CHAPTER 7

ACIDS AND BASES

Nature of Acids and Bases

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

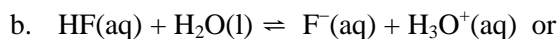$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \quad K = K_w = [H^+][OH^-]$

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

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

c. $C_5H_5N(aq) + H_2O(l) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq) \quad K = K_b = \dfrac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$
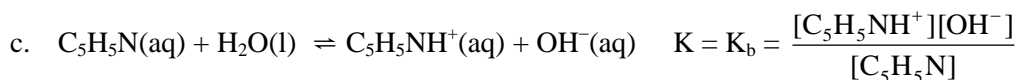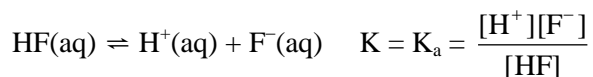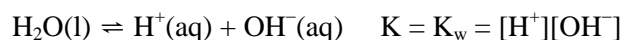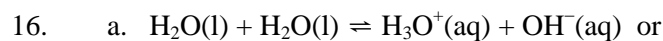
17.   An acid is a proton (H^+) donor, and a base is a proton acceptor. A conjugate acid-base pair differs by only a proton (H^+) in the formulas.

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

18. $\underset{\text{Acid}}{NH_3} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\substack{\text{Conjugate} \\ \text{Base}}}{NH_2^-} + \underset{\substack{\text{Conjugate} \\ \text{Acid}}}{NH_4^+}$
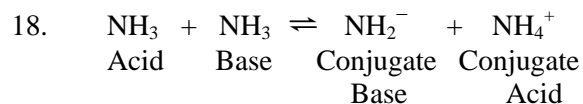
One of the NH_3 molecules acts as a base and accepts a proton to form NH_4^+. The other NH_3 molecule acts as an acid and donates a proton to form NH_2^-. NH_4^+ is the conjugate acid of the NH_3 base. In the reverse reaction, NH_4^+ donates a proton. NH_2^- is the conjugate base of the NH_3 acid. In the reverse reaction, NH_2^- accepts a proton. Conjugate acid-base pairs only differ by a H^+ in the formula.

19.   a.   The first equation is for the reaction of some generic acid, HA, with H_2O.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
Acid   Base   Conjugate   Conjugate
                         Acid of H_2O Base of HA
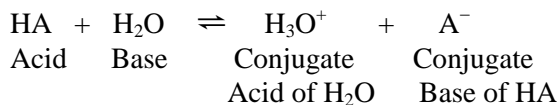
HA is the proton donor (the acid) and H_2O is the proton acceptor (the base). In the reverse reaction, H_3O^+ is the proton donor (the acid) and A^- is the proton acceptor (the base).

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

$$B + HX \rightleftharpoons BH^+ + X^-$$
Base   Acid   Conjugate   Conjugate
                         Acid of B   Base of HX
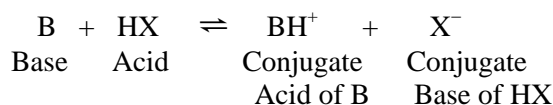
B is the proton acceptor (the base) and HX is the proton donor (the acid). When B accepts a proton, the central atom goes from having 3 bonded hydrogens to 4 bonded hydrogens. In the reverse reaction, BH^+ is the proton donor (the acid) and X^- is the proton acceptor (the base).
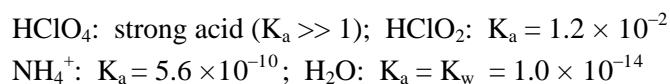
b.   Arrhenius acids produce H^+ in solution. So HA in the first equation is an Arrhenius acid. However, in the second equation, H^+ is not a product, so HX is not an Arrhenius acid. Both HA in the first equation and HX in the second equation are proton donors, so both are considered Brønsted-Lowry acids.

For the bases in the two equations, H_2O and B, neither of them produce OH^- in their equations, so neither of them are Arrhenius bases. Both H_2O and B accept protons, so both are Brønsted-Lowry bases.

20.   Strong acids have a $K_a \gg 1$ and weak acids have $K_a < 1$. Table 7.2 in the text lists some K_a values for weak acids. K_a values for strong acids are hard to determine so they are not listed in the text. However, there are only a few common strong acids so if you memorize the strong acids, then all other acids will be weak acids. The strong acids to memorize are HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4.
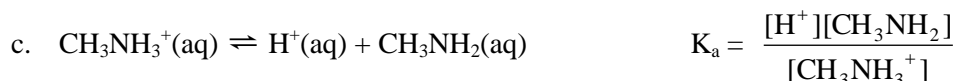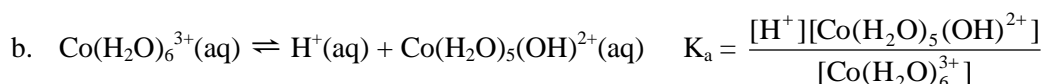
a. $HClO_4$ is a strong acid.
b.   HOCl is a weak acid ($K_a = 3.5 \times 10^{-8}$).
c. H_2SO_4 is a strong acid.
d. H_2SO_3 is a weak diprotic acid because the K_{a1} and K_{a2} values are less than 1.

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

$HClO_4$: strong acid ($K_a \gg 1$); $HClO_2$: $K_a = 1.2 \times 10^{-2}$
NH_4^+: $K_a = 5.6 \times 10^{-10}$; H_2O: $K_a = K_w = 1.0 \times 10^{-14}$

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

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

23.   The dissociation reaction (the K_a reaction) of an acid in water commonly omits water as a reactant.   We will follow this practice.   All dissociation reactions produce H^+ and the conjugate base of the acid that is dissociated.
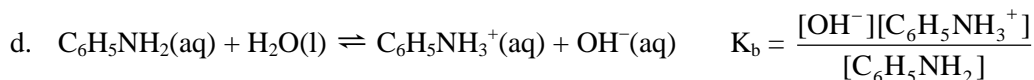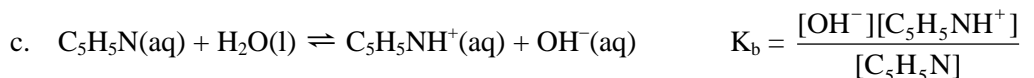
a. $HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$ $K_a = \dfrac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$

b. $Co(H_2O)_6^{3+}(aq) \rightleftharpoons H^+(aq) + Co(H_2O)_5(OH)^{2+}(aq)$ $K_a = \dfrac{[H^+][Co(H_2O)_5(OH)^{2+}]}{[Co(H_2O)_6^{3+}]}$

c. $CH_3NH_3^+(aq) \rightleftharpoons H^+(aq) + CH_3NH_2(aq)$ $K_a = \dfrac{[H^+][CH_3NH_2]}{[CH_3NH_3^+]}$
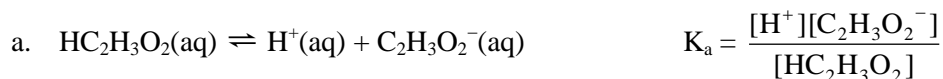
24.   a. $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$. Only the forward reaction is indicated because $HClO_4$ is a strong acid and is basically 100% dissociated in water. For acids, the dissociation reaction is commonly written without water as a reactant. The common abbreviation for this reaction is $HClO_4(aq) \rightarrow H^+(aq) + ClO_4^-(aq)$. This reaction is also called the K_a reaction because the equilibrium constant for this reaction is designated as K_a.

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

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

$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$ or $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$
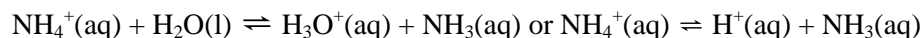
25.   a.   HCl is a strong acid, and water is a very weak acid with $K_a = K_w = 1.0 \times 10^{-14}$. HCl is a much stronger acid than H_2O.

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

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

26.   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 HOC_6H_5 (K_a for HCN > K_a for HOC_6H_5), $OC_6H_5^-$ will be a stronger base than CN^-.

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

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

2. All other acids and bases are weak and will have K_a and K_b values of less than 1 but greater than K_w (10^{-14}). Reference Table 7.2 for K_a values for some weak acids and Table 7.3 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

28. The NH_4^+ ion is a weak acid because it lies between H_2O and H_3O^+ (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 H_3O^+ (H^+). Weak acids only partially dissociate in water and have K_a values of between 10^{-14} and 1.

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

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

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

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

b. $CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$ $K_b = \dfrac{[OH^-][HCN]}{[CN^-]}$

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

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

31.   a. H_2O and $CH_3CO_2^-$

b.   An acid-base reaction can be thought of as a competition between two opposing bases. Because this equilibrium lies far to the left ($K_a < 1$), $CH_3CO_2^-$ is a stronger base than H_2O.

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:

$$CH_3CO_2^- + H_2O \rightleftharpoons CH_3CO_2H + OH^-$$
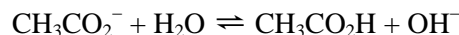
Now the competition is between $CH_3CO_2^-$ and OH^- for the proton. Hydroxide ion is the strongest base possible in water. The preceding equilibrium lies far to the left resulting in a K_b value of less than 1. Those species we specifically call weak bases ($10^{-14} < K_b < 1$) lie between H_2O and OH^- in base strength. Weak bases are stronger bases than water but are weaker bases than OH^-.

Autoionization of Water and pH Scale

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

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

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

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

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

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

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

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

33.   At 25°C, the relationship $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ always holds for aqueous solutions. When $[H^+]$ is greater than 1.0×10^{-7} M, the solution is acidic; when $[H^+]$ is less than 1.0×10^{-7} M, the solution is basic; when $[H^+] = 1.0 \times 10^{-7}$ M, the solution is neutral. In terms of $[OH^-]$, an acidic solution has $[OH^-] < 1.0 \times 10^{-7}$ M, a basic solution has $[OH^-] > 1.0 \times 10^{-7}$ M, and a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$ M. At 25°C, pH + pOH = 14.00.

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

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

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

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

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

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

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

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

       Note that pH is greater than 14.00 when $[OH^-]$ is greater than 1.0 M (an extremely basic solution). Also note the the pH is negative when $[H^+]$ is greater than 1.0 M (an extremely acidic solution).

34.   At 25°C: $K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$ and pH + pOH = 14.00; neutral solution:

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

       Acidic solution at 25°C:

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

       Basic solution at 25°C:

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

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

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

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

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

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

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

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

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

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

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

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

            $pH = -\log[H^+] = -\log(2.34 \times 10^{-7}) = 6.631$

            A neutral solution of water at 50.°C has:

                $[H^+] = [OH^-]$; $[H^+] = 2.34 \times 10^{-7}\ M$; $pH = 6.631$

            Obviously, the condition that $[H^+] = [OH^-]$ is the most general definition of a neutral
            solution.

       c. | Temp (°C) | Temp (K) | 1/T (K^{-1}) | K_w | ln K_w |
            |---|---|---|---|---|
            | 0 | 273 | 3.66×10^{-3} | 1.14×10^{-15} | -34.408 |
            | 25 | 298 | 3.36×10^{-3} | 1.00×10^{-14} | -32.236 |
            | 35 | 308 | 3.25×10^{-3} | 2.09×10^{-14} | -31.499 |
            | 40. | 313 | 3.19×10^{-3} | 2.92×10^{-14} | -31.165 |
            | 50. | 323 | 3.10×10^{-3} | 5.47×10^{-14} | -30.537 |

From the graph: $37°C = 310.$ K; $1/T = 3.23 \times 10^{-3}$ K^{-1}

$$\ln K_w = -31.38,\ K_w = e^{-31.38} = 2.35 \times 10^{-14}$$
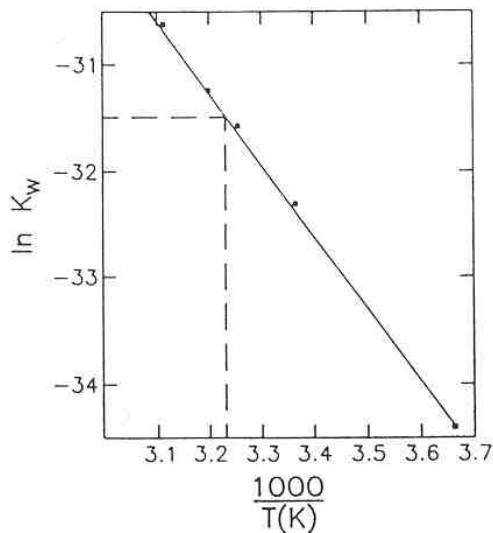
d.   At 37°C, $K_w = 2.35 \times 10^{-14} = [H^+][OH^-] = [H^+]^2$, $[H^+] = 1.53 \times 10^{-7}$ M

$$pH = -\log[H^+] = -\log(1.53 \times 10^{-7}) = 6.815$$

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

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

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

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

     $pOH = 14.00 - 8.59 = 5.41$; basic

c. $pH = -\log(0.027) = 1.57$; $pOH = 14.00 - 1.57 = 12.43$

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

d. $pH = 14.0 - 12.2 = 1.8$; $[H^+] = 10^{-1.8} = 1.6 \times 10^{-2} \, M$

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

Solutions of Acids

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

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

4.2 mL of 12 M HCl with enough water added to make 1600 mL of solution will result in a solution having $[H^+] = 3.2 \times 10^{-2} \, M$ and pH = 1.50.

40. $[H^+] = 10^{-5.10} = 7.9 \times 10^{-6} \, M$; $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

Because HNO_3 is a strong acid, we have a $7.9 \times 10^{-6} \, M \, HNO_3$ solution.

$$0.2500 \, \text{L} \times \frac{7.9 \times 10^{-6} \, \text{mol} \, HNO_3}{\text{L}} \times \frac{63.02 \, \text{g} \, HNO_3}{\text{mol} \, HNO_3} = 1.2 \times 10^{-4} \, \text{g} \, HNO_3$$

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

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

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

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

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

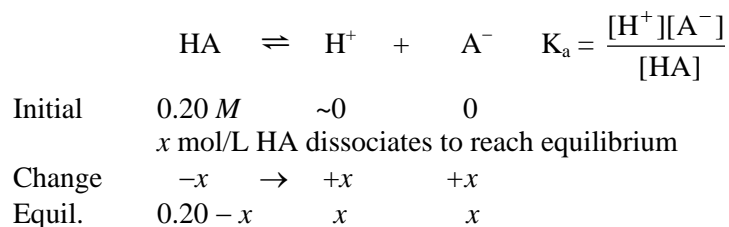42.   Both are strong acids, which are assumed to completely dissociate in water.

