When strong acid or strong base is added to a bicarbonate/carbonate mixture, the strong acid/base is neutralized. The reaction goes to completion, resulting in the strong acid/base being replaced with a weak acid/base, which results in a new buffer solution. The reactions are:

\[
\text{H}^+(\text{aq}) + \text{CO}_3^{2-} (\text{aq}) \rightarrow \text{HCO}_3^- (\text{aq}); \quad \text{OH}^- (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightarrow \text{CO}_3^{2-} (\text{aq}) + \text{H}_2\text{O(l)}
\]

15.23

a. This is a weak acid problem. Let \( \text{HC}_3\text{H}_5\text{O}_2 = \text{HOPr} \) and \( \text{C}_3\text{H}_5\text{O}_2^- = \text{OPr}^- \).

\[
\text{HOPr} \rightleftharpoons \text{H}^+ + \text{OPr}^- \quad K_a = 1.3 \times 10^{-5}
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.100 M</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.100 – x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = 1.3 \times 10^{-5} = [\text{H}^+][\text{OPr}^-] / [\text{HOPr}] = x^2 / 0.100 - x \approx x^2 / 0.100
\]

\[
x = [\text{H}^+] = 1.1 \times 10^{-3} \text{ M; pH} = 2.96 \quad \text{Assumptions are good by the 5% rule.}
\]

b. This is a weak base problem (\( \text{Na}^+ \) has no acidic/basic properties).

\[
\text{OPr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOPr} + \text{OH}^- \quad K_b = K_w / K_a = 7.7 \times 10^{-10}
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.100 M</th>
<th>0</th>
<th>0.100 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.100 – x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_b = 7.7 \times 10^{-10} = [\text{HOPr}][\text{OH}^-] / [\text{OPr}^-] = x^2 / 0.100 - x \approx x^2 / 0.100
\]

\[
x = [\text{OH}^-] = 8.8 \times 10^{-6} \text{ M; pOH} = 5.06; \text{pH} = 8.94 \quad \text{Assumptions good.}
\]

c. pure \( \text{H}_2\text{O}, [\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M; pH} = 7.00 

d. This solution contains a weak acid and its conjugate base. This is a buffer solution. We will solve for the pH using the weak acid equilibrium reaction.

\[
\text{HOPr} \rightleftharpoons \text{H}^+ + \text{OPr}^- \quad K_a = 1.3 \times 10^{-5}
\]

<table>
<thead>
<tr>
<th>Initial</th>
<th>0.100 M</th>
<th>0</th>
<th>0.100 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.100 – x</td>
<td>x</td>
<td>0.100 + x</td>
</tr>
</tbody>
</table>

\[
1.3 \times 10^{-5} = (0.100 + x) (x) / (0.100 - x) \approx (0.100)(x) / 0.100 = x = [\text{H}^+]
\]
\[ [H^+] = 1.3 \times 10^{-5}; \text{pH} = 4.89 \] Assumptions good.

Alternatively, we can use the Henderson-Hasselbalch equation to calculate the pH of buffer solutions.

\[ \text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}]} = \text{pK}_a + \log (0.100) / (0.100) = -\log (1.3 \times 10^{-5}) = 4.89 \]

The Henderson-Hasselbalch equation will be valid when an assumption of the type \(0.1 + x \approx 0.1\) that we just made in this problem is valid. From a practical standpoint, this will almost always be true for useful buffer solutions. If the assumption is not valid, the solution will have such a low buffering capacity that it will be of no use to control the pH. Note: The Henderson-Hasselbalch equation can only be used to solve for the pH of buffer solutions.

