Page 667 # 9,11

9) a

11)a polyprotic acid can lose more than one H^+ in an acid-base reaction. C_6H_6 is not a polyprotic acid or any kind of acid because its H atoms are not ionizable.

Exercise 15.4 A) pH = 4.331

Exercise 15.4B) pH = 12.624

Exercise 15.5A) The solution is basic. The concentration of OH^- comes mainly from the dissociation of NaOH and a small amount from the self-ionization of water.

Exercise 15.5B) The NaOH and HCl react to neutralize each other. The solution is neutral.

23. (a) $HOClO_2 + H_2O \rightleftharpoons H_3O^+ + OClO_2^-$
acid 1 base 2 acid 2 base 1
(b) $HSeO_4^- + NH_3 \rightleftharpoons NH_4^+ + SeO_4^{2-}$
acid 1 base 2 acid 2 base 1
(c) $HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$
acid 1 base 2 base 1 acid 2
(d) $C_5H_5NH^+ + H_2O \rightleftharpoons C_5H_5N + H_3O^+$
acid 1 base 2 base 1 acid 2

24. (a) $HSO_4^- + F^- \rightleftharpoons HF + SO_4^{2-}$
acid1 base 2 acid 2 base 1
(b) $NH_4^+ + Cl^- \rightleftharpoons NH_3 + HCl$
acid 1 base 2 base 1 acid 2
(c) $HCl + CH_3COO^- \rightleftharpoons CH_3COOH + Cl^-$
acid 1 base 2 acid 2 base 1
(d) $CH_3OH + Br^- \rightleftharpoons HBr + CH_3O^-$
acid 1 base 2 acid 2 base 1
(d) < (b) < (a) < (c)

25. $H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$
$H_2PO_4^- + H_2O \rightarrow OH^- + H_3PO_4$

26. $HSO_3^- + OH^- \rightarrow H_2O + SO_3^{2-}$
$HSO_3^- + HBr \rightarrow H_2SO_3 + Br^-$

37. (a) $[H_3O^+] = 10^{-pH} = 10^{-2.91} = 1.2 \times 10^{-3}$ M
(b) $[H_3O^+] = 10^{-9.26} = 5.5 \times 10^{-10}$ M
(c) $[H_3O^+] = 10^{-4.35} = 4.5 \times 10^{-5}$ M
(d) $[H_3O^+] = 10^{-3.94} = 1.1 \times 10^{-4}$ M

38. (a) pOH = 14.00 - pH = 14.00 - 13.70 = 0.30 $[OH^-] = 10^{-0.30} = 0.50$ M
(b) pOH = 14.00 – 3.65 = 9.65 $[OH^-] = 10^{-9.65} = 2.2 \times 10^{-10}$ M
(c) pOH = 14.00 – 7.42 = 6.58 $[OH^-] = 10^{-6.58} = 2.6 \times 10^{-7}$ M

39. (a) $[H_3O^+] = 0.039$ M pH = 1.41
(b) $[OH^-] = 0.070$ M pOH = 1.15 pH = 12.85
(c) $[H_3O^+] = 0.65$ M pH = 0.19
(d) $[OH^-] = 2 \times 2.5 \times 10^{-4}$ M $= 5.0 \times 10^{-4}$ M pOH = 3.30 pH = 10.70

40. (a) pOH = 14.00 - pH = 14.00 - 1.41 = 12.59
(b) pOH = 14.00 – 12.85 = 1.15
(c) pOH = 14.00 – 0.19 = 13.81
(d) pOH = 14.00 – 10.70 = 3.30

41. (a) $[OH^-]$ = 0.073 M pOH = 1.14
(b) $[OH^-]$ = 1.75 M pOH = −0.24
(c) $[OH^-]$ = 2 × 0.045 M = 0.090 M pOH = 1.05
(d) $[H_3O^+] = 9.1 \times 10^{-2}$ pH = 1.04 pOH = 12.96

42. (a) pH = 14.00 – 1.14 = 12.86
(b) pH = 14.00 – (−0.24) = 14.24
(c) pH = 14.00 – 1.05 = 12.95
(d) pH = 1.04

15.6A $CH_3CH_2COOH + H_2O \rightleftharpoons CH_3CH_2COO^- + H_3O^+$

$$K_a = 1.3 \times 10^{-5} = \frac{[H_3O^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

$[CH_3CH_2COOH] = 0.250 - [H_3O^+]$

Assumption: Self-ionization of water is negligible, so that $[H_3O^+] = [CH_3CH_2COO^-]$.

$$K_a = 1.3 \times 10^{-5} = \frac{[H_3O^+]^2}{0.250 - [H_3O^+]}$$

Assume $0.250 >> [H_3O^+]$.