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

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

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

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

   b.   This picture is the result of 1 out of 10 HA molecules dissociating.
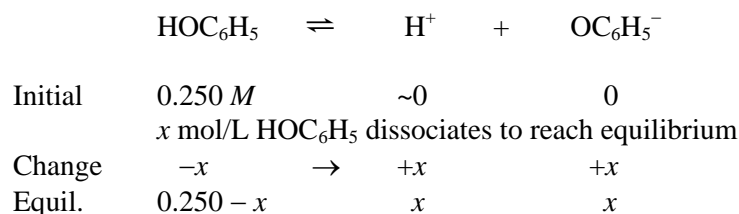
   Percent dissociation $= \dfrac{1}{10} \times 100 = 10\%$ (an exact number)

	HA	$\rightleftharpoons$	H^+	$+$	A^-	$K_a = \dfrac{[H^+][A^-]}{[HA]}$
Initial	0.20 M		~0		0	

   x mol/L HA dissociates to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.20 - x$		x		x

   $[H^+] = [A^-] = x = 0.10 \times 0.20\ M = 0.020\ M;\quad [HA] = 0.20 - 0.020 = 0.18\ M$

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

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

	HOC_6H_5	$\rightleftharpoons$	H^+	$+$	$OC_6H_5^-$
Initial	0.250 M		~0		0

   x mol/L HOC_6H_5 dissociates to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.250 - x$		x		x

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

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

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

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

	HCN	$\rightleftharpoons$	H^+	$+$	CN^-
Initial	0.250 M		~0		0

   x mol/L HCN dissociates to reach equilibrium

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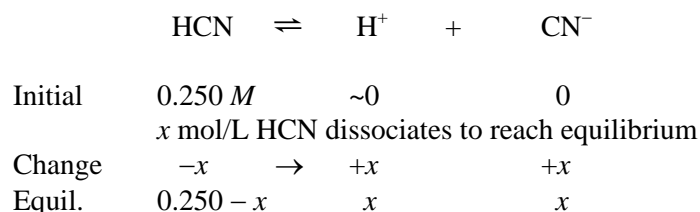
$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250} \quad \text{(assuming } x \ll 0.250\text{)}$$

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

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

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

$$HNO_2 \quad \rightleftharpoons \quad H^+ \quad + \quad NO_2^-$$

Initial	0.250 M	~0	0

x mol/L HNO_2 dissociates to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.250 - x$		x	x

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

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

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

All the assumptions are good. The H^+ contribution from water (1×10^{-7} M) is negligible, and x is small compared to 0.250 (percent error = 4.0%). If the percent error is less than 5% for an assumption, we will consider it a valid assumption (called the 5% rule). Finishing the problem: $x = 0.010 \ M = [H^+]$; $pH = -\log(0.010) = 2.00$

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

$$CH_3CO_2H \quad \rightleftharpoons \quad H^+ \quad + \quad CH_3CO_2^-$$

Initial	0.250 M	~0	0

x mol/L CH_3CO_2H dissociates to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.250 - x$		x	x

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

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

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

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

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

Initial   0.10 M ~0   0
              x mol/L $HC_2H_2ClO_2$ dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil. $0.10 - x$ x x

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

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

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

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

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

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

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

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

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.

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

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

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

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

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

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

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

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

Initial   0.22 M ~0   0
               x mol/L $HClO_2$ dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil. $0.22 - x$ x x

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

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

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

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

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

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

$$HC_9H_7O_4 \; \rightleftharpoons \; H^+ \; + \; C_9H_7O_4^-$$

Initial   0.0152 M ~0   0

                x mol/L $HC_9H_7O_4$ dissociates to reach equilibrium

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

Equil. $0.0152 - x$ x x

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

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

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

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

50. $HBz \; \rightleftharpoons \; H^+ \; + \; Bz^-$ $HBz = C_6H_5CO_2H$
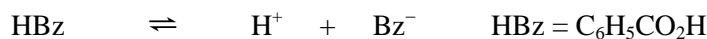
Initial   C   ~0   0   C = $[HBz]_0$ = concentration of HBz that
                                                                dissolves to give saturated solution.

                x mol/L HBz dissociates to reach equilibrium

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

Equil. $C - x$ x x

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

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

$$C - 1.6 \times 10^{-3} = \frac{(1.6 \times 10^{-3})^2}{6.4 \times 10^{-5}} = 4.0 \times 10^{-2}, \; C = (4.0 \times 10^{-2}) + (1.6 \times 10^{-3}) = 4.2 \times 10^{-2} \; M$$

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

$$\frac{4.2 \times 10^{-2} \, \text{mol} \, C_6H_5CO_2H}{L} \times \frac{122.1 \, \text{g} \, C_6H_5CO_2H}{\text{mol} \, C_6H_5CO_2H} \times 0.100 \, L = 0.51 \text{ g per 100. mL solution}$$

51.   Major species: HIO_3, H_2O; major source of H^+: HIO_3 (a weak acid, $K_a = 0.17$)

$$HIO_3 \quad \rightleftharpoons \quad H^+ \quad + \quad IO_3^-$$

Initial   0.010 M ~0   0

          x mol/L HIO_3 dissociates to reach equilibrium

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

Equil. $0.010 - x$ x x

$$K_a = 0.17 = \frac{[H^+][IO_3^-]}{[HIO_3]} = \frac{x^2}{0.010-x} \approx \frac{x^2}{0.010}, \quad x = 0.041; \quad \text{check assumption.}$$

Assumption is horrible (x is more than 400% of 0.010). When the assumption is this poor, it is generally quickest to solve exactly using the quadratic formula (see Appendix 1 in text). Using the quadratic formula and carrying extra significant figures:

$$0.17 = \frac{x^2}{0.010-x}, \quad x^2 = 0.17(0.010 - x), \quad x^2 + (0.17)x - 1.7 \times 10^{-3} = 0$$

$$x = \frac{-0.17 \pm [(0.17)^2 - 4(1)(-1.7 \times 10^{-3})]^{1/2}}{2(1)} = \frac{-0.17 \pm 0.189}{2}, \quad x = 9.5 \times 10^{-3} \, M$$

$$(x \text{ must be positive})$$

$$x = 9.5 \times 10^{-3} \, M = [H^+]; \quad pH = -\log(9.5 \times 10^{-3}) = 2.02$$

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

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

Initial   0.100 M ~0   0

          x mol/L $HC_3H_5O_2$ dissociates to reach equilibrium

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

Equil. $0.100 - x$ x x

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$CCl_3CO_2H \quad \rightleftharpoons \quad H^+ \quad + \quad CCl_3CO_2^-$$

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

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

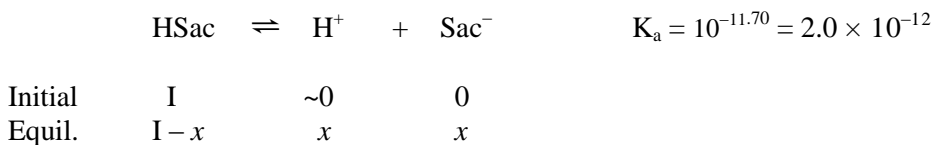$$K_a = \frac{(4.0 \times 10^{-2})^2}{0.050 - (4.0 \times 10^{-2})} = 0.16$$

55.   HX $\rightleftharpoons$ H^+ + X^-

Initial   I   ~0   0   where I = $[HX]_0$
                 x mol/L HX dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil.   I − x x x
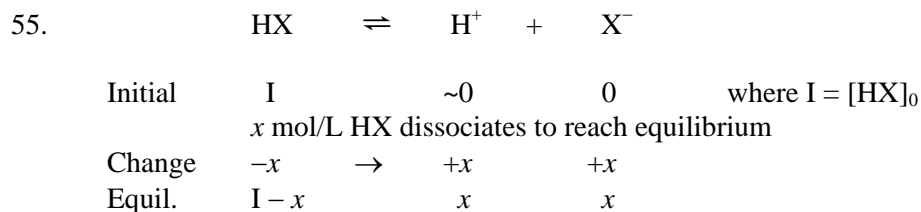
From the problem, $x = 0.25(I)$ and I − $x = 0.30$ M.

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

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

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

                        HSac $\rightleftharpoons$ H^+ + Sac^- $K_a = 10^{-11.70} = 2.0 \times 10^{-12}$

Initial   I   ~0   0
Equil.   I − x x x
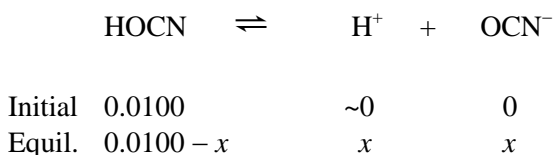
$$K_a = 2.0 \times 10^{-12} = \frac{x^2}{I-x}; \ x = [H^+] = 10^{-5.75} = 1.8 \times 10^{-6} \ M$$

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

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

57.   pH = 2.77, $[H^+] = 10^{-2.77} = 1.7 \times 10^{-3} \ M$

                  HOCN $\rightleftharpoons$ H^+ + OCN^-

Initial   0.0100   ~0   0
Equil.   0.0100 − x x x

$x = [H^+] = [OCN^-] = 1.7 \times 10^{-3} \ M$; [HOCN] = 0.0100 − x = 0.0100 − 0.0017 = 0.0083 M

$$K_a = \frac{[H^+][OCN^-]}{[HOCN]} = \frac{(1.7 \times 10^{-3})^2}{8.3 \times 10^{-3}} = 3.5 \times 10^{-4}$$

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

$$\text{HF} \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{F}^-$$

Initial   1.0 M ~0   0

x mol/L HF dissociates to reach equilibrium

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

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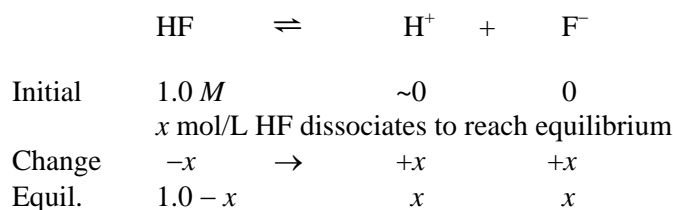
$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$x = [\text{H}^+] = 2.7 \times 10^{-2} \, M$; pH $= -\log(2.7 \times 10^{-2}) = 1.57$; assumptions good.
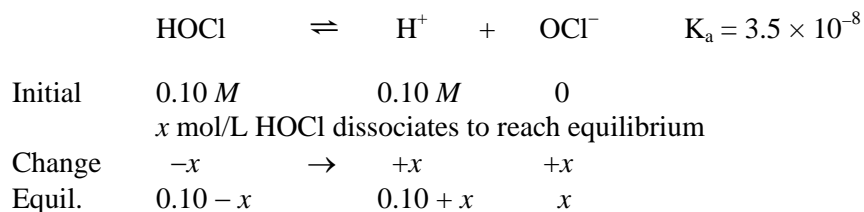
Solving for $[\text{OC}_6\text{H}_5^-]$ using $\text{HOC}_6\text{H}_5 \rightleftharpoons \text{H}^+ + \text{OC}_6\text{H}_5^-$ equilibrium:

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

$$[\text{OC}_6\text{H}_5^-] = 5.9 \times 10^{-9} \, M$$

Note that this answer indicates that only $5.9 \times 10^{-9} \, M$ HOC_6H_5 dissociates, which indicates that HF is truly the only significant producer of H^+ in this solution.
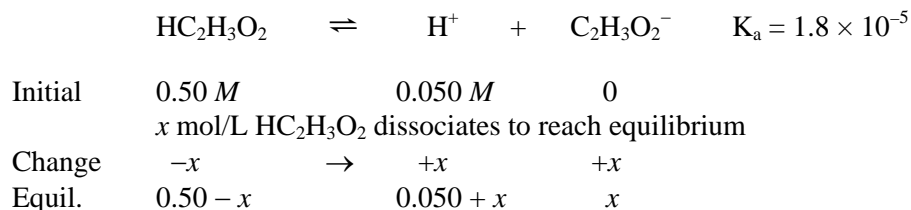
59.   a.   HCl is a strong acid. It will produce 0.10 M H^+. HOCl is a weak acid. Let's consider the equilibrium:

$$\text{HOCl} \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{OCl}^- \qquad K_a = 3.5 \times 10^{-8}$$

Initial   0.10 M 0.10 M 0

x mol/L HOCl dissociates to reach equilibrium

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

Equil. $0.10 - x$ $0.10 + x$ x

$$K_a = 3.5 \times 10^{-8} = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(0.10 + x)(x)}{0.10 - x} \approx x, \ x = 3.5 \times 10^{-8} \, M$$

Assumptions are great (x is 0.000035% of 0.10). We are really assuming that HCl is the only important source of H^+, which it is. The $[\text{H}^+]$ contribution from HOCl, x, is negligible. Therefore, $[\text{H}^+] = 0.10 \, M$; pH $= 1.00$.

b. HNO_3 is a strong acid, giving an initial concentration of H^+ equal to 0.050 M. Consider the equilibrium:
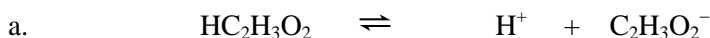
$$\text{HC}_2\text{H}_3\text{O}_2 \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{C}_2\text{H}_3\text{O}_2^- \qquad K_a = 1.8 \times 10^{-5}$$

Initial   0.50 M 0.050 M 0

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

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

Equil. $0.50 - x$ $0.050 + x$ x

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

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

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

60.   In all parts of this problem, acetic acid ($HC_2H_3O_2$) is the best weak acid present. We must solve a weak acid problem.

a. $HC_2H_3O_2$ $\rightleftharpoons$ H^+ + $C_2H_3O_2^-$

Initial   0.50 M   ~0   0
                x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil. $0.50 - x$ x x

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

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

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

b.   The setup for solutions b and c are similar to solution a except that the final equation is different because the new concentration of $HC_2H_3O_2$ is different.

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

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

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

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

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

Assumption that x is negligible is borderline (6.0% error). We should solve exactly. Using the method of successive approximations (see Appendix 1 of the text):

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

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

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

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

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

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

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

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

$$HC_2H_3O_2 \quad\rightleftharpoons\quad H^+ \quad + \quad C_2H_3O_2^-$$

Initial	C	~0	0

where C = $[HC_2H_3O_2]_0$

x mol/L $HC_2H_3O_2$ dissociates to reach equilibrium

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

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

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

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

A $6 \times 10^{-2} \, M$ acetic acid solution will have pH = 3.0.

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

$$HA \quad\rightleftharpoons\quad H^+ \quad + \quad A^-$$

Initial	0.15 M	~0	0

x mol/L HA dissociates to reach equilibrium

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

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

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

Solutions of Bases

63.   a. $C_6H_5NH_2$ b. $C_6H_5NH_2$ c. OH^- d. CH_3NH_2

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

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

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

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

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

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

$$[Ba(OH)_2] = 3.2 \times 10^{-4}\ M\ OH^- \times \frac{1\,M\ Ba(OH)_2}{2\,M\ OH^-} = 1.6 \times 10^{-4}\ M\ Ba(OH)_2$$

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

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

$[OH^-] = 2(0.00040) = 8.0 \times 10^{-4}\ M$; $pOH = -\log[OH^-] = 3.10$; $pH = 14.00 - pOH$
$= 10.90$

b. $\dfrac{25\,g\ KOH}{L} \times \dfrac{1\,mol\,KOH}{56.1\,g\ KOH} = 0.45$ mol KOH/L

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

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

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

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

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

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

$pH = 14.00 - pOH = 14.00 - 1.00 = 13.00$

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

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

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

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

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

$$0.8000\ L \times \frac{3.6 \times 10^{-3}\ mol\ KOH}{L} \times \frac{56.1\ g\ KOH}{mol\ KOH} = 0.16\ g\ KOH$$

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

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

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

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

71.   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^+.

