Chapter 17

2)

a) HCl and CH_3COOH are both acids. A buffer must have an acid/base conjugate pair.
b) NaH_2PO_4 and Na_2HPO_4 are an acid/base conjugate pair. They will make an
      excellent buffer.
c) H_2CO_3 and $NaHCO_3$ are also an acid/base conjugate pair and they will make an
      excellent buffer. The carbonic acid/bicarbonate buffer plays an important role in
      maintaining the pH of your blood at a constant value.

4) Solutions containing acid-base buffers are resistant to change in the pH of the solution
when H_3O^+ or OH^- is added or removed. Buffers are effective when the concentrations of
the weak acid (NH_4^+) and conjugate base (NH_3) are large compared to the amount of
H_3O^+ or OH^- ions added or removed. When H_3O^+ is added to the solution from an
external source, such as HCl, some of the base NH_3 of the buffer is converted to
NH_4^+(thus using up most of the protons added); when hydroxide ions are added to the
solution (from NaOH), protons are dissociated from some of the $NH_4^+$of the buffer,
converting them to NH_3 (and thus using up most of the OH- added). However, because of
the presence of the weak acid and conjugate base in solution, the change in H_3O^+ or OH^-
concentration is small relative to the amounts of these species present in solution and the
change in pH will be small.

15) Buffers works best when the pK_a corresponds to the desired pH. To determine
      which choice is best, we need to look up the pK_a (or Ka) values associated with
      each acid/base conjugate pair. Recall $pK_a = -logK_a$

H_3PO_4/NaH_2PO_4 $K_a = 7.5 \times 10^{-3}$ pKa = 2.1
NaH_2PO_4/Na_2HPO_4 $K_a = 6.2 \times 10^{-8}$ pKa = 7.2
Na_2HPO_4/Na_3PO_4 $K_a = 3.6 \times 10^{-13}$ pKa = 12

      The best buffer choice for pH 7 is NaH_2PO_4/Na_2HPO_4.

19)

a) A concentration of hydronium (H_3O^+) ions of 4.5×10^{-3} M will generate a pH of 2.3
($pH = -log[H_3O^+]$). The best choice from Table 7.1 is lactic acid/lactate since it as a pK_a
of 3.85. However, note that phosphoric acid, with a pK_a of 2.1, would actually be better.

b) A concentration of hydronium (H_3O^+) ions of 5.2×10^{-8} M will generate a pH of 7.3
($pH = -log[H_3O^+]$). The best choice from Table 7.1 is NaH_2PO_4/Na_2HPO_4 since it as a
pK_a of 7.2.

c) A concentration of hydronium (H_3O^+) ions of 8.3 x 10^{-6} M will generate a pH of 5.1 (pH = -log[H_3O^+]). The best choice from Table 7.1 is acetic acid/acetate since it as a pK_a of 4.7.

d) A concentration of hydronium (H_3O^+) ions of 9.7 x 10^{-11} M will generate a pH of 10 (pH = -log[H_3O^+]). The best choice from Table 7.1 is HCO_3^-/CO_3^{-2} since it as a pK_a of 10.3.

23) How many grams of benzoic acid must be added to the 1 L solution?

> We know the following: We have 14.4 g sodium benzoate.
> We want a pH of 3.88

> We can look up in appendix F that the K_a for benzoic acid is 6.3 x 10^{-5}.

> Using the looked up K_a value, we can calculate the pK_a value.
> pK_a = -logK_a = 4.2

> We can calculate that the MW of sodium benzoate is 144 g/mol. This lets us calculate the concentration of benzoate to be 0.10 M.

> The Henderson-Hasselbalch equation is:

$$pH = pKa + \log \frac{[A-]}{[HA]}$$

> We know all of these values now except HA. Plugging into the equation:

$$3.88 = 4.2 + \log \frac{0.1}{x} \qquad x = 0.21 \text{ M}$$

Thus, we need 0.21 mols in the 1 liter solution. The MW of benzoic acid is 122.6 g/mol, requiring 25.6 g = 26 g using sig fig.

27)

a) CH_3COOH/CH_3COONa is an acid/base conjugate pair and will form a buffer.

b) The sodium hydroxide will react completely with the acetic acid to form water and sodium acetate. This is the same acid/base conjugate pair discussed in part a).

c) HCl and acetic acid are both acids. No conjugate base is present and a buffer is not formed.

d) The addition of 0.3 mol of sodium hydroxide consumes all of the acetic acid. Thus, there is no acid present, only base. Without the acid present, a buffer is not formed.

29) You can solve this problem using ICE tables and the equilibrium constant to determine the $[H_3O^+]$ or you can more conveniently solve the problem using the Henderson-Hasselbalch equation.

Part 1. Calculate the pH change upon adding 10.0 mL 0.10 M NaOH to 90 mL water.

10.0 mL	0.10 mol		= 0.010 M NaOH
	1000 mL	0.100 L	

$[OH-] = 0.010$ M   since NaOH is a strong base that dissociates 100%
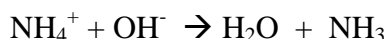
$pOH = -\log[0.010] = 2.0$ $pH = 14 - pOH = 12$

Could also solve by $K_w = 1 \times 10^{-14} = [H_3O^+][OH^-] = [H_3O^+] \times 0.010$
$\qquad\qquad [H_3O^+] = 1.0 \times 10^{-12}$ $pH = -\log(1.0 \times 10^{-12}) = 12$

Since the pH of water is 7, the total pH change in this chase is five pH units (or five orders of magnitude in $[H_3O^+]$).