$[H_3O^+] = 1.8 \times 10^{-3}$ M

Assumption is good.

pH = 2.74

15.6B $$[C_6H_4NO_2OH] = \frac{2.1\text{ g}}{\text{L}} \times \frac{\text{mole}}{139\text{ g}} = 0.015\text{ M}$$

$C_6H_4NO_2OH + H_2O \rightleftharpoons H_3O^+ + C_6H_4NO_2O^-$

Initial, M:	0.015	≈ 0	–
Change, M:	-y	+y	+y
Equilibrium, M:	0.015 -y	y	y

$$Ka = \frac{[H_3O^+][C_6H_4NO_2O^-]}{[C_6H_4NO_2OH]} = \frac{y^2}{0.015 - y} = 6.0 \times 10^{-8}$$

Assume 0.015 >> y.

$y^2 = 9.0 \times 10^{-10}$

$y = 3.0 \times 10^{-5} = [H_3O^+]$ Assumption is good.

$pH = -\log[H_3O^+] = -\log(3.0 \times 10^{-5}) = 4.52$

31. (a) H_2Se is stronger because it has a larger anion radius and lower bond dissociation energy than H_2S, so the H^+ is easier to remove.

(b) $HClO_3$ is stronger because Cl is more electronegative than I. The electron density is pulled alway from the —OH bond more in $HClO_3$ than in HIO_3.

(c) H_3AsO_4 is stronger than $H_2PO_4^-$ because the H^+ does not have to be removed from a -2 ion , only a -1 ion.

(d) HBr is stronger because Br is to the right of Se in the periodic table, so the ΔEN is greater between H and Br than between H and Se.

(e) HN_3 is stronger because the ΔEN is greater between N and H than between C and H.

(f) HNO_3 is stronger. The H^+ is separated from NO_3^- against a pull of -1, not -2, as in SO_4^{2-}.

47. (a) $K_a = 4.9 \times 10^{-5} = \dfrac{[H^+][C_8H_7O_2^-]}{[HC_8H_7O_2]}$

$$4.9 \times 10^{-5} = \frac{[H^+]^2}{0.22}$$

$[H^+]^2 = 1.08 \times 10^{-5}$

$[H^+] = 3.28 \times 10^{-3}$ M

pH = 2.48

(b) $M = \dfrac{32.9 \text{ g HCOOH}}{L} \times \dfrac{\text{mol HCOOH}}{46.03 \text{ g HCOOH}} = 0.715$ M

$$1.8 \times 10^{-4} = \frac{[H_3O^+][HCOO^-]}{[HCOOH]} = \frac{[H_3O^+]^2}{0.715}$$

$[H_3O^+] = 1.1 \times 10^{-2}$ M

pH = 1.95

48. (a) $K_b = 6.3 \times 10^{-10} = \dfrac{[OH^-][C_9H_7NH^+]}{[C_9H_7N]}$

$$6.3 \times 10^{-10} = \frac{[OH^-]^2}{0.084}$$

$[OH^-]^2 = 5.3 \times 10^{-11}$

$[OH^-] = 7.3 \times 10^{-6}$ M

pOH = 5.14

pH = 8.86

(b) $[NH_2OH] = \dfrac{5.65 \text{ g}}{226 \text{ mL}} \times \dfrac{\text{mL}}{10^{-3} \text{ L}} \times \dfrac{\text{mol}}{33.03 \text{ g}} = 0.757$ M

$$9.1 \times 10^{-9} = \frac{[OH^-][NH_3OH^+]}{[NH_2OH]} = \frac{[OH^-]^2}{0.757}$$

$[OH^-] = 8.30 \times 10^{-5}$

pOH = 4.08

pH = 9.92

45. $[OH^-] = 2 \times 0.0062 = 0.0124$ M pOH = 1.91 pH = 12.09
The $Ba(OH)_2$ is more basic and, thus, has the higher pH..