72.   These are solutions of weak bases in water.

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

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

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

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

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

Initial	0.40 *M*	0	~0
Equil.	0.40 − *x*	*x*	*x*

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

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

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

$$C_2H_5NH_2 \ + \ H_2O \ \rightleftharpoons \ C_2H_5NH_3^+ \ + \ OH^- \qquad K_b = 5.6 \times 10^{-4}$$

Initial	0.20 *M*	0	~0
	x mol/L $C_2H_5NH_2$ reacts with H_2O to reach equilibrium		
Change	−*x*	→ +*x*	+*x*
Equil.	0.20 − *x*	*x*	*x*

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

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

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:

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

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

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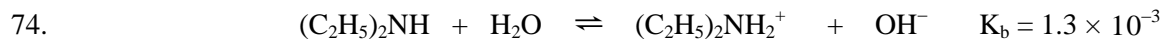
Initial	0.050 *M*	0	~0
	x mol/L $(C_2H_5)_2NH$ reacts with H_2O to reach equilibrium		
Change	−*x*	→ +*x*	+*x*
Equil.	0.050 − *x*	*x*	*x*

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

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

Using successive approximations:

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

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

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

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

$$H_2NNH_2 \; + \; H_2O \quad \rightleftharpoons \quad H_2NNH_3^+ \; + \; OH^- \quad K_b = 3.0 \times 10^{-6}$$

Initial	2.0 M		0	~0

x mol/L H_2NNH_2 reacts with H_2O to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$2.0 - x$		x	x

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

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

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

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

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

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

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

77. $$\frac{5.0 \times 10^{-3} \; g}{0.0100 L} \times \frac{1 \, mol}{299.4 \; g} = 1.7 \times 10^{-3} \; M = [\text{codeine}]_0; \quad \text{let cod} = \text{codeine } (C_{18}H_{21}NO_3).$$

Solving the weak base equilibrium problem:

$$\text{cod} \; + \; H_2O \; \rightleftharpoons \; codH^+ \; + \; OH^- \qquad K_b = 10^{-6.05} = 8.9 \times 10^{-7}$$

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

x mol/L codeine reacts with H_2O to reach equilibrium

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

$$K_b = 8.9 \times 10^{-7} = \frac{x^2}{(1.7 \times 10^{-3} - x)} \approx \frac{x^2}{1.7 \times 10^{-3}} \; , \quad x = 3.9 \times 10^{-5} \; ; \quad \text{assumptions good.}$$

$[OH^-] = 3.9 \times 10^{-5} \; M; \; [H^+] = K_w/[OH^-] = 2.6 \times 10^{-10} \; M; \; pH = -\log[H^+] = 9.59$

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

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

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

$$PT \quad + \quad H_2O \quad \rightleftharpoons \quad PTH^+ \quad + \quad OH^-$$

Initial	0.016 M		0	~0

x mol/L of PT reacts with H_2O to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$0.016 - x$		x	x

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

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

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

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

Initial	I		0	~0	I $= [HONH_2]_0$
Equil.	I $- x$		x	x	

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

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

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

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

81.   To solve for percent ionization, just solve the weak base equilibrium problem.

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

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

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

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

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

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

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

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

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

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

       Initial   0.10 M 0   ~0
       Equil.   0.10 $- x$ x x
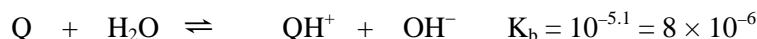
       $4.38 \times 10^{-4} = \dfrac{x^2}{0.10 - x} \approx \dfrac{x^2}{0.10}$, $x = 6.6 \times 10^{-3}$; assumption fails the 5% rule (x is

       6.6% of 0.10).   Using successive approximations and carrying extra significant figures:

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

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

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

                            Q + H_2O $\rightleftharpoons$ QH^+ + OH^- $K_b = 10^{-5.1} = 8 \times 10^{-6}$

       Initial $1.6 \times 10^{-3}\ M$ 0   ~0
                    x mol/L quinine reacts with H_2O to reach equilibrium
       Change $-x$ $\rightarrow$ $+x$ $+x$
       Equil. $1.6 \times 10^{-3} - x$ x x

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

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

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

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

Polyprotic Acids

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

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

Initial		2.0 M	2.0 M	0

x mol/L HSO_4^- dissociates to reach equilibrium

Change		$-x$	$\rightarrow$	$+x$	$+x$
Equil.		$2.0 - x$		$2.0 + x$	x

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

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

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

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

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

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

Initial		0.0050 M	0.0050 M	0

x mol/L HSO_4^- dissociates to reach equilibrium

Change		$-x$	$\rightarrow$	$+x$	$+x$
Equil.		$0.0050 - x$		$0.0050 + x$	x

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

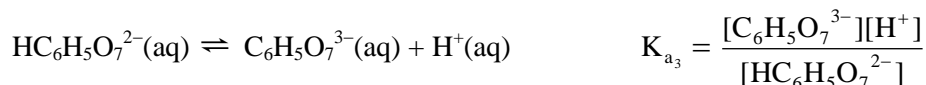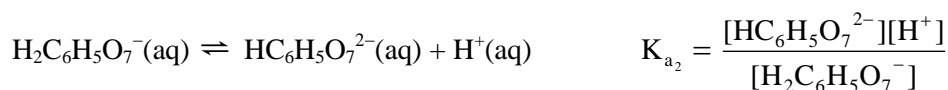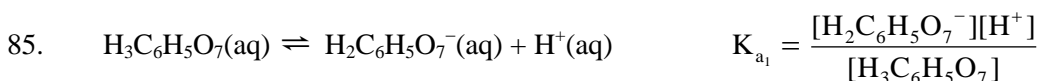Using the quadratic formula:

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

$$x = \frac{-0.017 \pm (2.9 \times 10^{-4} + 2.4 \times 10^{-4})^{1/2}}{2} = \frac{-0.017 \pm 0.023}{2}, \ x = 3.0 \times 10^{-3} M$$
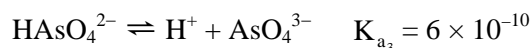
$$[H^+] = 0.0050 + x = 0.0050 + 0.0030 = 0.0080 \ M; \ pH = 2.10$$

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

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

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

 　　 $HC_6H_5O_7^{2-}(aq) \rightleftharpoons C_6H_5O_7^{3-}(aq) + H^+(aq)$ 　　　　$K_{a_3} = \dfrac{[C_6H_5O_7^{3-}][H^+]}{[HC_6H_5O_7^{2-}]}$
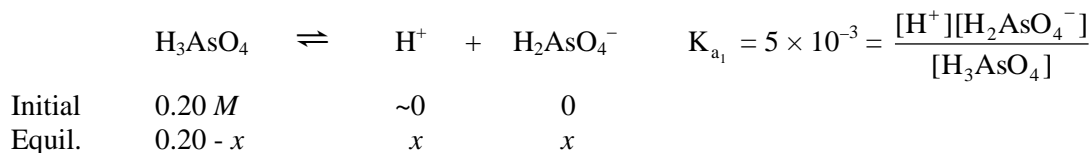
86. H_2CO_3 is a weak acid with $K_{a_1} = 4.3 \times 10^{-7}$ and $K_{a_2} = 4.8 \times 10^{-11}$. The $[H^+]$ concentration in solution will be determined from the K_{a_1} reaction because $K_{a_1} \gg K_{a_2}$. Because $K_{a_1} \ll 1$, the $[H^+] < 0.10 \ M$; only a small percentage of the $0.10 \ M \ H_2CO_3$ will dissociate into HCO_3^- and H^+. So statement a best describes the $0.10 \ M \ H_2CO_3$ solution. H_2SO_4 is a strong acid as well as a very good weak acid ($K_{a_1} \gg 1$, $K_{a_2} = 1.2 \times 10^{-2}$). All of the $0.10 \ M \ H_2SO_4$ solution will dissociate into $0.10 \ M \ H^+$ and $0.10 \ M \ HSO_4^-$. However, because HSO_4^- is a good weak acid due to the relatively large K_a value, some of the $0.10 \ M \ HSO_4^-$ will dissociate into some more H^+ and SO_4^{2-}. Therefore, the $[H^+]$ will be greater than $0.10 \ M$ but will not reach $0.20 \ M$ because only some of $0.10 \ M \ HSO_4^-$ will dissociate. Statement c is best for a $0.10 \ M \ H_2SO_4$ solution.

87.   The reactions are:

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

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

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

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

$$H_3AsO_4 \rightleftharpoons H^+ + H_2AsO_4^- \qquad K_{a_1} = 5 \times 10^{-3} = \frac{[H^+][H_2AsO_4^-]}{[H_3AsO_4]}$$

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

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

Solving by the method of successive approximations:

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

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

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

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

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

$K_{a_3} = 6 \times 10^{-10} = \dfrac{[H^+][AsO_4^{3-}]}{[HAsO_4^{2-}]} = \dfrac{(3 \times 10^{-2})[AsO_4^{3-}]}{8 \times 10^{-8}}$
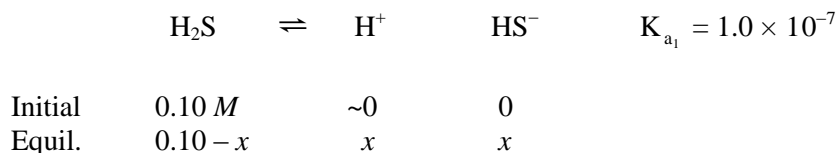
$[AsO_4^{3-}] = 1.6 \times 10^{-15} \approx 2 \times 10^{-15}\ M$; assumption good.

So in 0.20 M analytical concentration of H_3AsO_4:

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

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

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

$$H_2S \rightleftharpoons H^+ \qquad HS^- \qquad K_{a_1} = 1.0 \times 10^{-7}$$

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

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

$$pH = -\log(1.0 \times 10^{-4}) = 4.00$$
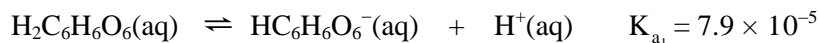
Use the K_{a_2} reaction to determine $[S^{2-}]$.

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

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

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

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

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

$$H_2C_6H_6O_6(aq) \rightleftharpoons HC_6H_6O_6^-(aq) + H^+(aq) \qquad K_{a_1} = 7.9 \times 10^{-5}$$

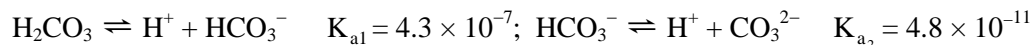|	0.0142 M	0	~ 0
Initial			
Equil.	$0.0142 - x$	x	x

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

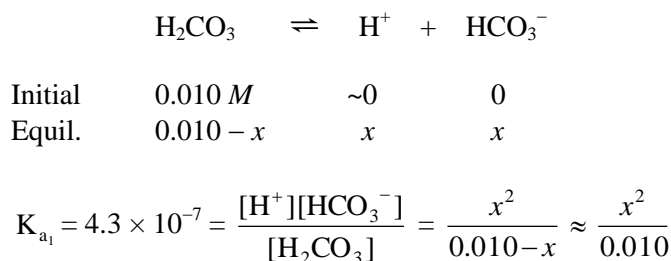Solving by the method of successive approximations:

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

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

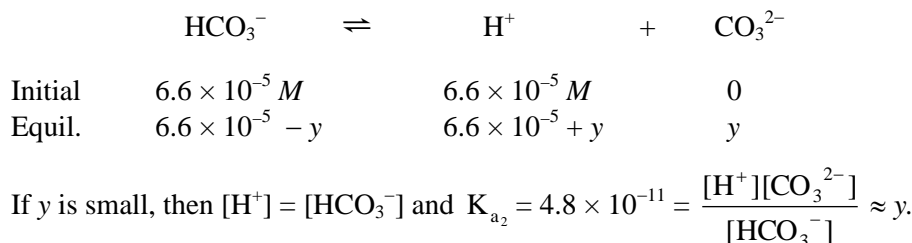90.   The relevant reactions are:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \quad K_{a1} = 4.3 \times 10^{-7}; \ HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad K_{a_2} = 4.8 \times 10^{-11}$$

Initially, we deal only with the first reaction (since $K_{a1} \gg K_{a_2}$), and then let those results control values of concentrations in the second reaction.

$$H_2CO_3 \quad \rightleftharpoons \quad H^+ \quad + \quad HCO_3^-$$

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

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

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

$$HCO_3^- \quad \rightleftharpoons \quad H^+ \quad + \quad CO_3^{2-}$$

Initial $6.6 \times 10^{-5}\, M$ $6.6 \times 10^{-5}\, M$ 0
Equil. $6.6 \times 10^{-5} - y$ $6.6 \times 10^{-5} + y$ y

If y is small, then $[H^+] = [HCO_3^-]$ and $K_{a_2} = 4.8 \times 10^{-11} = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \approx y.$

$y = [CO_3^{2-}] = 4.8 \times 10^{-11}\, M$;   assumptions good.

The amount of H^+ from the second dissociation is $4.8 \times 10^{-11}\, M$ or:

$$\frac{4.8 \times 10^{-11}}{6.6 \times 10^{-5}} \times 100 = 7.3 \times 10^{-5}\%$$

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

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

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

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

Acid-Base Properties of Salts

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

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

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

Initial   1.0 M 0   ~0 $K_b = 1.4 \times 10^{-11}$

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

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

Equil. $1.0 - x$ x x

$$K_b = 1.4 \times 10^{-11} = \frac{[HF][OH^-]}{[F^-]}, \quad 1.4 \times 10^{-11} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$x = [OH^-] = 3.7 \times 10^{-6} \ M$; assumptions good

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

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

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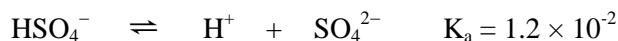
Initial   0.10 M ~0   0

Equil. $0.10 - x$ x x

$$1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, \quad x = 0.035$$
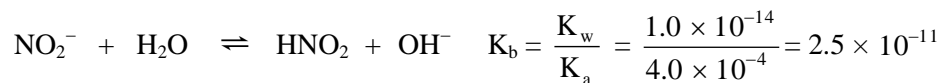
Assumption is not good (x is 35% of 0.10). Using successive approximations:

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

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

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

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

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

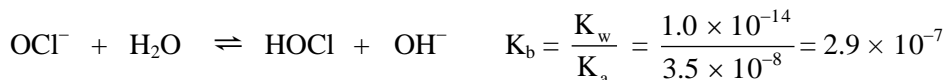Initial   0.12 M 0   ~0

Equil. $0.12 - x$ x x

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

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

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

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

Initial   0.45 M 0   ~0
Equil.   0.45 $- x$ x x

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

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

c. $NH_4ClO_4 \rightarrow NH_4^+ + ClO_4^-$: NH_4^+ is a weak acid. ClO_4^- is the conjugate base of a strong acid. ClO_4^- has no basic (or acidic) properties.
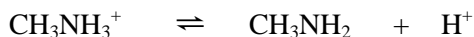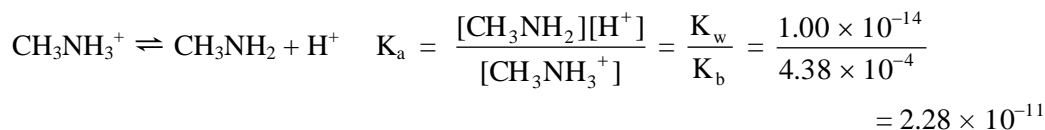
$$NH_4^+ \qquad \rightleftharpoons \qquad NH_3 \; + \; H^+ \qquad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$
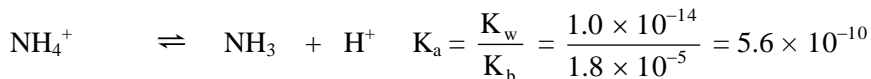
Initial   0.40 M 0   ~0
Equil.   0.40 $- x$ x x

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

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

94.   a. $CH_3NH_3Cl \rightarrow CH_3NH_3^+ + Cl^-$: $CH_3NH_3^+$ is a weak acid. Cl^- is the conjugate base of a strong acid. Cl^- has no basic (or acidic) properties.
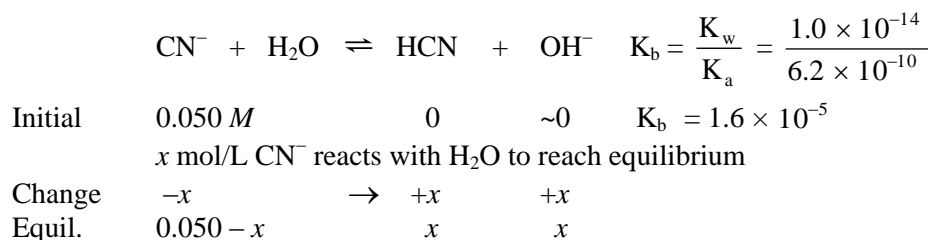
$$CH_3NH_3^+ \rightleftharpoons CH_3NH_2 + H^+ \qquad K_a = \frac{[CH_3NH_2][H^+]}{[CH_3NH_3^+]} = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{4.38 \times 10^{-4}}$$

$$= 2.28 \times 10^{-11}$$

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

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

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

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

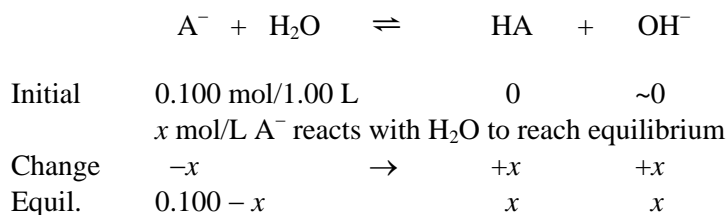b. $NaCN \rightarrow Na^+ + CN^-$: CN^- is a weak base. Na^+ has no acidic (or basic) properties.