15.25

0.100 M HC\textsubscript{3}H\textsubscript{5}O\textsubscript{2}: percent dissociation = \(\frac{[H^+]}{[HC_3H_5O_2]}\times100 = 1.1 \times 10^{-3} \text{ M} / 0.100 \text{ M} = 1.1\%\)

0.100 M HC\textsubscript{3}H\textsubscript{5}O\textsubscript{2} + 0.100 M NaC\textsubscript{3}H\textsubscript{5}O\textsubscript{2}: % dissociation = \(1.3 \times 10^{-5} / 0.100 \times 100 = 1.3 \times 10^{-2} \%\)

The percent dissociation of the acid decreases from 1.1% to 1.3 \times 10^{-2} \% when C\textsubscript{3}H\textsubscript{5}O\textsubscript{2} is present. This is known as the common ion effect. The presence of the conjugate base of the weak acid inhibits the acid dissociation reaction.

14.27

a. We have a weak acid HOPr = HC\textsubscript{3}H\textsubscript{5}O\textsubscript{2}) and a strong acid (HCl) present. The amount of H\textsuperscript{+} donated by the weak acid will be negligible as compared to the 0.020 M H\textsuperscript{+} from the strong acid. To prove it let’s consider the weak equilibrium reaction:

\[ \text{HOPr} \rightleftharpoons \text{H}^+ + \text{OPr}^- \quad \text{K}_a = 1.3 \times 10^{-5} \]

Initial 0.100 M 0.020 M 0
\(x \text{ mol/L HOPr dissociates to reach equilibrium}\)
Change \(-x\) \(+x\) \(+x\)
Equil. \(0.100 - x\) \(0.020\) \(+x\) \(x\)

\[ \text{K}_a = 1.3 \times 10^{-5} = \frac{(0.020 + x)(x)}{(0.100 - x)} \approx \frac{(0.020)(x)}{0.100}, x = 6.5 \times 10^{-5} \text{ M} \]

\[ [H^+] = 0.020 + x = 0.020 \text{ M}; \text{pH} = 1.70 \] Assumptions good \((x = 6.5 \times 10^{-5} \text{ which is <<0.020}).\)

b. Added H\textsuperscript{+} reacts completely with the best base present, OP\textsuperscript{r}. Since all species present are in the same volume of solution, we can use molarity units to do the stoichiometry part of the problem (instead of moles). The stoichiometry problem is:

\[ \text{OPr}^- + \text{H}^+ \rightarrow \text{HOPr} \]

Before 0.100 M 0.020 M 0
Change \(-0.020\) \(-0.020\) \(+0.020\)
After 0.080 0 0.020 M

Reacts completely
After reaction, a weak acid, HOPr, and its conjugate base, OPr\(^-\), are present. This is a buffer solution. Using the Henderson-Hasselbalch equation where \( pK_a = -\log(1.3 \times 10^{-5}) = 4.89 \):

\[
pH = pK_a + \log \left[ \frac{\text{Base}}{\text{Acid}} \right] = 4.89 + \log \left(\frac{0.080}{0.020}\right) = 5.49 \quad \text{Assumptions good.}
\]

c. This is a strong acid problem. \([H^+] = 0.020 \text{ M}; \text{pH} = 1.70\]

d. Added \(H^+\) reacts completely with the best base present, OPr\(^-\).

\[
\text{OPr}^- + H^+ \rightarrow \text{HOPr}
\]

<table>
<thead>
<tr>
<th>Before</th>
<th>0.100 M</th>
<th>0.020 M</th>
<th>0.100 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-0.020</td>
<td>-0.020</td>
<td>+0.020</td>
</tr>
<tr>
<td>After</td>
<td>0.080</td>
<td>0</td>
<td>0.120</td>
</tr>
</tbody>
</table>

A buffer solution results (weak acid + conjugate base). Using the Henderson-Hasselbalch equation:

\[
pH = pK_a + \log \left[ \frac{\text{Base}}{\text{Acid}} \right] = 4.89 + \log \left(\frac{0.080}{0.120}\right) = 4.71
\]

15.29

a. \(\text{OH}^-\) will react completely with the best acid present, HOPr.

