NAME_____________________

CHEMISTRY 220: FALL 2000

Third Examination: November 15 2000

Inspect your final answer and indicate significant figures where appropriate. If you run out of time, show how you would complete the problem - you will get partial credit. Use the reverse side of the paper if you need more space.

Q.1. (20 points) A buffer solution is made from a 1.00 L solution of 0.100 M benzoic acid, C₆H₅COOH, by adding solid NaOH. The pH of the resulting solution is 4.00 and the pKₐ for benzoic acid is 4.202.

a) Write down charge and mass balance equations for the buffer solution

\[ \text{Charge balance: } [\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{A}^-] \]

b) How much NaOH (in mol) was added to the 1.00 L solution of benzoic acid to give a pH of 4.00?

c) If 0.0500 mol of HCl was added to the buffer solution, what would be the new pH?

\[ \text{a) Mass balance for benzoic acid/benzoate: }  \]
\[ F = 0.100 M = [\text{H}^+] + [\text{A}^-] \]

\[ \text{Charge balance: } [\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{A}^-] \]

\[ \text{b) Since } \text{pH} = 4.00 \]
\[ 4.00 = 4.202 + \log \left( \frac{[\text{A}^-]}{[\text{H}^+]} \right) \]
\[ \log \left( \frac{[\text{A}^-]}{[\text{H}^+]} \right) = -0.202 \Rightarrow \frac{[\text{A}^-]}{[\text{H}^+]} = 0.628 \]
\[ \text{or } [\text{H}^+] = 1.59 \times 10^{-3} \text{ M} \]

\[ \text{From mole eqn: } [\text{OH}^-] + [\text{H}^+] = 0.100 M \]
\[ [\text{A}^-] + 1.59 \times 10^{-3} [\text{A}^-] = 0.100 M \Rightarrow [\text{A}^-] = 0.0386 \text{ M} \]

\[ \text{Since A}^- \text{ could only come from reaction of } \text{H}^+ \text{ with OH}^- \text{,} \]
\[ \text{mol } \text{A}^- = \text{ mol OH}^- \]
\[ \text{mol NaOH added } = 0.0386 \text{ mol A}^- \times \]

\[ \text{c) If 0.0500 mol HCl added, this is more than amount of A}^- \text{, i.e.} \]
\[ [\text{A}^-] + [\text{OH}^-] \rightarrow [\text{HA}] + [\text{H}^+] \]
\[ 0.0386 + 0.0500 = 0.0386 + 0.0500 - 0.0386 \]
\[ \Rightarrow [\text{H}^+]_{\text{excess}} = 0.0114 \text{ M} \]
\[ \Rightarrow \text{pH} = 1.943 \Rightarrow \text{ANS: pH} = 1.943 \]
Q2. (20 points). Calculate the pH of each of the following solutions (assume 1.00 L and that the following species are added in solid form). Identify which solutions are buffers.

a) 0.100 mol \( \text{H}_3\text{PO}_4 \) + 0.100 mol \( \text{Na}_3\text{PO}_4 \)  
Buffer

b) 0.100 mol \( \text{H}_3\text{PO}_4 \) + 0.0500 mol \( \text{NaH}_2\text{PO}_4 \)  
Buffer

c) 0.100 mol \( \text{H}_3\text{PO}_4 \) + 0.0500 mol \( \text{Na}_2\text{HPO}_4 \)  
Buffer

d) 0.100 mol \( \text{Na}_2\text{HPO}_4 \) + 0.100 mol \( \text{Na}_3\text{PO}_4 \)  
Buffer

For phosphoric acid, \( pK_1 = 2.13 \); \( pK_2 = 7.20 \); \( pK_3 = 12.13 \)

\( a \) The acid, \( \text{H}_3\text{PO}_4 \), will react with the base, \( \text{PO}_4^{3-} \).

\[ \text{H}_3\text{PO}_4 + \text{PO}_4^{3-} \rightarrow \text{H}_2\text{PO}_4^- + \text{H}_2\text{PO}_4^{2-} \]