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

Initial   0.050 M 0   ~0 $K_b = 1.6 \times 10^{-5}$

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

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

Equil. $0.050 - x$ x x

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

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

95.   All these salts contain Na^+, which has no acidic/basic properties and a conjugate base of a weak acid (except for NaCl, where Cl^- is a neutral species). All conjugate bases of weak acids are weak bases since K_b values for these species are between K_w and 1. To identify the species, we will use the data given to determine the K_b value for the weak conjugate base. From the K_b value and data in Table 7.2 of the text, we can identify the conjugate base present by calculating the K_a value for the weak acid. We will use A^- as an abbreviation for the weak conjugate base.

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

Initial   0.100 mol/1.00 L   0   ~0

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

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

Equil. $0.100 - x$ x x

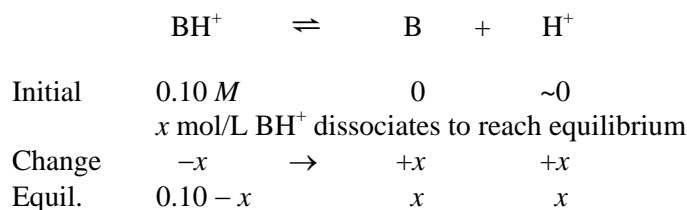$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{0.100 - x} \; ; \text{ from the problem, pH = 8.07:}$$

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

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

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

From Table 7.2 of the text, this K_a value is closest to HF. Therefore, the unknown salt is NaF.

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

$$BH^+ \quad \rightleftharpoons \quad B \quad + \quad H^+$$

Initial   0.10 M 0   ~0

x mol/L BH^+ dissociates to reach equilibrium

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

Equil.   0.10 − x x x

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

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

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

From Table 7.3 of the text, this K_b value is closest to CH_3NH_2, so the unknown salt is CH_3NH_3Cl.

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

$$B^- \quad + \quad H_2O \quad \rightleftharpoons \quad HB \quad + \quad OH^-$$

Initial   0.050 M 0   ~0

Equil.   0.050 − x x x
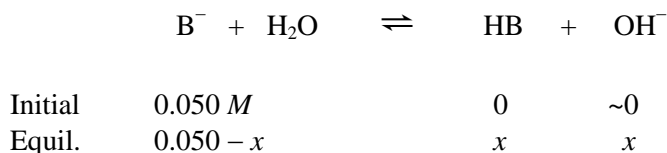
From pH = 9.00: pOH = 5.00, $[OH^-] = 10^{-5.00} = 1.0 \times 10^{-5} \, M = x$.

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

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

$$HB \quad \rightleftharpoons \quad H^+ \quad + \quad B^-$$

Initial   0.010 M ~ 0   0

Equil.   0.010 − x x x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-9}}, \quad 5.0 \times 10^{-6} = \frac{x^2}{0.010-x} \approx \frac{x^2}{0.010}$$
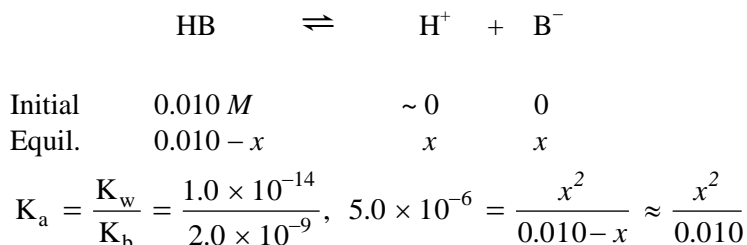
$x = [H^+] = 2.2 \times 10^{-4} \, M;$ pH = 3.66; assumptions good.

98. $C_2H_5NH_3Cl \rightarrow C_2H_5NH_3^+ + Cl^-;$ $C_2H_5NH_3^+$ is the conjugate acid of the weak base $C_2H_5NH_2$ ($K_b = 5.6 \times 10^{-4}$). As is true for all conjugate acids of weak bases, $C_2H_5NH_3^+$ is a weak acid. Cl^- has no basic (or acidic) properties. Ignore Cl^-. Solving the weak acid problem:

$$C_2H_5NH_3^+ \quad \rightleftharpoons \quad C_2H_5NH_2 \quad + \quad H^+ \quad K_a = K_w/5.6 \times 10^{-4} = 1.8 \times 10^{-11}$$

Initial   0.25 M 0   ~0

              x mol/L $C_2H_5NH_3^+$ dissociates to reach equilibrium

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

Equil.   0.25 $- x$ x x

$$K_a = 1.8 \times 10^{-11} = \frac{[C_2H_5NH_2][H^+]}{[C_2H_5NH_3^+]} = \frac{x^2}{0.25 - x} \approx \frac{x^2}{0.25} \quad \text{(assuming } x \ll 0.25)$$

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

$[C_2H_5NH_2] = [H^+] = 2.1 \times 10^{-6} \, M$; $[C_2H_5NH_3^+] = 0.25 \, M$; $[Cl^-] = 0.25 \, M$

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

99.   Reference Table 7.6 of the text.

a. $Sr(NO_3)_2 \rightarrow Sr^{2+} + 2 \, NO_3^-$ neutral; Sr^{2+} and NO_3^- have no effect on pH.

b. $C_2H_5NH_3CN \rightarrow C_2H_5NH_3^+ + CN^-$ basic; $C_2H_5NH_3^+$ is a weak acid
($K_a = K_w/K_{b,C_2H_5NH_2} = 1.0 \times 10^{-14}/5.6 \times 10^{-4} = 1.8 \times 10^{-11}$), and CN^- is a weak base
($K_b = K_w/K_{a, HCN} = 1.0 \times 10^{-14}/6.2 \times 10^{-10} = 1.6 \times 10^{-5}$). Because $K_{b, CN^-} > K_{a, C_2H_5NH_3^+}$,
the solution of $C_2H_5NH_3CN$ will be basic.

c. $C_5H_5NHF \rightarrow C_5H_5NH^+ + F^-$ acidic; $C_5H_5NH^+$ is a weak acid
($K_a = K_w/K_{b,C_5H_5N} = 5.9 \times 10^{-6}$), and F^- is a weak base ($K_b = K_w/K_{a, HF} = 1.4 \times 10^{-11}$).
Because $K_{a, C_5H_5NH^+} > K_{b, F^-}$, the solution of C_5H_5NHF will be acidic.

d. $NH_4C_2H_3O_2 \rightarrow NH_4^+ + C_2H_3O_2^-$ neutral; NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$), and
$C_2H_3O_2^-$ is a weak base ($K_b = K_w/K_{a, HC_2H_3O_2} = 5.6 \times 10^{-10}$). Because $K_{a, NH_4^+} = K_{b, C_2H_3O_2^-}$, the solution of $NH_4C_2H_3O_2$ will have pH $= 7.00$.

e. $NaHCO_3 \rightarrow Na^+ + HCO_3^-$ basic; ignore Na^+; HCO_3^- is a weak acid ($K_{a_2} = 4.8 \times 10^{-11}$),
and HCO_3^- is a weak base ($K_b = K_w/K_{a_1, H_2CO_3} = 2.3 \times 10^{-8}$) . HCO_3^- is a stronger base
than an acid because $K_b > K_a$. Therefore, the solution is basic.

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

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

101.   a.   These are strong acids like HCl, HBr, HI, HNO_3, H_2SO_4, or $HClO_4$.

b. These are salts of the conjugate acids of the bases in Table 7.3. These conjugate acids are all weak acids. NH_4Cl, $CH_3NH_3NO_3$, and $C_2H_5NH_3Br$ are three examples. Note that the anions used to form these salts are conjugate bases of strong acids; this is so because they have no acidic or basic properties in water (with the exception of HSO_4^-, which has weak acid properties).

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

d. These are salts of the conjugate bases of the neutrally charged weak acids in Table 7.2. The conjugate bases of weak acids are weak bases themselves. Three examples are $NaClO_2$, $KC_2H_3O_2$, and CaF_2. The cations used to form these salts are Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, or 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.

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

102. Reference Table 7.6 of the text and the solution to Exercise 103 for some generalizations on acid-base properties of salts. The letters in parenthesis is(are) the generalization(s) listed in Exercise 103 that identifies that species.

$CaBr_2$:   Neutral; Ca^{2+} and Br^- have no acidic/basic properties (f and g).

KNO_2: NO_2^- is a weak base, $K_b = (1.0 \times 10^{-14})/(4.0 \times 10^{-4}) = 2.5 \times 10^{-11}$ (c and d). Ignore K^+ (f).

$HClO_4$:   Strong acid (a)

HNO_2:   Weak acid, $K_a = 4.0 \times 10^{-4}$ (c)

$HONH_3ClO_4$: $HONH_3^+$ is a weak acid, $K_a = K_w/K_{b,HONH_2} = (1.0 \times 10^{-14})/(1.1 \times 10^{-8})$
                    $= 9.1 \times 10^{-7}$ (c and e). Ignore ClO_4^- (g).

NH_4NO_2: NH_4^+ is a weak acid, $K_a = 5.6 \times 10^{-10}$ (c and e). NO_2^- is a weak base, $K_b = 2.5 \times 10^{-11}$ (c and d). Because the K_a value for NH_4^+ is a slightly larger than K_b for NO_2^-, the solution will be slightly acidic with a pH a little lower than 7.0.

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

Most acidic → most basic: $HClO_4 > HNO_2 > HONH_3ClO_4 > NH_4NO_2 > CaBr_2 > KNO_2$

103.   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, $Ca(OH)_2$, $Sr(OH)_2$, 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 7.2 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 7.3 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 7.2 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 7.3 of the text.

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

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

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

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

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

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

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

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

         HBr: Strong acid

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

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

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

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

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

   $NaOH$:   Strong base

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

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

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

   HNO_3:   Strong acid

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

106. Major species: Na^+, PO_4^{3-} (a weak base), and H_2O; the K_b value for PO_4^{3-} is much larger than the K_b values for HPO_4^{2-} and $H_2PO_4^-$. We can ignore the contribution of OH^- from the K_b reactions for HPO_4^{2-} and $H_2PO_4^-$.

$$K_b \text{ for } PO_4^{3-} = \frac{K_w}{K_{a_3}} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-13}} = 0.021$$

Note: K_b for $HPO_4^- = K_w/K_{a_2} = 1.6 \times 10^{-7}$ and K_b for $H_2PO_4^- = K_w/K_{a_1} = 1.3 \times 10^{-12}$. Indeed, K_b for $PO_4^{3-} \gg K_b$ values for HPO_4^- and and $H_2PO_4^-$.

$$PO_4^{3-} \quad + \quad H_2O \quad \rightleftharpoons \quad HPO_4^{2-} \quad + \quad OH^- \qquad K_b = 0.021$$

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

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

using the quadratic equation:

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

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

$$Co(H_2O)_6^{3+} \quad \rightleftharpoons \quad Co(H_2O)_5(OH)^{2+} \quad + \quad H^+ \qquad K_a = 1.0 \times 10^{-5}$$

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

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

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

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

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

Initial	0.200 M	0.200 M	0	0
Change	$-x$	$-x$ $\rightarrow$	$+x$	$+x$
Equil.	$0.200 - x$	$0.200 - x$	x	x

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

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

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

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

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

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

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

Solutions of Dilute Acids and Bases

109.   We can't neglect the $[H^+]$ contribution from H_2O since this is a very dilute solution of the strong acid. Following the strategy developed in Section 7.10 of the text, we first determine the charge balance equation and then manipulate this equation to get into one unknown.

[Positive charge] = [negative charge]

$$[H^+] = [Cl^-] + [OH^-] = 7.0 \times 10^{-7} + \frac{K_w}{[H^+]} \quad \text{(because } [Cl^-] = 7.0 \times 10^{-7} \text{ and } [OH^-] = \frac{K_w}{[H^+]})$$

$$\frac{[H^+]^2 - K_w}{[H^+]} = 7.0 \times 10^{-7}, \ [H^+]^2 - (7.0 \times 10^{-7})[H^+] - 1.0 \times 10^{-14} = 0$$

Using the quadratic formula to solve:

$$[H^+] = \frac{-(-7.0 \times 10^{-7}) \pm [(-7.0 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})]^{1/2}}{2(1)}$$

$$[H^+] = 7.1 \times 10^{-7} \ M; \ pH = -\log(7.1 \times 10^{-7}) = 6.15$$

110.   We can't neglect the $[H^+]$ contribution from H_2O since this is a very dilute solution of the strong acid. Following the strategy developed in Section 7.10 of the text, we first determine the charge balance equation and then manipulate this equation to get into one unknown.

Charge balance: $[H^+] = [NO_3^-] + [OH^-], \ [H^+] = [NO_3^-] + K_w/[H^+]$

$$[H^+]^2 - 1.0 \times 10^{-14} = [H^+](5.0 \times 10^{-8}), \ [H^+]^2 - (5.0 \times 10^{-8})[H^+] - 1.0 \times 10^{-14} = 0$$

Using the quadratic formula: $[H^+] = 1.3 \times 10^{-7} \ M; \ pH = 6.89$

111.   HBrO $\rightleftharpoons$ H^+ + BrO^- $K_a = 2 \times 10^{-9}$

Initial	$1.0 \times 10^{-6} \ M$		~0	0

x mol/L HBrO dissociates to reach equilibrium

Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	$1.0 \times 10^{-6} - x$		x	x

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

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

112. C_6H_5OH $\rightleftharpoons$ $C_6H_5O^-$ + H^+ $C_6H_5OH = $ phenol
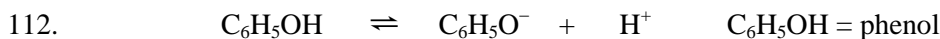
Initial	$4.0 \times 10^{-5} \ M$	0	~0
Equil.	$4.0 \times 10^{-5} - x$	x	x

$$K_a = \frac{x^2}{(4.0 \times 10^{-5} - x)}, \ 1.6 \times 10^{-10} \approx \frac{x^2}{4.0 \times 10^{-5}}, \ x = [H^+] = 8.0 \times 10^{-8} \ M$$

Check assumptions. The assumption that the H^+ contribution from water is negligible is poor. Whenever the calculated pH is greater than 6.0 ($[H^+] < 1 \times 10^{-6} \ M$) for an acid solution, the H^+ contribution from water should be considered. From Section 7.9 of the text, try $[H^+] = (K_a[HA]_0 + K_w)^{1/2}$.