\[
\text{HOPr} + \text{OH}^- \rightarrow \text{OPr}^- + \text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Before</th>
<th>0.100 M</th>
<th>0.020 M</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change</td>
<td>-0.020</td>
<td>-0.020</td>
<td>+0.020</td>
</tr>
<tr>
<td>After</td>
<td>0.080</td>
<td>0</td>
<td>0.020</td>
</tr>
</tbody>
</table>

A buffer solution results after the reaction. Using the Henderson-Hasselbalch equation:

\[
pH + pK_a + \log \left[ \frac{\text{Base}}{\text{Acid}} \right] = 4.89 + \log \left(\frac{0.020}{0.080}\right) = 4.29
\]

15.31

b. We have a weak base and a strong base present at the same time. The amount of \(\text{OH}^-\) added by the weak base will be negligible compared to the 0.020 M \(\text{OH}^-\) from the strong base. To prove it, let’s consider the weak base equilibrium:

\[
\text{OPr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOPr} + \text{OH}^- \quad K_b = 7.7 \times 10^{-10}
\]

Initial | 0.100 M | 0 | 0.020 M \\
\(x\) mol/L \(\text{OPr}^-\) reacts with \(\text{H}_2\text{O}\) to reach equilibrium \\
Change | -\(x\) | +\(x\) | +\(x\) \\
Equil. | \(0.100 - x\) | \(x\) | \(0.020 + x\)

\[
K_b = 7.7 \times 10^{-10} = (x)(0.020 + x) / (0.100 - x) \approx (x)(0.020) / (0.100), x = 3.9 \times 10^{-9} \text{ M}
\]

\[
[\text{OH}^-] = 0.020 + x = 0.020 \text{ M}; \text{pOH} = 1.70; \text{pH} = 12.30 \quad \text{Assumptions good.}
\]
c. 
This is a strong base in water. \([\text{OH}^-] = 0.020 \, \text{M}; \, \text{pOH} = 1.70; \, \text{pH} = 12.30\)

d. 
OH\(^-\) will react completely with HOPr, the best acid present.

\[
\begin{array}{ccc}
\text{HOPr} & \text{+} & \text{OH}\(^-\) \rightarrow \text{OPr}\(^-\) & \text{+} & \text{H}_2\text{O} \\
\hline
\text{Before} & 0.100 \, \text{M} & 0.020 \, \text{M} & 0.100 \, \text{M} \\
\text{Change} & -0.020 & -0.020 & +0.020 & \text{Reacts completely} \\
\text{After} & 0.080 & 0 & 0.120
\end{array}
\]

Using the Henderson-Hasselbalch equation to solve for the pH of the resulting buffer solution:

\[
\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}]} = 4.89 + \frac{0.120}{0.080} = 5.07
\]

15.31
Consider all of the results to Exercises 15.23, 15.27, and 15.29:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Initial pH</th>
<th>after added acid</th>
<th>after added base</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>2.96</td>
<td>1.70</td>
<td>4.29</td>
</tr>
<tr>
<td>b</td>
<td>8.94</td>
<td>5.49</td>
<td>12.30</td>
</tr>
<tr>
<td>c</td>
<td>7.00</td>
<td>1.70</td>
<td>12.30</td>
</tr>
<tr>
<td>d</td>
<td>4.89</td>
<td>4.71</td>
<td>5.07</td>
</tr>
</tbody>
</table>

15.33
Major species: HNO\(_2\), NO\(_2\)^-\), and Na\(^+\). Na\(^+\) has no acidic or basic properties. One appropriate equilibrium reaction you can use is the K\(_a\) reaction of HNO\(_2\) which contains both HNO\(_2\) and NO\(_2\)^-\). However, you could also use the K\(_b\) reaction for NO\(_2\)^-\) and come up with the same answer.

