO}_2$  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  $O_2$  is not released by hemoglobin in the cells. Breathing into a paper bag increases  $CO_2$  in the blood, thus increasing  $[H^+]$ , which shifts the hemoglobin reaction left.

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

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

- (1) There are only a few common strong acids and strong bases, all of which should be memorized. Common strong acids =  $HCl$ ,  $HBr$ ,  $HI$ ,  $HNO_3$ ,  $HClO_4$ , and  $H_2SO_4$ . Common strong bases =  $LiOH$ ,  $NaOH$ ,  $KOH$ ,  $RbOH$ ,  $CsOH$ ,  $Ca(OH)_2$ ,  $Sr(OH)_2$ , and  $Ba(OH)_2$ .
- (2) All other acids and bases are weak and will have  $K_a$  and  $K_b$  values of less than 1 but greater than  $K_w$  ( $1.0 \times 10^{-14}$ ). Reference Table 13.2 for  $K_a$  values for some weak acids and Table 13.3 for  $K_b$  values for some weak bases. There are too many weak acids and weak bases to memorize them all. Therefore, use the tables of  $K_a$  and  $K_b$  values to help you identify weak acids and weak bases. Appendix 5 contains more complete tables of  $K_a$  and  $K_b$  values.

- |  |   |
|--|---|
| a. weak acid ( $K_a = 4.0 \times 10^{-4}$ )  | b. strong acid                              |
| c. weak base ( $K_b = 4.38 \times 10^{-4}$ ) | d. strong base                              |
| e. weak base ( $K_b = 1.8 \times 10^{-5}$ )  | f. weak acid ( $K_a = 7.2 \times 10^{-4}$ ) |
| g. weak acid ( $K_a = 1.8 \times 10^{-4}$ )  | h. strong base                              |
| i. strong acid                               |   |

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

- a. Memorize the following strong acids:  $HCl$ ,  $HBr$ ,  $HI$ ,  $HNO_3$ ,  $HClO_4$ , and  $H_2SO_4$
- b. Memorize the following strong bases:  $LiOH$ ,  $NaOH$ ,  $KOH$ ,  $RbOH$ ,  $CsOH$ ,  $Ca(OH)_2$ ,  $Sr(OH)_2$ , and  $Ba(OH)_2$
- c. Weak acids have a  $K_a$  value of less than 1 but greater than  $K_w$ . Some weak acids are listed in Table 13.2 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 13.3 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 13.2 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 13.3 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:  $F^-$  is the conjugate base of the weak acid HF, so  $F^-$  is a weak base. The  $K_b$  value for  $F^- = K_w/K_{a, HF} = 1.4 \times 10^{-11}$ .  $Na^+$  has no acidic or basic properties.  
 NaI: Neutral ( $pH = 7.0$ );  $Na^+$  and  $I^-$  have no acidic/basic properties.

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

- b.  $\text{NH}_4\text{Br}$ :  $\text{NH}_4^+$  is a weak acid ( $K_a = 5.6 \times 10^{-10}$ ), and  $\text{Br}^-$  is a neutral species.  
 $\text{HBr}$ : Strong acid  
 $\text{KBr}$ : Neutral;  $\text{K}^+$  and  $\text{Br}^-$  have no acidic/basic properties.  
 $\text{NH}_3$ : Weak base,  $K_b = 1.8 \times 10^{-5}$

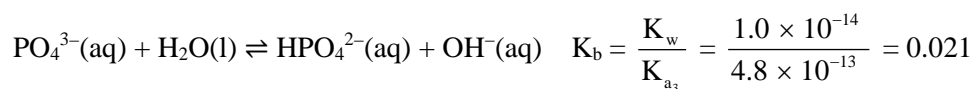
Increasing pH: HBr < NH<sub>4</sub>Br < KBr < NH<sub>3</sub>  
Most acidic Most basic

- c.  $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_3$ :  $\text{C}_6\text{H}_5\text{NH}_3^+$  is a weak acid ( $K_a = K_w / K_{b, \text{C}_6\text{H}_5\text{NH}_2} = 1.0 \times 10^{-14} / 3.8 \times 10^{-10} = 2.6 \times 10^{-5}$ ), and  $\text{NO}_3^-$  is a neutral species.
- $\text{NaNO}_3$ : Neutral;  $\text{Na}^+$  and  $\text{NO}_3^-$  have no acidic/basic properties.
- $\text{NaOH}$ : Strong base
- $\text{HOC}_6\text{H}_5$ : Weak acid ( $K_a = 1.6 \times 10^{-10}$ )
- $\text{KOC}_6\text{H}_5$ :  $\text{OC}_6\text{H}_5^-$  is a weak base ( $K_b = K_w / K_{a, \text{HOC}_6\text{H}_5} = 6.3 \times 10^{-5}$ ), and  $\text{K}^+$  is a neutral species.
- $\text{C}_6\text{H}_5\text{NH}_2$ : Weak base ( $K_b = 3.8 \times 10^{-10}$ )
- $\text{HNO}_3$ : Strong acid

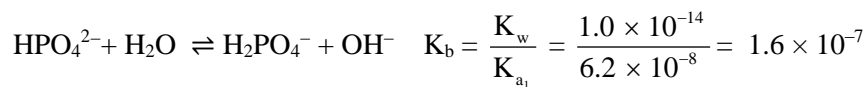
This is a little more difficult than the previous parts of this problem because two weak acids and two weak bases are present. Between the weak acids,  $\text{C}_6\text{H}_5\text{NH}_3^+$  is a stronger weak acid than  $\text{HOC}_6\text{H}_5$  since the  $K_a$  value for  $\text{C}_6\text{H}_5\text{NH}_3^+$  is larger than the  $K_a$  value for  $\text{HOC}_6\text{H}_5$ . Between the two weak bases, because the  $K_b$  value for  $\text{OC}_6\text{H}_5^-$  is larger than the  $K_b$  value for  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $\text{OC}_6\text{H}_5^-$  is a stronger weak base than  $\text{C}_6\text{H}_5\text{NH}_2$ .

Increasing pH:  $\text{HNO}_3 < \text{C}_6\text{H}_5\text{NH}_3\text{NO}_3 < \text{HOC}_6\text{H}_5 < \text{NaNO}_3 < \text{C}_6\text{H}_5\text{NH}_2 < \text{KOC}_6\text{H}_5 < \text{NaOH}$   
 Most acidic Most basic

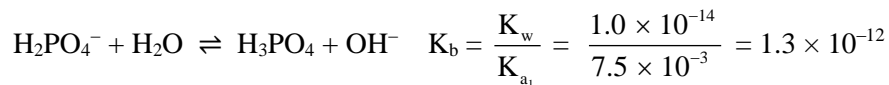
183.  $\text{PO}_4^{3-}$  is the conjugate base of  $\text{HPO}_4^{2-}$ . The  $K_a$  value for  $\text{HPO}_4^{2-}$  is  $K_{a_3} = 4.8 \times 10^{-13}$ .



$\text{HPO}_4^{2-}$  is the conjugate base of  $\text{H}_2\text{PO}_4^-$  ( $K_{a_2} = 6.2 \times 10^{-8}$ ).



$\text{H}_2\text{PO}_4^-$  is the conjugate base of  $\text{H}_3\text{PO}_4$  ( $K_{a_1} = 7.5 \times 10^{-3}$ ).



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 ( $\text{HPO}_4^{2-}$ ).