$[H^+] = [(1.6 \times 10^{-10})(4.0 \times 10^{-5}) + (1.0 \times 10^{-14})]^{1/2} = 1.3 \times 10^{-7} M$

This equation will work if $[HA]_0 = 4.0 \times 10^{-5} \gg \dfrac{[H^+]^2 - K_w}{[H^+]} = 5.3 \times 10^{-8}$. Assumption good.

$[H^+] = 1.3 \times 10^{-7} M$; pH = 6.89

Note: If the assumption that $([H^+]^2 - K_w)/[H^+] \ll K_a$ is bad, then the full equation derived in Section 7.9 of the text should be used.

113.   HCN $\rightleftharpoons$ H$^+$ +   CN$^-$ $K_a = 6.2 \times 10^{-10}$

Initial $5.0 \times 10^{-4} M$ ~0   0
Equil. $5.0 \times 10^{-4} - x$ x x

$K_a = \dfrac{x^2}{(5.0 \times 10^{-4} - x)} \approx \dfrac{x^2}{5.0 \times 10^{-4}} = 6.2 \times 10^{-10}$, $x = 5.6 \times 10^{-7}$; check assumptions.

The assumption that the H$^+$ contribution from water is negligible is poor. Whenever the calculated pH is greater than 6.0 for a weak acid, the water contribution to $[H^+]$ must be considered. From Section 7.9 in text:

if $\dfrac{[H^+]^2 - K_w}{[H^+]} \ll [HCN]_0 = 5.0 \times 10^{-4}$, then we can use $[H^+] = (K_a[HCN]_o + K_w)^{1/2}$.

Using this formula: $[H^+] = [(6.2 \times 10^{-10})(5.0 \times 10^{-4}) + (1.0 \times 10^{-14})]^{1/2}$, $[H^+] = 5.7 \times 10^{-7} M$

Checking assumptions: $\dfrac{[H^+]^2 - K_w}{[H^+]} = 5.5 \times 10^{-7} \ll 5.0 \times 10^{-4}$

Assumptions good. pH $= -\log(5.7 \times 10^{-7}) = 6.24$

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

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

H$_2$O $\rightleftharpoons$ H$^+$ + OH$^-$ $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$
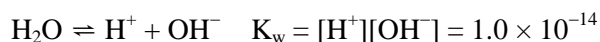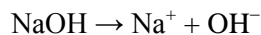
This solution, like all solutions, must be charged balanced; that is, [positive charge] = [negative charge]. For this problem, the charge balance equation is:

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

Substituting into the charge balance equation:

$$1.0 \times 10^{-7} + \frac{1.0 \times 10^{-14}}{[OH^-]} = [OH^-], \ [OH^-]^2 - (1.0 \times 10^{-7})[OH^-] - 1.0 \times 10^{-14} = 0$$
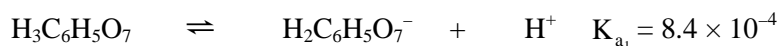
Using the quadratic formula to solve:

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

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

Additional Exercises

115. Because the values of K_{a_1} and K_{a_2} are fairly close to each other, we should consider the amount of H^+ produced by the K_{a_1} and K_{a_2} reactions.

$$H_3C_6H_5O_7 \ \rightleftharpoons \ H_2C_6H_5O_7^- \ + \ H^+ \quad K_{a_1} = 8.4 \times 10^{-4}$$

	$H_3C_6H_5O_7$	$H_2C_6H_5O_7^-$	H^+
Initial	0.15 M	0	~0
Equil.	0.15 - x	x	x

$$8.4 \times 10^{-4} = \frac{x^2}{0.15 - x} \approx \frac{x^2}{0.15}, \ x = 1.1 \times 10^{-2}; \quad \text{assumption fails the 5\% rule.}$$

Solving more exactly using the method of successive approximations:

$$8.4 \times 10^{-4} = \frac{x^2}{(0.15 - 1.1 \times 10^{-2})}, \ x = 1.1 \times 10^{-2} \ M \quad \text{(consistent answer)}$$

Now let's solve for the H^+ contribution from the K_{a_2} reaction.

$$H_2C_6H_5O_7^- \ \rightleftharpoons \ HC_6H_5O_7^{2-} \ + \ H^+ \qquad K_{a_2} = 1.8 \times 10^{-5}$$
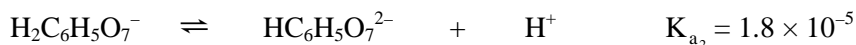
	$H_2C_6H_5O_7^-$	$HC_6H_5O_7^{2-}$	H^+
Initial	$1.1 \times 10^{-2} \ M$	0	$1.1 \times 10^{-2} \ M$
Equil.	$1.1 \times 10^{-2} - x$	x	$1.1 \times 10^{-2} + x$

$$1.8 \times 10^{-5} = \frac{x(1.1 \times 10^{-2} + x)}{(1.1 \times 10^{-2} - x)} \approx \frac{x(1.1 \times 10^{-2})}{1.1 \times 10^{-2}}, \ x = 1.8 \times 10^{-5} \ M; \ \text{assumption good}$$
$$\text{(0.2\% error).}$$

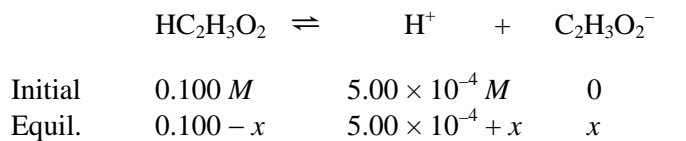At most, $1.8 \times 10^{-5} \ M \ H^+$ will be added from the K_{a_2} reaction.

$$[H^+]_{total} = (1.1 \times 10^{-2}) + (1.8 \times 10^{-5}) = 1.1 \times 10^{-2} \ M$$

Note that the H^+ contribution from the K_{a_2} reaction was negligible compared to the H^+ contribution from the K_{a_1} reaction even though the two K_a values only differed by a factor of 50. Therefore, the H^+ contribution from the K_{a_3} reaction will also be negligible since $K_{a_3} < K_{a_2}$.

Solving: $pH = -\log(1.1 \times 10^{-2}) = 1.96$

116.   At a pH = 0.00, the $[H^+] = 10^{-0.00} = 1.0\ M$. Begin with 1.0 L × 2.0 mol/L NaOH = 2.0 mol
        OH^-. We will need 2.0 mol HCl to neutralize the OH^- plus an additional 1.0 mol excess to
        reduce to a pH of 0.00. We need 3.0 mol HCl total to achieve pH = 0.00.

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

$$HC_2H_3O_2 \rightleftharpoons \qquad H^+ \quad + \quad C_2H_3O_2^-$$

Initial	0.100 M	$5.00 \times 10^{-4}\ M$	0
Equil.	$0.100 - x$	$5.00 \times 10^{-4} + x$	x

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

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

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

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

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

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

$$CB^- \quad + \quad H_2O \quad \rightleftharpoons \quad HCB \quad + \quad OH^-$$

Initial	0.20 M	0	~0
Equil.	0.20 - x	x	x
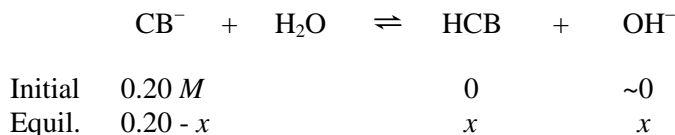
Because pH = 8.65, pOH = 5.35 and $[OH^-] = 10^{-5.35} = 4.5 \times 10^{-6}\ M = x$.

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

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

$$HCB \quad \rightleftharpoons \quad H^+ \quad + \quad CB^-$$

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

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-10}},\ 1.0 \times 10^{-4} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$
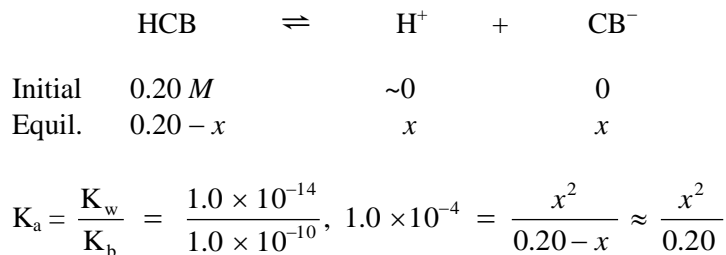
$$x = [H^+] = 4.5 \times 10^{-3}\ M;\ pH = 2.35;\ \text{assumptions good.}$$

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

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

120. $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ $K = \dfrac{[H_2CO_3]}{[CO_2]}$
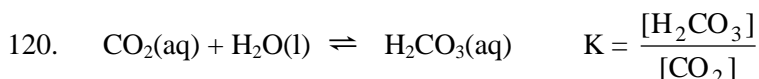
        During exercise: $[H_2CO_3] = 26.3$ mM and $[CO_2] = 1.63$ mM, so: $K = \dfrac{26.3 \text{ m}M}{1.63 \text{ m}M} = 16.1$

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

121.   0.50 M HA, $K_a = 1.0 \times 10^{-3}$; 0.20 M HB, $K_a = 1.0 \times 10^{-10}$; 0.10 M HC, $K_a = 1.0 \times 10^{-12}$

        Major source of H^+ is HA because its K_a value is significantly larger than other K_a values.

        $$HA \rightleftharpoons H^+ + A^-$$

        Initial   0.50 M ~0   0
        Equil.   0.50 $- x$ x x

        $K_a = \dfrac{x^2}{0.50 - x}$, $1.0 \times 10^{-3} \approx \dfrac{x^2}{0.50}$, $x = 0.022$ $M = [H^+]$, $\dfrac{0.022}{0.50} \times 100 = 4.4\%$ error

        Assumption good. Let's check out the assumption that only HA is an important source of H^+.

        For HB: $1.0 \times 10^{-10} = \dfrac{(0.022)[B^-]}{(0.20)}$, $[B^-] = 9.1 \times 10^{-10}$ M

        At <u>most</u>, HB will produce an additional 9.1×10^{-10} M H^+. Even less will be produced by HC. Thus our original assumption was good. $[H^+] = 0.022$ M.

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

        a.   Hacr $\rightleftharpoons$ H^+ +   acr$^-$

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

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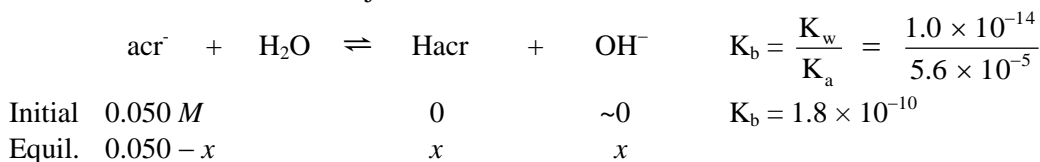
Assumptions good.

b. Percent dissociation $= \dfrac{2.4 \times 10^{-3}}{0.10} \times 100 = 2.4\%$

c. For 0.010% dissociation: $[acr^-] = 1.0 \times 10^{-4}(0.10) = 1.0 \times 10^{-5} \, M$

$$K_a = \frac{[H^+][acr^-]}{[Hacr]}, \quad 5.6 \times 10^{-5} = \frac{[H^+](1.0 \times 10^{-5})}{0.10 - (1.0 \times 10^{-5})}, \quad [H^+] = 0.56 \, M$$

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

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

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-5}}$$

$$K_b = 1.8 \times 10^{-10}$$

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

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

123.   The light bulb is bright because a strong electrolyte is present; that is, a solute is present that dissolves to produce a lot of ions in solution. The pH meter value of 4.6 indicates that a weak acid is present. (If a strong acid were present, the pH would be close to zero.) Of the possible substances, only HCl (strong acid), NaOH (strong base), and NH_4Cl are strong electrolytes. Of these three substances, only NH_4Cl contains a weak acid (the HCl solution would have a pH close to zero, and the NaOH solution would have a pH close to 14.0). NH_4Cl dissociates into NH_4^+ and Cl^- ions when dissolved in water. Cl^- is the conjugate base of a strong acid, so it has no basic (or acidic properties) in water. NH_4^+, however, is the conjugate acid of the weak base NH_3, so NH_4^+ is a weak acid and would produce a solution with a pH = 4.6 when the concentration is ~1.0 M. NH_4Cl is the solute.

124.   For H_3PO_4, $K_{a_1} = 7.5 \times 10^{-3}$, $K_{a_2} = 6.2 \times 10^{-8}$, and $K_{a_3} = 4.8 \times 10^{-13}$.   Because K_{a_1} is much larger than K_{a_2} and K_{a_3}, the dominant H^+ producer is H_3PO_4, and the H^+ contributed from $H_2PO_4^-$ and HPO_4^{2-} can be ignored Solving the weak acid problem in the typical manner.
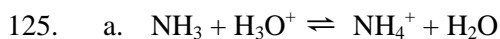
	H_3PO_4	$\rightleftharpoons$	$H_2PO_4^-$	+	H^+
Initial	0.007 M		0		~0
Equil.	$0.007 - x$		x		x
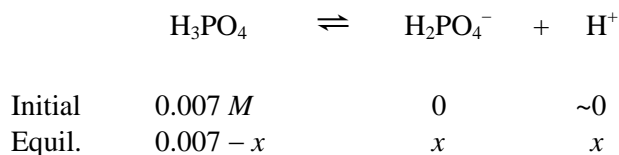
$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} = \frac{x^2}{0.007 - x} \approx \frac{x^2}{0.007}$$

$x = 7.5 \times 10^{-3}$; assumption is horrible because x is 100% of 0.007. We will use the quadratic equation to solve exactly.
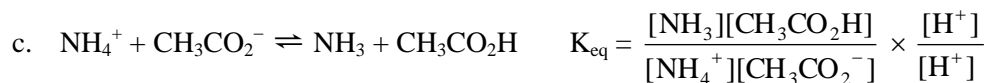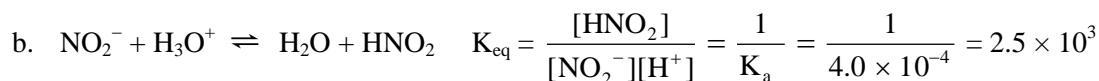
$$7.5 \times 10^{-3} = \frac{x^2}{0.007 - x}, \quad x^2 = 5 \times 10^{-5} - (7.5 \times 10^{-3})x, \quad x^2 + (7.5 \times 10^{-3})x - 5 \times 10^{-5} = 0$$

