1. **True or False Statements** [2 pts each]
   
a) When a strong acid is added to a buffer solution, the pH of the solution does not change.  
**FALSE**, a buffer resists change in pH.

b) When F\(^-\) is added to a hydrofluoric acid solution (HF), the pH of the solution increases.  
**TRUE**

c) The pH of a particular HCN/CN\(^-\) buffer is 9. This indicates that [HCN] < [CN\(^-\)]. \([K_a(HCN) = 4.9 \times 10^{-10}]\)  
**FALSE**, p\(K_a\) = 9.31. More acid is needed to decrease pH to 9.

2. You wish to prepare a buffer of pH = 6.50. Which of the following buffers would be most effective at that pH? [3 pts]
   
a) \(\text{NH}_4^+/\text{NH}_3\) \(K_b(\text{NH}_3) = 1.8 \times 10^{-5}\)  
b) \(\text{C}_5\text{H}_5\text{NH}^+\)/\(\text{C}_5\text{H}_5\text{N}\) \(K_b(\text{C}_5\text{H}_5\text{N}) = 1.7 \times 10^{-9}\)

c) \(\text{H}_2\text{CO}_3/\text{HCO}_3^-\) \(K_a(\text{H}_2\text{CO}_3) = 4.2 \times 10^{-7}\)  
d) \(\text{HCN}/\text{CN}^-\) \(K_a(\text{HCN}) = 4.9 \times 10^{-10}\)

e) \(\text{HF}/\text{F}^-\) \(K_a(\text{HF}) = 7.1 \times 10^{-4}\)

3. Identify the buffer systems below by circling which ones are effective buffers. [3 pts]
   
a) \(\text{HBr}/\text{NaBr}\)  
b) \(\text{NH}_3/\text{NH}_4\text{NO}_3\)  
c) \(\text{HCl}/\text{KOH}\)

d) \(\text{NaHCO}_3/\text{Na}_2\text{CO}_3\)  
e) \(\text{CH}_3\text{COOH}/\text{KCH}_3\text{COO}\)  
f) \(\text{HF}/\text{NaCH}_3\text{COO}\)

4. A buffer solution is composed of 1.0 \(M\) \(\text{NH}_3\) and 1.0 \(M\) \(\text{NH}_4\text{Cl}\). Which of the following represents the reaction that occurs when HCl is added to the buffer? [3 pts]
   
a) \(\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{Cl}^-\)  
b) \(\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}\)  
c) \(\text{HCl} + \text{NH}_4^+ \rightarrow \text{H}_2\text{Cl}^+ + \text{NH}_3\)  
d) \(\text{HCl} + \text{NH}_4^+ \rightarrow \text{NH}_5^{2+} + \text{Cl}^-\)

e) \(\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl}\)

5. The pH of a formic acid-formate buffer (HCOOH/HCOO\(^-\)) is 3.25. Calculate the ratio of the concentration of formic acid (HCOOH) to that of the formate ion (HCOO\(^-\)). \([K_a(\text{HCOOH}) = 1.7 \times 10^{-4}]\) [4 pts]

\[
K_a = \frac{[\text{H}_3\text{O}^+] [\text{HCOO}^-]}{[\text{HCOOH}]} \\
\frac{[\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{K_a}{[\text{H}_3\text{O}^+]} = \frac{1.7 \times 10^{-4}}{5.62 \times 10^{-4}} = 0.302 \\
\frac{[\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{1}{0.302} = 3.31
\]

\[
\text{pH} = \log \left[ \frac{\text{base}}{\text{acid}} \right] = pK_a + \log \left[ \frac{\text{base}}{\text{acid}} \right] \\
3.25 = -\log(1.7 \times 10^{-4}) + \log \left[ \frac{\text{base}}{\text{acid}} \right] \\
-0.520 = \log \left[ \frac{\text{base}}{\text{acid}} \right] = \log \left[ \frac{\text{base}}{\text{acid}} \right] = 0.302
\]

\[
\frac{[\text{base}]}{[\text{acid}]} = 0.302 \\
\frac{[\text{acid}]}{[\text{base}]} = \frac{1}{0.302} = 3.31
\]
6. Calculate the pH of the buffer system made up of 0.50 M C₆H₅COOH/0.75 M KC₆H₅COO.

\[ K_a(C_6H_5COOH) = 6.5 \times 10^{-5} \] [4 pts]

\[
\begin{array}{l}
\text{C}_6\text{H}_5\text{COOH (aq)} + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{C}_6\text{H}_5\text{COO}^- (aq)
\end{array}
\]

\[
\begin{array}{c|c|c|c}
\text{Initial (M):} & 0.50 & 0 & 0.75 \\
\text{Change (M):} & -x & +x & +x \\
\text{Equilibrium (M):} & 0.50 - x & x & 0.75 + x \\
\end{array}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} \\
6.5 \times 10^{-5} = \frac{(x)(0.75 + x)}{(0.50 - x)} \approx \frac{(x)(0.75)}{(0.50)} \\
x = [\text{H}_3\text{O}^+] = 4.33 \times 10^{-5} M \\
\text{pH} = 4.33 + 0.176 = 4.50
\]

a) 2.24  b) 4.01  c) 4.19  d) 4.36  e) 9.64

7. Consider 1.00 L of a buffer which is 0.50 M HNO₂/0.50 M NaNO₂.

a) Calculate the pH of this buffer. \([K_a(HNO_2) = 4.5 \times 10^{-4}] \] [2 pts]

\[
\text{pH} = pK_a = -\log(4.5 \times 10^{-4}) = 3.35
\]

b) Calculate the pH of this buffer after the addition of 0.13 mol of NaOH. Assume that there is no change in volume upon addition of NaOH. \([K_a(HNO_2) = 4.5 \times 10^{-4}] \] [5 pts]

\[
\text{HNO}_2 + \text{OH}^- \rightleftharpoons \text{NO}_2^- + \text{H}_2\text{O}
\]

\[
\begin{array}{c|c|c|c}
\text{Initial (mol):} & 0.50 & 0.13 & 0.50 \\
\text{Change (mol):} & -0.13 & +0.13 & +0.13 \\
\text{Final (mol):} & 0.37 & 0 & 0.63 \\
\end{array}
\]

\[
\text{HNO}_2 (aq) + \text{H}_2\text{O (l)} \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{NO}_2^- (aq)
\]

\[
\begin{array}{c|c|c|c}
\text{Initial (M):} & 0.37 & 0 & 0.63 \\
\text{Change (M):} & -x & +x & +x \\
\text{Equilibrium (M):} & 0.37 - x & x & 0.63 + x \\
\end{array}
\]

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} \\
4.5 \times 10^{-4} = \frac{(x)(0.63 + x)}{(0.37 - x)} \approx \frac{(x)(0.63)}{(0.37)} \\
x = [\text{H}_3\text{O}^+] = 2.64 \times 10^{-4} M \\
\text{pH} = 3.58 + 0.231 = 3.81
\]