Part 2. Calculate the pH change upon adding 10.0 mL 0.10 M NaOH to 90 mL buffer containing 1.0 M NH_3 and 1.0 M NH_4Cl.

The key reaction with the buffer will be:

$$NH_4^+ + OH^- \rightarrow H_2O + NH_3$$

The strong base will react with the ammonium cation in the buffer and completely convert it to ammonia. The number of moles of base added are:

10.0 mL	0.10 mol	= 0.0010 mol NaOH
	1000 mL	

The number of moles of NH_4^+ and NH_3 present are:

1.0 mol	90 mL	= 0.090 mol
1000 mL		

So we start with 0.090 mol of both NH_4^+ and NH_3. After complete reaction with 0.0010 mol NaOH the resulting amounts of each are:

$0.090 - 0.0010 = 0.089$ mol NH_4^+
$0.090 + 0.0010 = 0.091$ mol NH_3

To use Henderson-Hasselbalch equation we need to know the pK_a value.

$1 \times 10^{-14} = K_a * K_b$ $K_a = 1 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$ (or look up in table)

So,

$$pH = pKa + \log \frac{[A-]}{[HA]}$$

We know all of these values now except pH. Plugging into the equation:

$$pH = -\log(5.6 \times 10^{-10}) + \log \frac{0.91}{0.89} = 9.25 + 0.0096 = 9.26 \text{ or } 9.3$$

The pH of the buffer before adding NaOH was

$$pH = -\log(5.6 \times 10^{-10}) + \log 1 = 9.25$$

The pH shift of the buffered sample is 0.01 pH units. Note that within the 2 significant digits of the problem this is essentially no change.

So, the upon addition of 10 mL 1.0 M NaOH, the buffered system shifts by ~0.01 pH units where the unbuffered system shifts by 5 pH units.

Ch 5.

38)

a) S +6, 0 -2

b) H +1, N +5, O -2

c) K +1, Mn +7, O -2

d) H+1, O -2

e) Li +1, O -2, H +1

f) C 0, H +1, Cl -1

42)

a) $CrCl_3$ = +3

b) Na_2CrO_4 = Cr+6

c) $K_2Cr_2O_7$ = Cr+6

43) The only redox reaction is (b). In this reaction calcium metal (Ca^0) is oxidized by oxygen gas to Ca +2. The oxygen is reduced from O (0) to O -2. Reaction (a) is a precipitation reaction and reaction (c) is an acid/base reaction.

50)

The strongest oxidizing agent is F_2. The strongest reducing agent is I^-.

51) & 52)

a) NR
b) NaBr + I_2,
Br is reduced, acting as the oxidizing agent and I^- is oxidized, acting as the reducing agent
c) NaF + Cl_2,
F is reduced, acting as the oxidizing agent and Cl^- is oxidized, acting as the reducing agent
d) NaCl +Br_2,
Cl is reduced, acting as the oxidizing agent and Br^- is oxidized, acting as the reducing agent

e) NR
f) NR

56)

a) NR
b) NR
c) NR
d) Au^{3+} + 3 Ag → Au + 3 Ag^+

106)

a) The metal halide compound should be formed. Magnesium Bromide ($MgBr_2$), Calcium Bromide ($CaBr_2$), Strontium Bromide ($SrBr_2$).

b) $Mg + Br_2 \rightarrow MgBr_2$, $Ca + Br_2 \rightarrow CaBr_2$, $Sr + Br_2 \rightarrow SrBr_2$

c) This is a redox reaction in each case. The metal is oxidize and the Bromine is reduced.

d) If the stoichiometry of the products is one metal per two bromine atoms, the ratio of product to metal mass should be 7.6, 5.0, and 2.8 for Mg, Ca, and Sr respectively. This is consistent with the leveling off point for each plot. The plots level off when an amount of metal is used that exceeds the amount of Br_2 available.

The plots become level at different masses of products because the molar mass of the metal is different and therefore the molar mass of the products is different. The ratios of the mass of the products should be Ca:Mg, Sr:Ca, Sr: Mg = 1.08, 1.24, and 1.34 to 1 respectively. This is in agreement with the ratios of the maximum weight values given in the graph.

113) Note: K_2SO_4 is one of the products of this reaction. It is NOT listed in the book.

The net ionic equation is:

$3 C_2H_5OH(aq) + 2 Cr_2O_7^{2-}(aq) + 16 H^+(aq) \rightarrow$

$\qquad 3 CH_3COOH(aq) + 4 Cr^{+3}(aq) + 11 H_2O(l)$
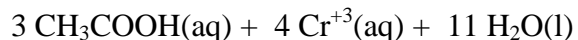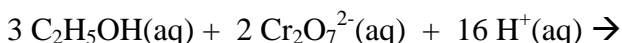
The oxidation number of one of the carbons and that of the Cr are changing.

The ethanol is being oxidized to acetic acid (C^{-1} to C^{+3}) and the Cr is being reduced (Cr^{+6} to Cr^{+3}). These carbon oxidation numbers come from counting as follows; ethanol: one monovalent O (-1) two H (+2) for a net effect at carbon of -1 and acetic acid: one monovalent O (--1), one bivalent O (-2) for a net effect at carbon of +3. You may have looked at the entire molecule and counted the carbon in ethanol as -4 and the carbon in acetic acid as 0. The result is the same: a net change in oxidation number of +4.

The $Cr_2O_7^{2-}$ is the oxidizing agent and the ethanol is the reducing agent.