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

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

125.   a. $NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$

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

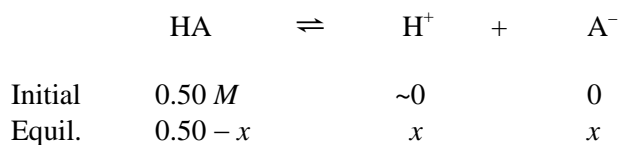b. $NO_2^- + H_3O^+ \rightleftharpoons H_2O + HNO_2$ $K_{eq} = \frac{[HNO_2]}{[NO_2^-][H^+]} = \frac{1}{K_a} = \frac{1}{4.0 \times 10^{-4}} = 2.5 \times 10^3$

c. $NH_4^+ + CH_3CO_2^- \rightleftharpoons NH_3 + CH_3CO_2H$ $K_{eq} = \frac{[NH_3][CH_3CO_2H]}{[NH_4^+][CH_3CO_2^-]} \times \frac{[H^+]}{[H^+]}$

$$K_{eq} = \frac{K_a \text{ for } NH_4^+}{K_a \text{ for } CH_3CO_2H} = \frac{K_w}{(K_b \text{ for } NH_3)(K_a \text{ for } CH_3CO_2H)}$$

$$K_{eq} = \frac{1.0 \times 10^{-14}}{(1.8 \times 10^{-5})(1.8 \times 10^{-5})} = 3.1 \times 10^{-5}$$

d. $H_3O^+ + OH^- \rightleftharpoons 2\, H_2O$ $K_{eq} = \frac{1}{K_w} = 1.0 \times 10^{14}$

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

f. $HNO_2 + OH^- \rightleftharpoons H_2O + NO_2^-$
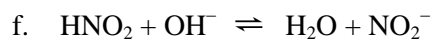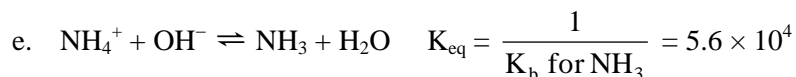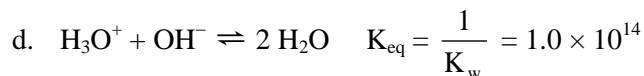
$$K_{eq} = \frac{[NO_2^-]}{[HNO_2][OH^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_a \text{ for } HNO_2}{K_w} = \frac{4.0 \times 10^{-4}}{1.0 \times 10^{-14}} = 4.0 \times 10^{10}$$

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

$$\text{HA} \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{A}^-$$

Initial   0.50 M ~0   0
Equil.   0.50 − x x x
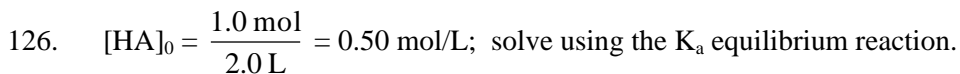
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{0.50 - x} ; \text{ in this problem, } [\text{HA}] = 0.45 \, M \text{ so:}$$

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

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

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

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

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

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

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

128. $50.0 \, \text{mL conc. HCl soln} \times \dfrac{1.19 \, \text{g}}{\text{mL}} \times \dfrac{38 \, \text{g HCl}}{100 \, \text{g conc. HCl soln}} \times \dfrac{1 \, \text{mol HCl}}{36.5 \, \text{g}} = 0.62 \, \text{mol HCl}$

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

$\text{HCl(aq)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ 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 H^+ in the final solution.

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

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

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

$$\text{NH}_3 \ + \ \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{NH}_4^+ \quad + \quad \text{OH}^- \qquad K_b = 1.8 \times 10^{-5}$$

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

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

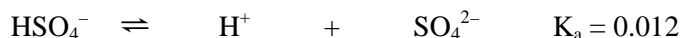$$(x \text{ is } 270\% \text{ of } 0.0100).$$

Using the quadratic formula:

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

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

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

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

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \quad K_a = 0.012$$

Initial	0.010 M	0.020 M	0
Equil.	0.010 − x	0.020 + x	x

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

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

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

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

$$= 0.0792 M$$

$$papH^+ \rightleftharpoons pap + H^+ \quad K_a = \frac{K_w}{K_{b,\text{ pap}}} = \frac{2.1 \times 10^{-14}}{8.33 \times 10^{-9}} = 2.5 \times 10^{-6}$$
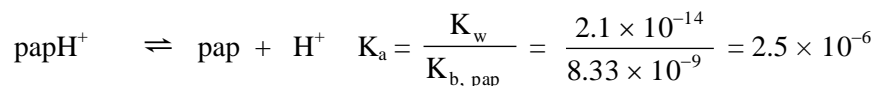
Initial	0.0792 M	0	~0
Equil.	0.0792 − x	x	x

$$K_a = 2.5 \times 10^{-6} = \frac{x^2}{0.0792 - x} \approx \frac{x^2}{0.0792}, \quad x = [H^+] = 4.4 \times 10^{-4} M$$
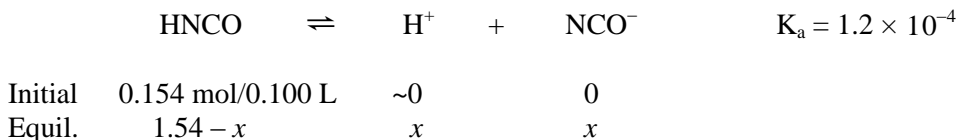
$$pH = -\log(4.4 \times 10^{-4}) = 3.36; \text{ assumptions good.}$$

132. $$10.0 \text{ g NaOCN} \times \frac{1 \text{ mol}}{65.01 \text{ g}} = 0.154 \text{ mol NaOCN}$$

$$10.0 \text{ g H}_2\text{C}_2\text{O}_4 \times \frac{1 \text{ mol}}{90.04 \text{ g}} = 0.111 \text{ mol H}_2\text{C}_2\text{O}_4$$
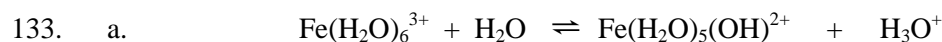
$$\frac{\text{Mol NaOCN}}{\text{Mol H}_2\text{C}_2\text{O}_4}\text{(actual)} = \frac{0.154\,\text{mol}}{0.111\,\text{mol}} = 1.39$$

The balanced reaction requires a larger 2 : 1 mole ratio. Therefore, NaOCN in the numerator is limiting. Because there is a 2 : 2 mole correspondence between mol NaOCN reacted and mol HNCO produced, 1.54 mol HNCO will be produced.

$$\text{HNCO} \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{NCO}^- \qquad\qquad K_a = 1.2 \times 10^{-4}$$

Initial   0.154 mol/0.100 L   ~0   0
Equil. $1.54 - x$ x x

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

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

133.   a. $\text{Fe(H}_2\text{O)}_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe(H}_2\text{O)}_5(\text{OH})^{2+} + \text{H}_3\text{O}^+$

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

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

$x = 2.4 \times 10^{-2}\, M;$ assumption is poor (24% error).

Using successive approximations:

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

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

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

b. $\dfrac{[\text{Fe(H}_2\text{O)}_5(\text{OH})^{2+}]}{[\text{Fe(H}_2\text{O)}_6^{3+}]} = \dfrac{0.0010}{0.9990}; \ K_a = 6.0 \times 10^{-3} = \dfrac{[\text{H}^+](0.0010)}{0.9990}$
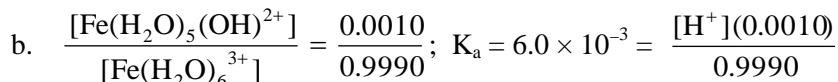
Solving: $[\text{H}^+] = 6.0\, M;$ pH $= -\log(6.0) = -0.78$

c.   Because of the lower charge, Fe^{2+}(aq) will not be as strong an acid as Fe^{3+}(aq). A solution of iron(II) nitrate will be less acidic (have a higher pH) than a solution with the same concentration of iron(III) nitrate.
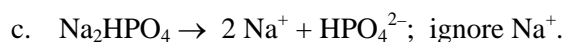
134.   a. $NH_4(HCO_3) \rightarrow NH_4^+ + HCO_3^-$

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

Solution is basic since HCO_3^- is a stronger base than NH_4^+ is as an acid. The acidic properties of HCO_3^- were ignored because K_{a_2} is very small (4.8×10^{-11}).
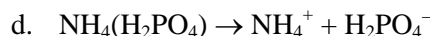
b. $NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$; ignore Na^+.
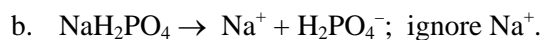
$K_{a_2, H_2PO_4^-} = 6.2 \times 10^{-8}; \quad K_{b, H_2PO_4^-} = \dfrac{K_w}{K_{a_1}} = \dfrac{1.0 \times 10^{-14}}{7.5 \times 10^{-3}} = 1.3 \times 10^{-12}$

Solution is acidic since $K_a > K_b$.

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

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

Solution is basic since $K_b > K_a$.

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

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

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

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

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

135. $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq); \quad Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq)$
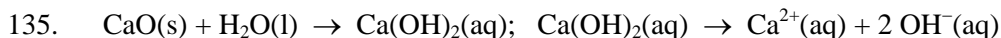
$[OH^-] = \dfrac{0.25\,g\,CaO \times \dfrac{1\,mol\,CaO}{56.08\,g} \times \dfrac{1\,mol\,Ca(OH)_2}{1\,mol\,CaO} \times \dfrac{2\,mol\,OH^-}{mol\,Ca(OH)_2}}{1.5\,L} = 5.9 \times 10^{-3}\,M$

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

Challenge Problems

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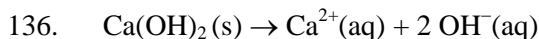
This is a very dilute solution of $Ca(OH)_2$, so we can't ignore the OH^- contribution from H_2O. From the dissociation of $Ca(OH)_2$ alone, $2[Ca^{2+}] = [OH^-]$. Including the H_2O autoionization into H^+ and OH^-, the overall charge balance is:
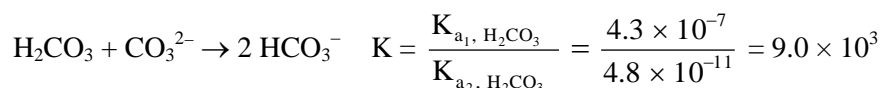
$2[Ca^{2+}] + [H^+] = [OH^-]$

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

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

137. $\dfrac{0.135\,mol\,CO_2}{2.50\,L} = 5.40 \times 10^{-2}\ mol\ CO_2/L = 5.40 \times 10^{-2}\, M\ H_2CO_3;\ 0.105\, M\ CO_3^{2-}$

The best acid (H_2CO_3) reacts with the best base present (CO_3^{2-}) for the principal equilibrium.

$H_2CO_3 + CO_3^{2-} \rightarrow 2\ HCO_3^-\quad K = \dfrac{K_{a_1,\,H_2CO_3}}{K_{a_2,\,H_2CO_3}} = \dfrac{4.3 \times 10^{-7}}{4.8 \times 10^{-11}} = 9.0 \times 10^3$

Because $K \gg 1$, assume all CO_2 (H_2CO_3) is converted into HCO_3^-; that is, 5.40×10^{-2} mol/L CO_3^{2-} is converted into HCO_3^-.

$[HCO_3^-] = 2(5.40 \times 10^{-2}) = 0.108\, M;\ [CO_3^{2-}] = 0.105 - 0.0540 = 0.051\, M$

Note: If we solve for the $[H_2CO_3]$ using these concentrations, we get $[H_2CO_3] = 2.5 \times 10^{-5}\, M$; our assumption that the reaction goes to completion is good (2.5×10^{-5} is 0.05% of 0.051). Whenever $K \gg 1$, always assume the reaction goes to completion.

To solve for the $[H^+]$ in equilibrium with HCO_3^- and CO_3^{2-}, use the K_a expression for HCO_3^-.

$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}\quad K_{a2} = 4.8 \times 10^{-11}$
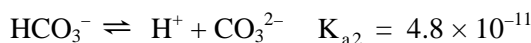
$4.8 \times 10^{-11} = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \dfrac{[H^+](0.051)}{0.108}$

$[H^+] = 1.0 \times 10^{-10};\ pH = 10.00;$ assumptions good.

138. $H_2O \rightleftharpoons H^+ + OH^-;\quad B + H_2O \rightleftharpoons HB^+ + OH^-$

$K_w = [H^+][OH^-];\quad K_b = \dfrac{[HB^+][OH^-]}{[B]}$

Charge balance: $[H^+] + [HB^+] = [OH^-];$ material balance: $[B]_o = [B] + [HB^+]$

So: $[OH^-] = [H^+] + [HB^+]$

$[OH^-] = \dfrac{K_w}{[OH^-]} + [HB^+]$ or: $[HB^+] = [OH^-] - \dfrac{K_w}{[OH^-]}$

$[B] = [B]_0 - [HB^+]$

$$[B] = [B]_0 - \left([OH^-] - \frac{K_w}{[OH^-]}\right)$$

$$K_b = \frac{\left([OH^-] - \frac{K_w}{[OH^-]}\right)[OH^-]}{[B]_0 - \left([OH^-] - \frac{K_w}{[OH^-]}\right)} = \frac{[OH^-]^2 - K_w}{[B]_0 - \frac{[OH^-]^2 - K_w}{[OH^-]}}$$

Assuming $[B]_0 \gg \dfrac{[OH^-]^2 - K_w}{[OH^-]}$, then:

$$K_b \approx \frac{[OH^-]^2 - K_w}{[B]_0}, \quad 6.1 \times 10^{-11} = \frac{[OH^-]^2 - 1.0 \times 10^{-14}}{2.0 \times 10^{-5}}$$

$[OH^-] = 1.1 \times 10^{-7}$; $pOH = 6.96$; $pH = 7.04$ (assumption good)

139.   Major species: H_2O, Na^+, and NO_2^-; NO_2^- is a weak base. $NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

Because this is a very dilute solution of a weak base, the OH^- contribution from H_2O must be considered. The weak base equations for dilute solutions are analogous to the weak acid equations derived in Section 7.9 of the text.

For A^- type bases ($A^- + H_2O \rightleftharpoons HA + OH^-$), the general equation is:

$$K_b = \frac{[OH^-]^2 - K_w}{[A^-]_0 - \frac{[OH^-]^2 - K_w}{[OH^-]}}$$

When $[A^-]_0 \gg \dfrac{[OH^-]^2 - K_w}{[OH^-]}$, then $K_b = \dfrac{[OH^-]^2 - K_w}{[A^-]_0}$ and:

$$[OH^-] = (K_b[A^-]_0 + K_w)^{1/2}$$

Try: $[OH^-] = \left(\dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} \times (6.0 \times 10^{-4}) + (1.0 \times 10^{-14})\right)^{1/2} = 1.6 \times 10^{-7}\,M$

Checking assumption: $6.0 \times 10^{-4} \gg \dfrac{(1.6 \times 10^{-7})^2 - (1.0 \times 10^{-14})}{1.6 \times 10^{-7}} = 9.8 \times 10^{-8}$

Assumption good. $[OH^-] = 1.6 \times 10^{-7}\,M$; $pOH = 6.80$; $pH = 7.20$

140.   a. $NaHCO_3(aq) \rightarrow Na^+(aq) + HCO_3^-(aq)$; $NaHSO_4 \rightarrow Na^+(aq) + HSO_4^-(aq)$

Na^+ has no acidic (or basic) properties. HCO_3^- is a weak acid with $K_a = 4.8 \times 10^{-11}$. HCO_3^- is also the conjugate base of the weak acid H_2CO_3, which makes it a weak base. HCO_3^- is amphoteric; the dominant equilibrium of the best acid reacting with the best base present in a bicarbonate solution is:

$$HCO_3^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + CO_3^{2-}(aq)$$
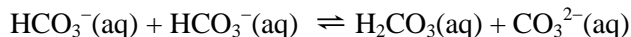
Because the best acid and best base present are the same species, adding more HCO_3^- adds both the acid and the base to the equilibrium at the same time. The H_2CO_3 and CO_3^{2-} concentrations are increased by the same proportions as more HCO_3^- is added. The proportional increase is determined only by the K_a value for HCO_3^- and the K_b value for HCO_3^-. Thus bicarbonate solutions are concentration independent.