Hence, the solution will contain 0.100 mol \( \text{H}_2\text{PO}_4^- \) and 0.100 mol \( \text{H}_2\text{PO}_4^- \). This is a buffer.

\[ \text{pH} = pK_2 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{PO}_4^2-]} = pK_2 = 7.20 \]

\( b \) This is a buffer for the system

\[ \text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+ \]

\[ \text{pH} = pK_1 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = pK_1 + \log \frac{0.0500}{0.100} \]

\[ = 1.83 \text{ A.N.S.} \]

\( c \) The acid, \( \text{H}_3\text{PO}_4 \), will react with the base \( \text{H}_2\text{PO}_4^- \).

\[ \text{H}_3\text{PO}_4 + \text{H}_2\text{PO}_4^- \rightarrow 2\text{H}_2\text{PO}_4^- \]

i.e. \( 0.0500 \) mol \( \text{H}_2\text{PO}_4^- \) will react with \( 0.0500 \) mol \( \text{H}_3\text{PO}_4 \) to give \( 0.100 \) mol \( \text{H}_2\text{PO}_4^- \) and leave

\( 0.0500 \) mol \( \text{H}_3\text{PO}_4 \)

\[ \text{pH} = pK_1 + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 2.13 + \log \frac{0.100}{0.050} \]

\[ = 2.43 \text{ A.N.S.} \]

\( d \) This is a buffer

\[ \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{PO}_4^{3-} \]

\[ \text{pH} = pK_3 + \log \frac{[\text{PO}_4^{3-}]}{[\text{H}_2\text{PO}_4^-]} = pK_3 = 12.13 \text{ A.N.S.} \]
Q. 3. (20 points) The graph below represents the titration curves of 10.00 mL of 0.100 M solutions of two dibasic bases titrated with 0.100 M HCl. Curve (a) is for a base with \( pK_{a1} = 4.00 \) and \( pK_{a2} = 9.00 \). Curve (b) is for nicotine, \( pK_{a1} = 6.15 \) and \( pK_{a2} = 10.85 \). Answer the following:

a) Indicate the equivalence points for each titration
b) Calculate (i.e. Don't read off the graph) the pH at points B, G, and D, I

c) Calculate the pH at points C and H

d) From the attached table of indicators, suggest appropriate indicators for the titration of each base to the first and second equivalence points

e) Show, with appropriate formulas, how you would calculate the pH of the solutions at points E and J (don't actually perform the numerical calculations)

f) Would you expect a sharp end point for the second end point for nicotine?

No - no sharp end point

\[
\begin{align*}
\text{HA}^- &
\end{align*}
\]

Since molarities of the bases and the HCl are both 0.100 M, the HCl volume to reach first equivalence point is 10.00 mL. To reach the second equivalence point requires additional 10.00 mL (i.e. 20 mL total).

For A_2:

First titration: \( A_2^- + H^+ \rightarrow HA^- \)

Second titration: \( HA^- + H^+ \rightarrow H_2A \)

b) Points B, C - half way to first equivalence point
i.e. \[ [HA^-] = [HA^+] \] \[ pK_{a2} \]

c) Points C, D. Intermediate species, \( HA^- \): \[ pH = \frac{1}{2}(pK_{a1} + pK_{a2}) \]

d) At points E, J, you have solution of \( H_2A \) (\( \text{pK}_{a1} = 0.033 \))
\[ \text{pH calculated as } \quad H_2A \approx H^+ + HA^- \]
\[ 0.033 - x < x < 0 \]
Q.5. (20 points) Glutamic acid is a triprotic amino acid and has the nominal formula:

\[
\text{HOOC-CH-CH}_2\text{CH}_2\text{COOH}
\]

\[
\text{NH}_2
\]