Solving the equilibrium problem (called a buffer problem):

\[
\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}^+ \\
\text{Initial} \quad 1.00 \, \text{M} \quad 1.00 \, \text{M} \quad 0 \\
\text{Change} \quad -x \quad +x \quad +x \\
\text{Equil.} \quad 1.00 - x \quad 1.00 - x \quad x
\]

\[
\text{K}_a = 4.0 \times 10^{-4} = \frac{[\text{NO}_2^-][\text{H}^+]}{[\text{HNO}_2]} = \frac{(1.00 + x)(x)}{(1.00 - x) \approx (1.00)(x) / 1.00} \quad \text{(assuming} \, x \ll 1.00) \\
\]

\[
x = 4.0 \times 10^{-4} \, \text{M} = [\text{H}^+] ; \quad \text{Assumptions good (} \, x \text{ is} \, 4.0 \times 10^{-2}\% \text{ of } 1.00). \\
\text{pH} = -\log (4.0 \times 10^{-4}) = 3.40
\]

Note: We would get the same answer using the Henderson-Hasselbalch equation. Use whichever method you prefer.

15.35
Major species after NaOH added: HNO\(_2\), NO\(_2\)^-, Na\(^+\) and OH\(^-\). The OH\(^-\) from the strong base will react with the best acid present (HNO\(_2\)). Any reaction involving a strong base is assumed to go to completion. Since all species present are in the same volume of solution, we can use molarity units to do the stoichiometry part of the problem (instead of moles). The stoichiometry problem is:
\[
\text{OH}^- + \text{HNO}_2 \rightarrow \text{NO}_2^- + \text{H}_2\text{O}
\]

Before: 0.10 mol/1.00 L 1.00 M 1.00 M
Change: -0.10 M -0.10 M +0.10 M Reacts completely
After: 0 0.90 1.10

After all the OH\(^-\) reacts, we are left with a solution containing a weak acid (HNO\(_2\)) and its conjugate base (NO\(_2^-\)). This is what we call a buffer problem. We will solve this buffer problem using the \(K_a\) equilibrium reaction.

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

Initial: 0.90 M 1.10 M 0

\(x\) mol/L HNO\(_2\) dissociates to reach equilibrium
Change: -\(x\) +\(x\) +\(x\)
Equil.: 0.90 - \(x\) 1.10 + \(x\) \(x\)

\[
K_a = 4.0 \times 10^{-4} = \frac{(1.10 + x)(x)}{(0.90 - x)} \approx \frac{(1.10)(x)}{(0.90)}, \quad x = [H^+] = 3.3 \times 10^{-4} \text{ M};
\]

\[
\text{pH} = 3.48; \quad \text{Assumptions good.}
\]

Note: The added NaOH to this buffer solution changes the pH only from 3.40 to 3.48. If the NaOH were added to 1.0 L of pure water, the pH would change from 7.00 to 13.00.

Major species after HCl added: HNO\(_2\), NO\(_2^-\), H\(^+\), Na\(^+\), Cl\(^-\); The added H\(^+\) from the strong acid will react completely with the best base present (NO\(_2^-\)).

\[
\text{H}^+ + \text{NO}_2^- \rightarrow \text{HNO}_2
\]

Before: 0.20 mol/1.00 L 1.00 M 1.00 M
Change: -0.20 M -0.20 M +0.20 M Reacts completely
After: 0 0.80 1.20

After all the H\(^+\) has reacted, we have a buffer solution (a solution containing a weak acid and its conjugate base). Solving the buffer problem:

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

Initial: 1.20 M 0.80 M 0
Equil.: 1.20 - \(x\) 0.80 + \(x\) \(x\)

\[
K_a = 4.0 \times 10^{-4} = \frac{(0.80 + x)(x)}{(1.20 - x)} \approx \frac{(0.80)(x)}{1.20}, \quad x = [H^+] = 6.0 \times 10^{-4} \text{ M};
\]

\[
\text{pH} = 3.22; \quad \text{Assumptions good.}
\]

Note: The added HCl to this buffer solution changes the pH only from 3.40 to 3.22. If the HCl were added to 1.0 L of pure water, the pH would change from 7.00 to 0.70.