For HSO_4^- solutions, the dominant equilibrium of the best acid reacting with the best base present is:

$$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$$
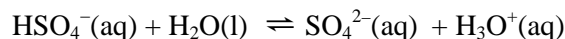
This is just the K_a reaction for HSO_4^-. HSO_4^- is the conjugate base of the strong acid H_2SO_4, so HSO_4^- is a much worse base than water. Water is the best base present in bisulfate solutions.

When more HSO_4^- is added, more H_3O^+ will be produced, resulting in a more acidic pH. The pH of HSO_4^- solutions does depend on the concentration of HSO_4^- present.

b.   The dominant equilibrium reaction is:

$$HCO_3^-(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + CO_3^{2-}(aq)$$
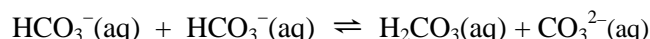
From this reaction, the equilibrium concentrations of H_2CO_3 and CO_3^{2-} must be equal to each other. If we add the K_{a_1} reaction for H_2CO_3 to the K_{a_2} reaction for HCO_3^-, the result is:

$$H_2CO_3 \rightleftharpoons 2\,H^+ + CO_3^{2-} \qquad K = K_{a_1} \times K_{a_2} = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]}$$
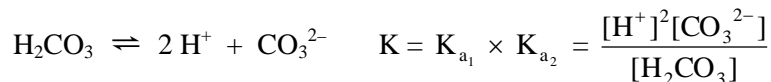
Because $[H_2CO_3] = [CO_3^{2-}]$: $[H^+]^2 = K_{a_1} \times K_{a_2}$

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

$$pH = \frac{pK_{a_1} + pK_{a_2}}{2} = \frac{-\log(4.3 \times 10^{-7}) - \log(4.8 \times 10^{-11})}{2}, \quad pH = \frac{6.37 + 10.32}{2} = 8.35$$
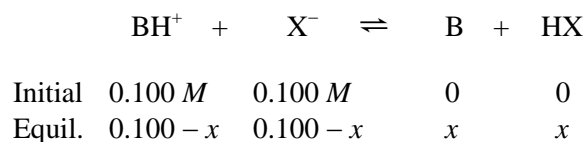
c. $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ $K_a = 1.2 \times 10^{-2}$

Initial   0.010 *M*   ~0   0
Equil.   0.010 − *x*   *x*   *x*

$$1.2 \times 10^{-2} = \frac{x^2}{0.010 - x}; \quad \text{solving using the quadratic equation:}$$

$$x = [H^+] = 6.5 \times 10^{-3} \, M; \quad pH = 2.19$$

141.   Major species: BH^+, X^-, and H_2O; because BH^+ is the best acid and X^- is the best base in solution, the principal equilibrium is:

$$BH^+ \quad + \quad X^- \quad \rightleftharpoons \quad B \quad + \quad HX$$

Initial   0.100 M 0.100 M 0   0
Equil.   0.100 − x 0.100 − x x x

$$K = \frac{K_{a, BH^+}}{K_{a, HX}} = \frac{[B][HX]}{[BH^+][X^-]}, \text{ where } [B] = [HX] \text{ and } [BH^+] = [X^-]$$

To solve for the K_a of HX, let's use the equilibrium expression to derive a general expression that relates pH to the pK_a for BH^+ and to the pK_a for HX.

$$\frac{K_{a, BH^+}}{K_{a, HX}} = \frac{[HX]^2}{[X^-]^2}; \quad K_{a,HX} = \frac{[H^+][X^-]}{[HX]}, \quad \frac{[HX]}{[X^-]} = \frac{[H^+]}{K_{a, HX}}$$

$$\frac{K_{a, BH^+}}{K_{a, HX}} = \frac{[HX]^2}{[X^-]^2} = \left(\frac{[H^+]}{K_{a, HX}}\right)^2, \quad [H^+]^2 = K_{a, BH^+} \times K_{a, HX}$$

Taking the −log of both sides: $\quad pH = \dfrac{pK_{a, BH^+} + pK_{a, HX}}{2}$

This is a general equation that applies to all BHX type salts. Solving the problem:

$$K_b \text{ for } B = 1.0 \times 10^{-3}; \quad K_a \text{ for } BH^+ = \frac{K_w}{K_b} = 1.0 \times 10^{-11}$$

$$pH = 8.00 = \frac{11.00 + pK_{a, HX}}{2}, \quad pK_{a, HX} = 5.00 \text{ and } K_a \text{ for } HX = 10^{-5.00} = 1.0 \times 10^{-5}$$

142.   Major species: NH_4^+, $C_2O_4^{2-}$, and H_2O; reacting the best acid with the best base:

$$NH_4^+ \quad + \quad C_2O_4^{2-} \quad \rightleftharpoons \quad NH_3 + HC_2O_4^- \qquad K = \frac{K_{a, NH_4^+}}{K_{a, HC_2O_4^-}}$$

Initial   0.200 M 0.100 M 0   0 $K = 9.2 \times 10^{-6}$
Change   −x −x →   +x +x
Equil.   0.200 − x 0.100 − x x x
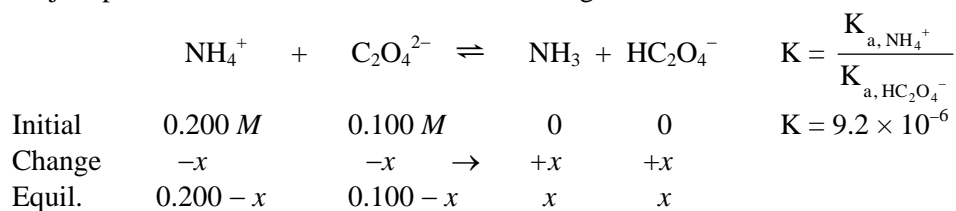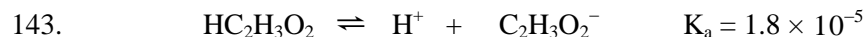
$$K = \frac{(x)(x)}{(0.200 - x)(0.100 - x)} = 9.2 \times 10^{-6}; \quad \text{solving: } x = 4.3 \times 10^{-4} \, M$$

Use either K_a expression to solve for $[H^+]$.

$$K_{a_2} = 6.1 \times 10^{-5} = \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]} = \frac{[H^+](0.100 - 4.3 \times 10^{-4})}{(4.3 \times 10^{-4})}, \quad [H^+] = 2.6 \times 10^{-7}\,M;$$
$$pH = 6.59$$

We get the same answer using the K_a equilibrium for NH_4^+.

$$K_a = 5.6 \times 10^{-10} = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{[H^+](4.3 \times 10^{-4})}{(0.200 - 4.3 \times 10^{-4})}, \quad [H^+] = 2.6 \times 10^{-7}\,M; \quad pH = 6.59$$
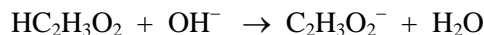
143. $HC_2H_3O_2 \;\rightleftharpoons\; H^+ \;+\; C_2H_3O_2^- \qquad K_a = 1.8 \times 10^{-5}$

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

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

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

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

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

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

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

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

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

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

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

$$HC_2H_3O_2 \;+\; OH^- \;\rightarrow\; C_2H_3O_2^- \;+\; H_2O$$
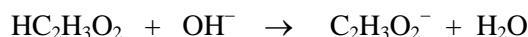
Before	1.00 M	0.50 M	0	
Change	-0.50	-0.50	$\rightarrow$	$+0.50$
After	0.50 M	0	0.50 M	
completion				

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

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

144.   Major species: H^+, HSO_4^-, and H_2O

Charge balance: $[H^+] = [OH^-] + [HSO_4^-] + 2[SO_4^{2-}]$

Material balance: $[HSO_4^-]_0 = [SO_4^{2-}] + [HSO_4^-] = 1.00 \times 10^{-7} \, M$ (from the $1.00 \times 10^{-7} \, M$ H_2SO_4)

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

$$K_a = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}; \;\; [HSO_4^-] = (1.00 \times 10^{-7}) - [SO_4^{2-}]$$

$$[H^+] = \frac{K_w}{[H^+]} + (1.00 \times 10^{-7}) - [SO_4^{2-}] + 2[SO_4^{2-}], \;\; [SO_4^{2-}] = [H^+] - \frac{K_w}{[H^+]} - (1.00 \times 10^{-7})$$

$$1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{[H^+]\left([H^+] - \dfrac{K_w}{[H^+]} - (1.00 \times 10^{-7})\right)}{(1.00 \times 10^{-7}) - [H^+] + \dfrac{K_w}{[H^+]} + (1.00 \times 10^{-7})}$$

This is a complicated expression to solve. Because this is such a dilute solution of H_2SO_4 ($1.00 \times 10^{-7} \, M$), the K_a equilibrium expression for HSO_4^- dictates that $[SO_4^{2-}] \gg [HSO_4^-]$. Let's assume that $[SO_4^{2-}] = 1.00 \times 10^{-7} \, M$ (assume most of the HSO_4^- dissociates):

$$[H^+] = \frac{K_w}{[H^+]} + (1.00 \times 10^{-7}) + [SO_4^{2-}] = \frac{K_w}{[H^+]} + 2.00 \times 10^{-7}$$
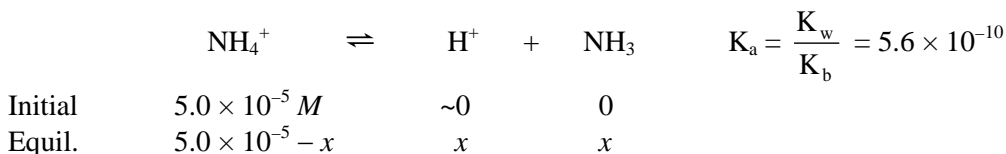
Solving: $[H^+] = 2.4 \times 10^{-7} \, M$; pH = 6.62

Assumption good: $\dfrac{[SO_4^{2-}]}{[HSO_4^-]} = \dfrac{K_a}{[H^+]} = \dfrac{1.2 \times 10^{-2}}{2.4 \times 10^{-7}} = 5.0 \times 10^4$.

We do have mostly SO_4^{2-} at equilibrium.

145.   Major species: H_2O, NH_3, H^+, and Cl^-; the H^+ from the strong acid will react with the best base present (NH_3). Because strong acids are great at donating protons, the reaction between H^+ and NH_3 essentially goes to completion, that is, until one or both of the reactants runs out. The reaction is:

$$NH_3 + H^+ \rightarrow NH_4^+$$

Because equal volumes of 1.0×10^{-4} M NH_3 and 1.0×10^{-4} M H^+ are mixed, both reactants are in stoichiometric amounts, and both reactants will run out at the same time. After reaction, only NH_4^+ and Cl^- remain. Cl^- has no basic properties since it is the conjugate base of a strong acid. Therefore, the only species with acid-base properties is NH_4^+, a weak acid. The initial concentration of NH_4^+ will be exactly one-half of 1.0×10^{-4} M since equal volumes of NH_3 and HCl were mixed. Now we must solve the weak acid problem involving 5.0×10^{-5} M NH_4^+.

	NH_4^+	$\rightleftharpoons$	H^+	$+$	NH_3	$K_a = \dfrac{K_w}{K_b} = 5.6 \times 10^{-10}$
Initial	5.0×10^{-5} M		~0		0	
Equil.	$5.0 \times 10^{-5} - x$		x		x	

$$K_a = \frac{x^2}{(5.0 \times 10^{-5} - x)} \approx \frac{x^2}{5.0 \times 10^{-5}} = 5.6 \times 10^{-10}, \ x = 1.7 \times 10^{-7} \ M; \ \text{check assumptions.}$$

We cannot neglect $[H^+]$ that comes from H_2O. As discussed in Section 7.9 of the text, assume $5.0 \times 10^{-5} \gg ([H^+]^2 - K_w)/[H^+]$. If this is the case, then:

$$[H^+] = (K_a[HA]_0 + K_w)^{1/2} = 1.9 \times 10^{-7} \ M; \ \text{checking assumption:}$$

$$\frac{[H^+]^2 - K_w}{[H^+]} = 1.4 \times 10^{-7} \ll 5.0 \times 10^{-5} \ \text{(assumption good)}$$

So: $[H^+] = 1.9 \times 10^{-7} \ M$; pH = 6.72

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

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

	HA	$\rightleftharpoons$	H^+	$+$	A^-
Initial	0.120 M		~0		0
Equil.	$0.120 - x$		x		x

where $x = [H^+] = 1.6 \times 10^{-2} \ M$

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

147.   0.0500 M HCO$_2$H (HA), K$_a$ = 1.77 × 10^{-4}; 0.150 M CH$_3$CH$_2$CO$_2$H (HB), K$_a$ = 1.34 × 10^{-5}

Because two comparable weak acids are present, each contributes to the total pH.

Charge balance: $[H^+] = [A^-] + [B^-] + [OH^-] = [A^-] + [B^-] + K_w/[H^+]$

Mass balance for HA and HB: 0.0500 = [HA] + [A$^-$] and 0.150 = [HB] + [B$^-$]

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

We have five equations and five unknowns. Manipulate the equations to solve.

$[H^+] = [A^-] + [B^-] + K_w/[H^+];\ [H^+]^2 = [H^+][A^-] + [H^+][B^-] + K_w$

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

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

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

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

Check assumptions: $[H^+][A^-] \approx 8.85 \times 10^{-6}$, $[A^-] \approx \dfrac{8.85 \times 10^{-6}}{3.30 \times 10^{-3}} \approx 2.68 \times 10^{-3}$

Assumed 0.0500 − [A$^-$] ≈ 0.0500. This assumption is borderline (2.68 × 10^{-3} is 5.4% of 0.0500). The HB assumption is good (0.4% error).

Using successive approximations to refine the [H$^+$][A$^-$] value:

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

Note: If we treat each acid separately:

    H$^+$ from HA = 2.9 × 10^{-3}
    H$^+$ from HB = 1.4 × 10^{-3}
    _____

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

This assumes the acids did not suppress each other's ionization. They do, and we expect the [H$^+$] to be less than 4.3 × 10^{-3} M. We get such an answer.

