pOH = 14.00 − 0.92 = 13.08; acidic

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

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

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

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

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

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

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

Solutions of Acids

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

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

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

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

57.   Strong acids are assumed to completely dissociate in water; for example; HCl(aq) + H_2O(l) → H_3O^+(aq) + Cl^-(aq) or HCl(aq) → 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 1.0×10^{-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.

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

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

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

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

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

	HNO_2	$\rightleftharpoons$	H^+	+	NO_2^-
Initial	0.250 M		~0		0
		x mol/L HNO_2 dissociates to reach equilibrium			
Change	$-x$	$\rightarrow$	$+x$		$+x$
Equil.	$0.250 - x$		x		x

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

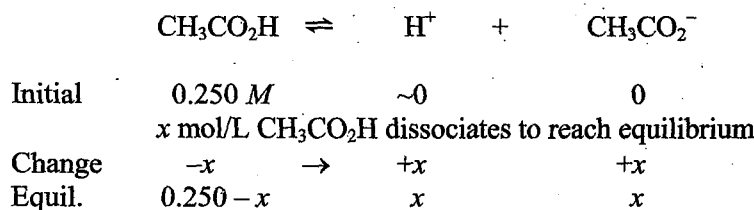$$4.0 \times 10^{-4} \approx \frac{x^2}{0.250}, \quad x = \sqrt{4.0 \times 10^{-4}(0.250)} = 0.010 \text{ } M$$

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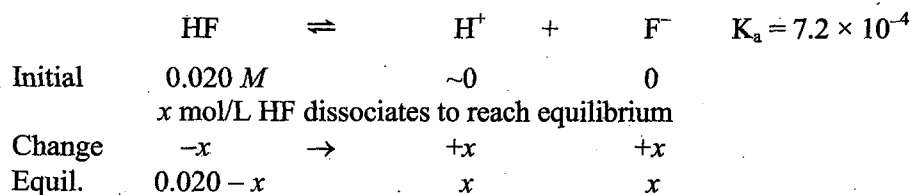
$$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$$

Initial   0.250 M ~0   0

             x mol/L CH_3CO_2H dissociates to reach equilibrium

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

Equil. $0.250 - x$ x x

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

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

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

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

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

Initial   0.020 M ~0   0

           x mol/L HF dissociates to reach equilibrium

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

Equil. $0.020 - x$ x x

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

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

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

The assumption $x \ll 0.020$ is not good (x is more than 5% of 0.020). We must solve $x^2/(0.020 - x) = 7.2 \times 10^{-4}$ exactly by using either the quadratic formula or the method of successive approximations (see Appendix 1 of the text). Using successive approximations, we let 0.016 M be a new approximation for [HF]. That is, in the denominator try $x = 0.0038$ (the value of x we calculated making the normal assumption) so that $0.020 - 0.0038 = 0.016$; then solve for a new value of x in the numerator.

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

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

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

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

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

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

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

67. $HC_3H_5O_2$ ($K_a = 1.3 \times 10^{-5}$) 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:
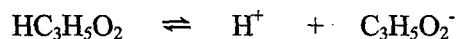
$$HC_3H_5O_2 \quad \rightleftharpoons \quad H^+ \quad + \quad C_3H_5O_2^-$$

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

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

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

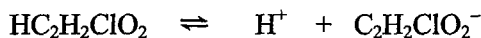Assumption follows the 5% rule (x is 1.1% of 0.100).

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

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

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

69.   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 $-x$ → $+x$ $+x$
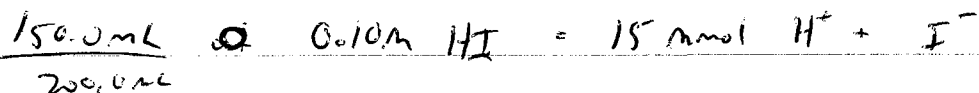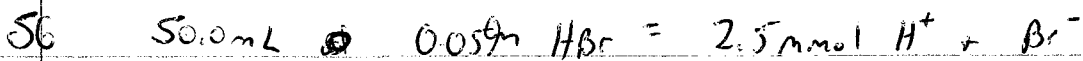Equil. $0.10 - x$ x x

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

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

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

56   50.0 mL @ 0.05m HBr = 2.5 mmol H^+ + Br^-

$\dfrac{150.0 mL \ @ \ 0.10m \ HI = 15 \ mmol \ H^+ + I^-}{200.0 mL}$

$[H^+] = \dfrac{15 + 2.5 \ mmol}{200 mL} = 0.0875 m$ $pH = -\log 0.0875 m$

$\boxed{pH = 1.06}$

$[Br^-] = \dfrac{2.5 \ mmol}{200.0 mL} = 0.0125 M$

$[I^-] = \dfrac{15 \ mmol}{200.0 mL} = 0.075 m$
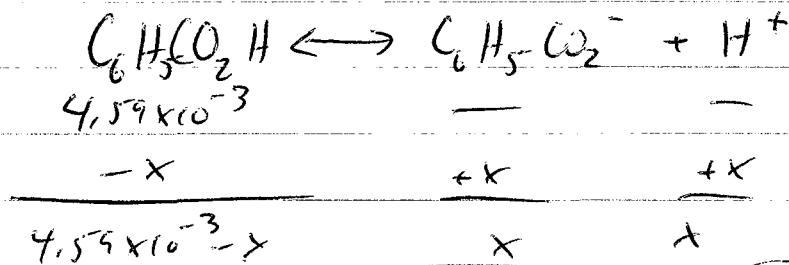
60   HBr = Strong Acid

$[H^+] = [HBr] = 10^{-pH} = 10^{-4.25} = 5.6 \times 10^{-5} M$

68    $0.56 g \ B.A. \left(\dfrac{1 \ mol}{122 g}\right) = 0.00459 \ mol$ $\Big|$ $K_a = 6.4 \times 10^{-5}$

$[B.A.] = \dfrac{0.00459 \ mol}{1.0 L} = 4.59 \times 10^{-3} M$

$$C_6H_5CO_2H \longleftrightarrow C_6H_5CO_2^- + H^+$$

4.59×10^{-3}	—	—
$-x$	$+x$	$+x$
$4.59 \times 10^{-3} - x$	x	x

$pH = \boxed{3.27}$

$K_a = \dfrac{[H^+][C_6H_5CO_2^-]}{(C_6H_5CO_2H)} = 6.4 \times 10^{-5} = \dfrac{x^2}{4.59 \times 10^{-3} \ (x)}$

$x = [H^+] = [C_6H_5CO_2^-]$ $\boxed{5.42 \times 10^{-4} m}$

$[C_6H_5CO_2H] = \dfrac{4.59 \times 10^{-3}}{5.42 \times 10^{-4}}$

68   Quadratic

$$6.4 \times 10^{-5} = \frac{x^2}{4.59 \times 10^{-3} - x}$$

$$2.94 \times 10^{-7} - 6.4 \times 10^{-5} x = x^2$$

$$0 = x^2 + 6.4 \times 10^{-5} x - 2.94 \times 10^{-7}$$

$[H^+] = \quad x = 5.11 \times 10^{-4} M = [C_6 H_5 CO_2^-]$

$pH \quad -\log 5.11 \times 10^{-4} M = 3.29$

$$[C_6 H_5 CO_2 H] = 4.59 \times 10^{-3} - 5.11 \times 10^{-4} = 0.00405 M$$