**15.37**

[HC\(_7\)H\(_5\)O\(_2\)] = \([21.5 \text{ g HC}_7\text{H}_5\text{O}_2 \times 1 \text{ mol HC}_7\text{H}_5\text{O}_2 / 122.12 \text{ g}] / 0.2000 \text{ L} = 0.880 \text{ M}\]

[C\(_7\)H\(_5\)O\(_2\)\(^-\)] = \([37.7 \text{ g NaC}_7\text{H}_5\text{O}_2 \times 1 \text{ mol NaC}_7\text{H}_5\text{O}_2 / 144.10 \text{ g} \times 1 \text{ mol C}_7\text{H}_5\text{O}_2^- / 1 \text{ mol NaC}_7\text{H}_5\text{O}_2 ] / 0.2000 \text{ L} = 1.31 \text{ M}\]
We have a buffer solution since we have both a weak acid and its conjugate base present at the same time. One can use the $K_a$ reaction or the $K_b$ reaction to solve. We will use the $a$ reaction for the acid component of the buffer.

$$\text{HC}_7\text{H}_5\text{O}_2 \rightleftharpoons \text{H}^+ + \text{C}_7\text{H}_5\text{O}_2^-$$

Initial: 0.880 M, 0, 1.31 M

$x$ mol/L of $\text{HC}_7\text{H}_5\text{O}_2$ dissociates to reach equilibrium

Change: $-x$, $+x$, $+x$

Equil: 0.880 $- x$, $x$, 1.31 $+ x$

$K_a = 6.4 \times 10^{-5} = (x)(1.31 + x) / (0.880 - x) \approx (x)(1.31) / (0.880)$, $x = [\text{H}^+] = 4.3 \times 10^{-5}$ M

$pH = -\log (4.3 \times 10^{-5}) = 4.37$; Assumptions good.

Alternatively, we can use the Henderson-Hasselbalch equation to calculate the pH of buffer solutions.

$$pH = pK_a + \log [\text{Base}] / [\text{Acid}] = pK_a + \log [\text{C}_7\text{H}_5\text{O}_2^-] / [\text{HC}_7\text{H}_5\text{O}_2]$$

$pH = -\log(6.4 \times 10^{-5}) + \log (1.31 / 0.880) = 4.19 + 0.173 = 4.36$

Within round-off error, this is the same answer we calculated solving the equilibrium problem using the $K_a$ reaction.

The Henderson-Hasselbalch equation will be valid when an assumption of the type $1.31 + x \approx 1.31$ that we just made in this problem is valid. From a practical standpoint, this will almost always be true for useful buffer solutions. If the assumption is not valid, the solution will have such a low buffering capacity that it will be of no use to control the pH. Note: The Henderson-Hasselbalch equation can only be used to solve for the pH of buffer solutions.

15.39

$[\text{H}^+]$ added = 0.010 mol / 0.25 L = 0.040 M; The added $\text{H}^+$ reacts completely with $\text{NH}_3$ to form $\text{NH}_4^+$.

a.

$$\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$$

Before: 0.050 M, 0.040 M, 0.15 M

Change: $-0.040$, $-0.040$, $+0.040$ Reacts completely

After: 0.010, 0, 0.19

A buffer solution still exists after $\text{H}^+$ reacts completely. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log [\text{NH}_3] / [\text{NH}_4^+] = -\log (5.6 \times 10^{-10}) + \log (0.010/0.19) = 9.25 + (-1.28) = 7.97$$

b.

$$\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$$

Before: 0.050 M, 0.040 M, 1.50

Change: $-0.040$, $-0.040$, $+0.040$ Reacts completely

After: 0.010, 0, 1.54
A buffer solution still exists. \[ \text{pH} = \text{pK}_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 9.25 + \log (0.46/1.54) = 8.73 \]

The two buffers differ in their capacity and not in pH (both buffers had an initial pH = 8.77). Solution b has the greater capacity because it has the largest concentration of weak acid and conjugate base. Buffers with greater capacities will be able to absorb more H\(^+\) or OH\(^-\) added.