148.   1.000 L × $\dfrac{1.00 \times 10^{-4}\ mol\,HA}{L}$ = 1.00 × 10^{-4} mol HA

25.0% dissociation gives:

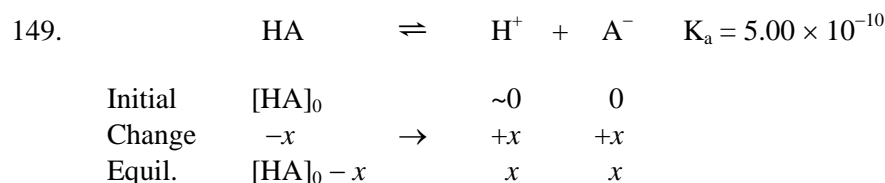$\text{mol H}^+ = 0.250 \times (1.00 \times 10^{-4}) = 2.50 \times 10^{-5} \text{ mol}$

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

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

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

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

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

149.   HA $\rightleftharpoons$ H$^+$ +   A$^-$ $K_a = 5.00 \times 10^{-10}$

Initial $[\text{HA}]_0$ ~0   0
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil. $[\text{HA}]_0 - x$ x x

From the problem: pH = 5.650, so $[\text{H}^+] = x = 10^{-5.650} = 2.24 \times 10^{-6} M$

$$5.00 \times 10^{-10} = \frac{x^2}{[\text{HA}]_0 - x} = \frac{(2.24 \times 10^{-6})^2}{([\text{HA}]_0 - 2.24 \times 10^{-6})}, \quad [\text{HA}]_0 = 1.00 \times 10^{-2} M$$

After the water is added, the pH of the solution is between 6 and 7, so the water contribution to the $[\text{H}^+]$ must be considered. The general expression for a very dilute weak acid solution is:

$$K_a = \frac{[\text{H}^+]^2 - K_w}{[\text{HA}]_0 - \dfrac{[\text{H}^+]^2 - K_w}{[\text{H}^+]}}$$

pH = 6.650; $[\text{H}^+] = 10^{-6.650} = 2.24 \times 10^{-7} M$; let V = volume of water added:
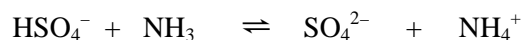
$$5.00 \times 10^{-10} = \frac{(2.24 \times 10^{-7})^2 - (1.00 \times 10^{-14})}{(1.00 \times 10^{-2})\left(\dfrac{0.0500}{0.0500 + V}\right) - \dfrac{(2.24 \times 10^{-7})^2 - (1.00 \times 10^{-14})}{2.24 \times 10^{-7}}}$$

Solving, V = 6.16 L of water were added.

150.   Major species = Na^+, HSO_4^-, NH_3, and H_2O; reaction: $HSO_4^- + NH_3 \rightleftharpoons SO_4^{2-} + NH_4^+$

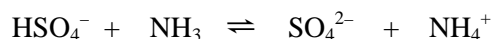$$K = \frac{[SO_4^{2-}][NH_4^+]}{[HSO_4^-][NH_3]} = \frac{K_{a, HSO_4^-}}{K_{a, NH_4^+}} = \frac{1.2 \times 10^{-2}}{5.6 \times 10^{-10}} = 2.1 \times 10^7$$

Because K is a large number, let the reaction go to completion, and then solve the back equilibrium problem.

$$HSO_4^- + NH_3 \rightleftharpoons SO_4^{2-} + NH_4^+$$

Before   0.10 M 0.10 M 0   0
After   0   0   0.10 M 0.10 M

Now allow the reaction to attain equilibrium:

$$HSO_4^- + NH_3 \rightleftharpoons SO_4^{2-} + NH_4^+$$

Initial	0	0	0.10 M	0.10 M
Change	$+x$	$+x$	$\leftarrow$ $-x$	$-x$
Equil.	x	x	$0.10 - x$	$0.10 - x$

$$\frac{(0.10 - x)^2}{x^2} \approx \frac{(0.10)^2}{x^2} = 2.1 \times 10^7, \ x = 2.2 \times 10^{-5} \ M; \ \text{assumptions good.}$$

$[HSO_4^-] = 2.2 \times 10^{-5} \ M; \quad [SO_4^{2-}] = 0.10 \ M$

$[NH_3] = 2.2 \times 10^{-5} \ M; \quad [NH_4^+] = 0.10 \ M$

Using one of the K_a equilibrium expressions to solve for $[H^+]$:

$$K_{a, HSO_4^-} = \frac{[H^+](0.10)}{2.2 \times 10^{-5}} = 1.2 \times 10^{-2}, \ [H^+] = 2.6 \times 10^{-6} \ M; \ pH = 5.59$$

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

$$K_{eq} = \frac{[H_2CO_3][CO_3^{2-}]}{[HCO_3^-][HCO_3^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_{a_2}}{K_{a_1}} = \frac{4.8 \times 10^{-11}}{4.3 \times 10^{-7}} = 1.1 \times 10^{-4}$$

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

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

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

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

d. $[H^+] = [(4.3 \times 10^{-7}) \times (4.8 \times 10^{-11})]^{1/2}$, $[H^+] = 4.5 \times 10^{-9} M$; pH = 8.35

152.   HA $\rightleftharpoons$ H^+ + A^- $K_a = 1.00 \times 10^{-6}$
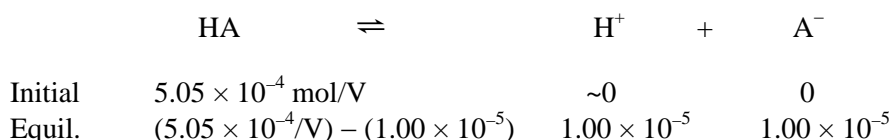
Initial   C   ~0   0   C = $[HA]_0$ for pH = 4.000
Equil.   C − 1.00×10^{-4} 1.00×10^{-4} 1.00×10^{-4} x = $[H^+] = 1.00 \times 10^{-4} M$
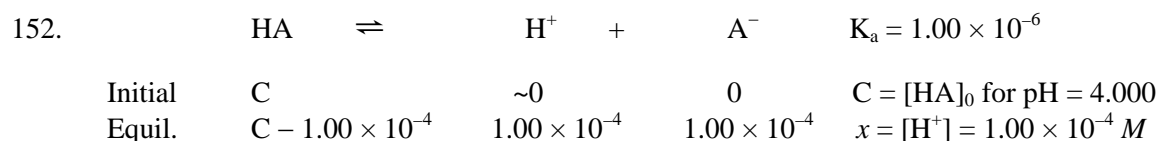
$$K_a = \frac{(1.00 \times 10^{-4})^2}{(C - 1.00 \times 10^{-4})} = 1.00 \times 10^{-6};\ \text{solving: C} = 0.0101\ M$$

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

                              HA $\rightleftharpoons$ H^+ + A^-

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

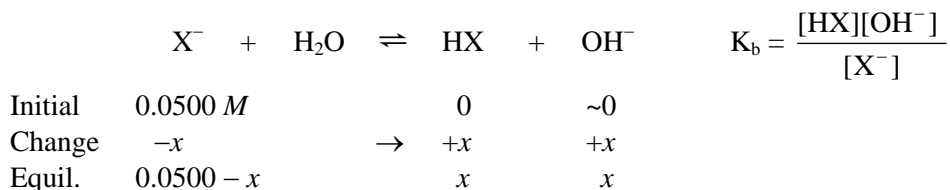$$K_a = \frac{(1.00 \times 10^{-5})^2}{(5.05 \times 10^{-4}/V) - (1.00 \times 10^{-5})} = 1.00 \times 10^{-6}$$

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

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

Marathon Problems

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

         Solution B:

                              X^- + H_2O $\rightleftharpoons$ HX   + OH^- $K_b = \dfrac{[HX][OH^-]}{[X^-]}$

Initial   0.0500 M   0   ~0
Change   −x   →   +x   +x
Equil.   0.0500 − x   x   x

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

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

Solution A:

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

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

Initial   0.100 M ~0   0
Change $-x$ $\rightarrow$ $+x$ $+x$
Equil. $0.100 - x$ x x
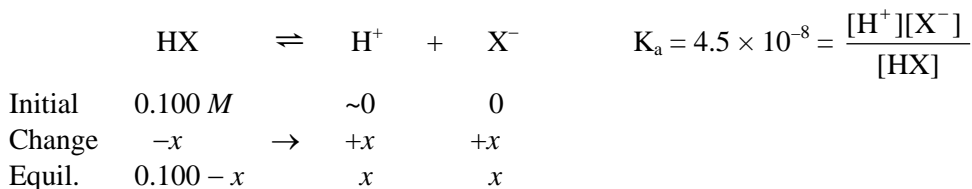
$K_a = 4.5 \times 10^{-8} = \dfrac{x^2}{0.100 - x} \approx \dfrac{x^2}{0.100}$, $\quad x = [H^+] = 6.7 \times 10^{-5} \, M$
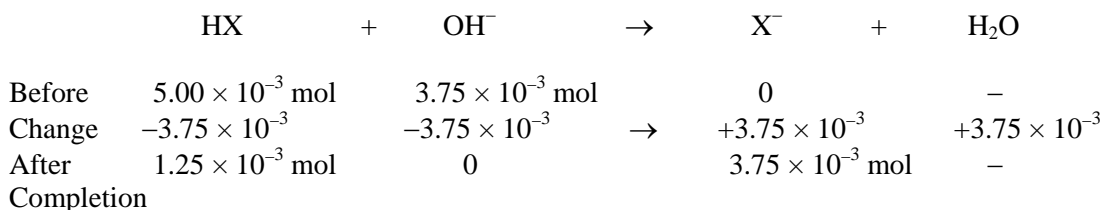
Assumptions good (x is 0.067% of 0.100); pH = 4.17

Solution C:

Major species: H_2O, HX ($K_a = 4.5 \times 10^{-8}$), Na^+, and OH^-; the OH^- from the strong base is exceptional at accepting protons. OH^- will react with the best acid present (HX), and we can assume that OH^- will react to completion with HX, that is, until one (or both) of the reactants runs out. Because we have added one volume of substance to another, we have diluted both solutions from their initial concentrations. What hasn't changed is the moles of each reactant. So let's work with moles of each reactant initially.

$$\text{Mol HX} = 0.0500 \, L \times \frac{0.100 \, mol \, HX}{L} = 5.00 \times 10^{-3} \, mol \, HX$$

$$\text{Mol } OH^- = 0.0150 \, L \times \frac{0.250 \, mol \, NaOH}{L} \times \frac{1 \, mol \, OH^-}{mol \, NaOH} = 3.75 \times 10^{-3} \, mol \, OH^-$$
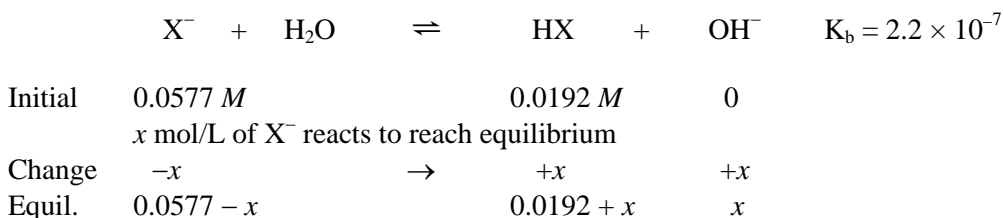
Now lets determine what is remaining in solution after OH^- reacts completely with HX. Note that OH^- is the limiting reagent.

$$HX \quad + \quad OH^- \quad \rightarrow \quad X^- \quad + \quad H_2O$$

Before 5.00×10^{-3} mol 3.75×10^{-3} mol   0 $-$
Change -3.75×10^{-3} -3.75×10^{-3} $\rightarrow$ $+3.75 \times 10^{-3}$ $+3.75 \times 10^{-3}$
After 1.25×10^{-3} mol   0 3.75×10^{-3} mol $-$
Completion

After reaction, the solution contains HX, X^-, Na^+ and H_2O. The Na^+ (like most +1 metal ions) has no effect on the pH of water. However, HX is a weak acid and its conjugate base, X^-, is a weak base. Since both K_a and K_b reactions refer to these species, we could use either reaction to solve for the pH; we will use the K_b reaction. To solve the equilibrium problem using the K_b reaction, we need to convert to concentration units since K_b is in concentration units of mol/L.

$$[HX] = \frac{1.25 \times 10^{-3} \, mol}{(0.0500 + 0.0150) \, L} = 0.0192 \, M; \quad [X^-] = \frac{3.75 \times 10^{-3} \, mol}{0.0650 L} = 0.0577 \, M$$

$[OH^-] = 0$ (We reacted all of it to completion.)

$$X^- \quad + \quad H_2O \quad \rightleftharpoons \quad HX \quad + \quad OH^- \qquad K_b = 2.2 \times 10^{-7}$$

Initial	0.0577 M		0.0192 M	0
	x mol/L of X^- reacts to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$	$+x$
Equil.	0.0577 $- x$		0.0192 $+ x$	x

$$K_b = 2.2 \times 10^{-7} = \frac{(0.0192 + x)x}{0.0577 - x} \approx \frac{(0.0192)\,x}{0.0577} \qquad \text{(assuming } x \text{ is} \ll 0.0192)$$

$$x = [OH^-] = \frac{(2.2 \times 10^{-7})(0.0577)}{0.0192} = 6.6 \times 10^{-7}\,M; \ \text{ assumptions great (} x \text{ is } 0.0034\% \text{ of}$$
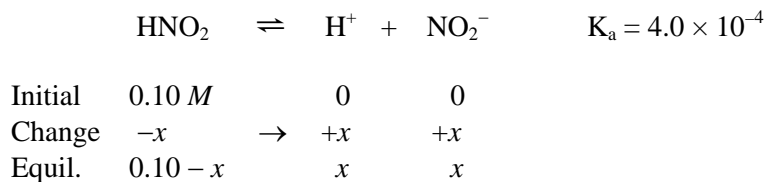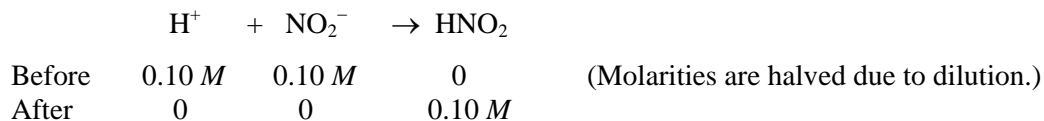$$0.0192).$$

$[OH^-] = 6.6 \times 10^{-7}\,M, \ \ pOH = 6.18, \ \ pH = 14.00 = 6.18 = 7.82 = pH$ of solution C

The combination is 4-17-7-82.

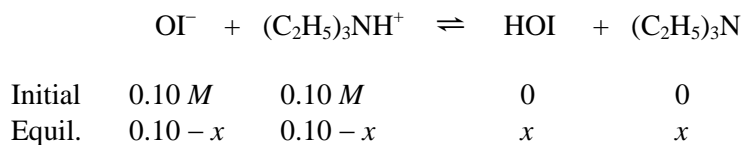154.   a.   Strongest acid from group I $= HCl$;   weakest base (smallest K_b) from group II $= NaNO_2$

0.20 M HCl + 0.20 M NaNO$_2$;   major species $= H^+$, Cl^-, Na^+, NO_2^-, and H_2O
Let the H^+ react to completion with the NO_2^-; then solve the back equilibrium problem.

$$H^+ \quad + \quad NO_2^- \quad \rightarrow HNO_2$$

Before	0.10 M	0.10 M	0	(Molarities are halved due to dilution.)
After	0	0	0.10 M	

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

Initial	0.10 M	0	0
Change	$-x$	$\rightarrow \ +x$	$+x$
Equil.	0.10 $- x$	x	x

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

b.   Weakest acid from group I $= (C_2H_5)_3NHCl$; best base from group II $= KOI$; The
dominant equilibrium will be the best base reacting with the best acid.

$$OI^- \ + \ (C_2H_5)_3NH^+ \quad \rightleftharpoons \quad HOI \ + \ (C_2H_5)_3N$$

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

$$K = \frac{K_{a,\ (C_2H_5)_3NH^+}}{K_{a,\ HOI}} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} \times \frac{1}{2.0 \times 10^{-11}} = 1.25 \text{ (carrying extra sig. fig.)}$$

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

So: $[HOI] = 0.053\ M$ and $[OI^-] = 0.10 - x = 0.047\ M$; using the K_a equilibrium constant for HOI to solve for $[H^+]$:

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

c. K_a for $(C_2H_5)_3NH^+ = \dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$

K_b for $NO_2^- = \dfrac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$

Because $K_a = K_b$, mixing $(C_2H_5)_3NHCl$ with $NaNO_2$ will result in a solution with $pH = 7.00$.