For glutamic acid, \( pK_1 = 2.17 \) (carboxylic acid); \( pK_2 = 4.42 \) (substituent carboxylic acid); \( pK_3 = 9.95 \) (ammonium)

a) Write down the actual structure of glutamic acid
b) Write down the chemical formulas of the four forms of glutamic acid and write the dissociation reactions of this triprotic acid
c) What is the pH of a 0.0500 M solution of glutamic acid?
d) What is the pH of a 0.0500 M solution of monosodium glutamate, \( \text{HOOC-CH-CH}_2\text{CH}_2\text{COONa} \)

\[
\text{NH}_2
\]

\[
\text{a)} \quad \text{HOOC-CH-CH}_2\text{CH}_2\text{COOH} \\
\text{b)} \quad \text{HOOC-CH-CH}_2\text{CH}_2\text{COONa}
\]

c) glutamic acid \( \text{H}_2\text{G} \) is \( \text{Ko} \)

first intermediate form

\[
pH = \frac{1}{2} (pK_1 + pK_2) = 3.30
\]

d) monosodium glutamate, \( \text{i.e. } \text{H}_2\text{G}^- \) in the second intermediate form

\[
pH = \frac{1}{2} (pK_2 + pK_3) = 7.19
\]

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Useful formulas: \( K_w = 1.00 \times 10^{-14} \) at 25°C. \( \text{pH} = 0.5(pK_1 + pK_2) \)
<table>
<thead>
<tr>
<th>Indicator</th>
<th>Transition range (pH)</th>
<th>Acid color</th>
<th>Base color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl violet</td>
<td>0.0–1.6</td>
<td>Yellow</td>
<td>Violet</td>
</tr>
<tr>
<td>Cresol red</td>
<td>0.2–1.8</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>1.2–2.8</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Cresol purple</td>
<td>1.2–2.8</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Erythrosine, disodium</td>
<td>2.2–3.6</td>
<td>Orange</td>
<td>Red</td>
</tr>
<tr>
<td>Methyl orange</td>
<td>3.1–4.4</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Congo red</td>
<td>3.0–5.0</td>
<td>Violet</td>
<td>Red</td>
</tr>
<tr>
<td>Ethyl orange</td>
<td>3.4–4.8</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Bromocresol green</td>
<td>3.8–5.4</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>Methyl red</td>
<td>4.8–6.0</td>
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<td>Yellow</td>
</tr>
<tr>
<td>Chlorophenol red</td>
<td>4.8–6.4</td>
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<td>Red</td>
</tr>
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<td>Bromocresol purple</td>
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<td>Purple</td>
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<tr>
<td>p-Nitrophenol</td>
<td>5.6–7.6</td>
<td>Colorless</td>
<td>Yellow</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Transition range (pH)</th>
<th>Acid color</th>
<th>Base color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litmus</td>
<td>5.0–8.0</td>
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<td>Blue</td>
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<td>Bromothymol blue</td>
<td>6.0–7.6</td>
<td>Yellow</td>
<td>Blue</td>
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<td>Phenol red</td>
<td>6.4–8.0</td>
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<td>Red</td>
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<tr>
<td>Neutral red</td>
<td>6.8–8.0</td>
<td>Red</td>
<td>Yellow</td>
</tr>
<tr>
<td>Cresol red</td>
<td>7.2–8.8</td>
<td>Yellow</td>
<td>Red</td>
</tr>
<tr>
<td>α-Naphtholphthalein</td>
<td>7.3–8.7</td>
<td>Pink</td>
<td>Green</td>
</tr>
<tr>
<td>Cresol purple</td>
<td>7.6–9.2</td>
<td>Yellow</td>
<td>Purple</td>
</tr>
<tr>
<td>Thymol blue</td>
<td>8.0–9.6</td>
<td>Yellow</td>
<td>Blue</td>
</tr>
<tr>
<td>Phenolphthalein</td>
<td>8.0–9.6</td>
<td>Colorless</td>
<td>Red</td>
</tr>
<tr>
<td>Thymolphthalein</td>
<td>8.3–10.5</td>
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<td>Blue</td>
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<td>Alizarin yellow</td>
<td>10.1–12.0</td>
<td>Yellow</td>
<td>Orange-red</td>
</tr>
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<td>Nitramine</td>
<td>10.8–13.0</td>
<td>Colorless</td>
<td>Orange-brown</td>
</tr>
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<td>Tropaeolin O</td>
<td>11.1–12.7</td>
<td>Yellow</td>
<td>Orange</td>
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