Chapter 17

2)  
a) HCl and CH$_3$COOH are both acids. A buffer must have an acid/base conjugate pair.
b) NaH$_2$PO$_4$ and Na$_2$HPO$_4$ are an acid/base conjugate pair. They will make an excellent buffer.
c) H$_2$CO$_3$ 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$_3$O$^+$ 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$_3$O$^+$ or OH$^-$ ions added or removed. When H$_3$O$^+$ 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$_3$O$^+$ 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$_a$ = -logKa

<table>
<thead>
<tr>
<th></th>
<th>Ka</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$PO$_4$/NaH$_2$PO$_4$</td>
<td>7.5 x 10$^{-3}$</td>
<td>2.1</td>
</tr>
<tr>
<td>NaH$_2$PO$_4$/Na$_2$HPO$_4$</td>
<td>6.2 x 10$^{-8}$</td>
<td>7.2</td>
</tr>
<tr>
<td>Na$_2$HPO$_4$/Na$_3$PO$_4$</td>
<td>3.6 x 10$^{-13}$</td>
<td>12</td>
</tr>
</tbody>
</table>

The best buffer choice for pH 7 is NaH$_2$PO$_4$/Na$_2$HPO$_4$.

19)  
a) A concentration of hydronium (H$_3$O$^+$) ions of 4.5 x 10$^{-3}$ M will generate a pH of 2.3 (pH = -log[H$_3$O$^+$]). 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$_3$O$^+$) ions of 5.2 x 10$^{-8}$ M will generate a pH of 7.3 (pH = -log[H$_3$O$^+$]). The best choice from Table 7.1 is NaH$_2$PO$_4$/Na$_2$HPO$_4$ since it as a pK$_a$ of 7.2.
c) A concentration of hydronium (H$_3$O$^+$) ions of $8.3 \times 10^{-6}$ 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$_3$O$^+$) ions of $9.7 \times 10^{-11}$ 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 $6.3 \times 10^{-5}$.

Using the looked up K$_a$ value, we can calculate the pK$_a$ value.
$pK_a = -\log K_a = 4.2$

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:

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

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

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

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$_3$COOH/CH$_3$COONa 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 $[\text{H}_3\text{O}^+]$ 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.

\[
\begin{array}{c|c|c|c}
10.0 \text{ mL} & 0.10 \text{ mol} & \text{= 0.010 M NaOH} \\
1000 \text{ mL} & 0.100 \text{ L} & \\
\end{array}
\]

$[\text{OH}^-] = 0.010 \text{ M}$ since NaOH is a strong base that dissociates 100%

$p\text{OH} = -\log[0.010] = 2.0$ \hspace{1cm} $p\text{H} = 14 - p\text{OH} = 12$

Could also solve by $K_w = 1 \times 10^{-14} = [\text{H}_3\text{O}^+] [\text{OH}^-] = [\text{H}_3\text{O}^+] \times 0.010$

$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-12}$ \hspace{1cm} $p\text{H} = -\log(1.0 \times 10^{-12}) = 12$

Since the pH of water is 7, the total pH change in this chase is five pH units (or five orders of magnitude in $[\text{H}_3\text{O}^+]$).

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$_4$Cl.

The key reaction with the buffer will be:

$$\text{NH}_4^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{NH}_3$$

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:

\[
\begin{array}{c|c|c|c}
10.0 \text{ mL} & 0.10 \text{ mol} & \text{= 0.0010 mol NaOH} \\
1000 \text{ mL} & & \\
\end{array}
\]

The number of moles of NH$_4^+$ and NH$_3$ present are:

\[
\begin{array}{c|c|c|c}
1.0 \text{ mol} & 90 \text{ mL} & \text{= 0.090 mol} \\
1000 \text{ mL} & & \\
\end{array}
\]
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.

\[ 1 \times 10^{-14} = K_a \times K_b \]

\[ K_a = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \] (or look up in table)

So,

\[ pH = pK_a + \log \frac{[A^-]}{[HA]} \]

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

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

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$_2$CrO$_4$ = Cr$^6$  

r)  K$_2$C$_{r2}$O$_7$ = 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  

56)

a) NR  
b) NR  
c) NR  
d) Au$^{3+}$ + 3 Ag $\rightarrow$ Au + 3 Ag$^+$
a) The metal halide compound should be formed. Magnesium Bromide (MgBr$_2$), Calcium Bromide (CaBr$_2$), Strontium Bromide (SrBr$_2$).

b) Mg + Br$_2$ → MgBr$_2$, Ca + Br$_2$ → CaBr$_2$, Sr + Br$_2$ → 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$_2$SO$_4$ is one of the products of this reaction. It is NOT listed in the book.

The net ionic equation is:

\[
3 \text{C}_2\text{H}_5\text{OH(aq)} + 2 \text{Cr}_2\text{O}_7^{2-}(aq) + 16 \text{H}^+(aq) \rightarrow \\
3 \text{CH}_3\text{COOH(aq)} + 4 \text{Cr}^{3+}(aq) + 11 \text{H}_2\text{O(l)}
\]

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$_2$O$_7^{2-}$ is the oxidizing agent and the ethanol is the reducing agent.