46. $[H_3O^+] = 0.00048 \times 2 = 0.00096$ M pH = 3.02
The vinegar (pH = 2.42) is more acidic. Even if both H^+ ionize, the pH of the $H_2SO_4(aq)$ can be no lower than 3.02.

49. $[H_3O^+] = 10^{-4.90} = 1.26 \times 10^{-5}$ M

$$K_a = \frac{[H_3O^+]^2}{[C_3H_5OH]} = 1.0 \times 10^{-10}$$

$$[C_3H_5OH] = \frac{(1.26 \times 10^{-5})^2}{1.0 \times 10^{-10}} = 1.6 \text{ M}$$

50. $[H_3O^+] = 10^{-3.10} = 7.94 \times 10^{-4}$ M, $K_a = 10^{-4.72} = 1.9 \times 10^{-5}$

$$K_a = \frac{[H_3O^+]^2}{[HN_3]} = \frac{[H_3O^+]^2}{M - 7.94 \times 10^{-4}} = 1.9 \times 10^{-5}$$

Assume $M >> 7.94 \times 10^{-4}$ M.

$$\frac{[H_3O^+]^2}{M} = \frac{(7.94 \times 10^{-4})^2}{M} = 1.9 \times 10^{-5}$$

$M = 3.3 \times 10^{-2}$

64. (a) $CH_3CH_2COO^- + H_2O \rightleftharpoons CH_3CH_2COOH + OH^-$
basic

(b) $Mg(NO_3)_2(aq)$ should be neutral because Mg^{2+} would be from a strong base and NO_3^- would be from a strong acid.

(c) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ $K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$

$CN^- + H_2O \rightleftharpoons HCN + OH^-$ $K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$

Because $K_a(NH_4^+)$ is smaller than $K_b(CN^-)$, hydrolysis of CN^- occurs more extensively than that of NH_4^+, and the solution will be basic.

81. $$[H_3O^+] = K_a \times \frac{[\text{acid}]}{[\text{base}]} = 1.8 \times 10^{-4} \times \frac{0.405}{0.326}$$

$[H_3O^+] = 2.24 \times 10^{-4}$ M

pH = 3.65

82. $$[H_3O^+] = \frac{K_w}{K_b}\frac{[\text{acid}]}{[\text{base}]} = \frac{10^{-14} \times 0.186}{4.2 \times 10^{-4} \times 0.245} = 1.8 \times 10^{-11} \text{ M}$$

pH = 10.74

95. In a strong base–strong acid titration; (1) the initial pH is high because the base is completely ionized; (2) at the half-neutralization point, the pH depends on the concentration of the base remaining (half has been neutralized); (3) at the equivalence point, the pH is 7.00 because neither cation nor anion ionize; (4) the steep portion of the curve is over a wide range; (5) the choice of indicators is extensive. Any indicator with a color change in the pH range of 4 to 10 will work. The same indicator can be used for either titration because the region of rapid pH change (steep portion of titration curve) is the same in either case; it is just appoached from a different direction. (Something not discussed in the text is that since it is easier to see the color change from a light to a dark color, usually the same indicator is not used for both types of titrations.)

96. In contrast to a strong base–strong acid titration, in the titration of a weak base by a strong acid: (1) the initial pH is lower because the weak base is only partially ionized; (2) at the half-neutralization point, pH = pK_b, in a buffer solution in which the concentrations of the weak base and its conjugate acid are equal; (3) the pH < 7 at the equivalence point because the cation of the weak base hydrolyzes; (4) the steep portion of the curve at the equivalence point is confined to a smaller pH range; (5) the choice of indicators is more limited. Only those with a color change in the pH range of about 3 to 6 will work (see curve on page 663).
The pH at the equivalence point of the weak base–strong acid titration is well below 7, whereas that of the weak acid–strong base titration is well above 7. Thus, the same indicator cannot be used for both titrations.