15.41

\[ \text{pH} = \text{pK}_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} ; \text{pK}_a = -\log (1.8 \times 10^{-5}) = 4.74 \]

Since the buffer components, \(\text{C}_2\text{H}_3\text{O}_2^-\) and \(\text{HC}_2\text{H}_3\text{O}_2\), are both in the same volume of water, the concentration ratio of \(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\) will equal the mol ratio of \(\frac{\text{mol C}_2\text{H}_3\text{O}_2^-}{\text{mol HC}_2\text{H}_3\text{O}_2}\).

\[ 5.00 = 4.74 + \log \left( \frac{\text{mol C}_2\text{H}_3\text{O}_2^-}{\text{mol HC}_2\text{H}_3\text{O}_2} \right) ; \text{mol HC}_2\text{H}_3\text{O}_2 = 0.5000 \text{ L} \times 0.200 \text{ mol/L} = 0.100 \text{ mol} \]

\[ 0.26 = \log \left( \frac{\text{mol C}_2\text{H}_3\text{O}_2^-}{0.100 \text{ mol}} \right) ; \text{mol C}_2\text{H}_3\text{O}_2^- = 10^{0.26} = 1.8 \text{ mol} \]

mass \(\text{NaC}_2\text{H}_3\text{O}_2\) = 0.18 mol \(\text{NaC}_2\text{H}_3\text{O}_2\) x 82.03 g/1 mol = 15 g \(\text{NaC}_2\text{H}_3\text{O}_2\)

15.43

\(\text{C}_5\text{H}_5\text{NH}^+ \rightleftharpoons \text{H}^+ + \text{C}_5\text{H}_5\text{N}\) \[ \text{K}_a = \frac{\text{K}_w}{\text{K}_b} = 1.0 \times 10^{-14} / 1.7 \times 10^{-9} = 5.9 \times 10^{-6} ; \text{pK}_a = -\log (5.9 \times 10^{-6}) = 5.23 \]

We will use the Henderson-Hasselbalch equation to calculate the concentration ratio necessary for each buffer.

\[ \text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}], \text{pH} = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}} \]

a. \[ 4.50 = 5.23 + \log \frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]} \]

\[ \log \left(\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}\right) = -0.73 \]

\[ [\text{C}_5\text{H}_5\text{N}] = [\text{C}_5\text{H}_5\text{NH}^+] = 10^{-0.73} = 0.19 \]

b. \[ 5.00 = 5.23 + \log \left(\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}\right) = -0.23 \]

\[ [\text{C}_5\text{H}_5\text{N}] = [\text{C}_5\text{H}_5\text{NH}^+] = 10^{-0.23} = 0.59 \]

c. \[ 5.23 = 5.23 + \log \left(\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}\right) \]

\[ [\text{C}_5\text{H}_5\text{N}] = [\text{C}_5\text{H}_5\text{NH}^+] = 10^{0.0} = 1.0 \]

d. \[ 5.50 = 5.23 + \log \left(\frac{[\text{C}_5\text{H}_5\text{N}]}{[\text{C}_5\text{H}_5\text{NH}^+]}\right) \]

\[ [\text{C}_5\text{H}_5\text{N}] = [\text{C}_5\text{H}_5\text{NH}^+] = 10^{0.27} = 1.9 \]
A best buffer has large and equal quantities of weak acid and conjugate base. For a best buffer, 
\[ \text{[acid]} = \text{[base]}, \] so 
\[ \text{pH} = \text{pK}_a + \log \left[ \frac{\text{Base}}{\text{Acid}} \right] = \text{pK}_a + 0 = \text{pK}_a \] (pH = \text{pK}_a).

The best acid choice for a pH = 7.00 buffer would be the weak acid with a pK\(_a\) close to 7.0 or K\(_a\) ≈ 1 x 10\(^{-7}\). HOCl is the best choice in Table 14.2 (K\(_a\) = 3.5 x 10\(^{-8}\); pK\(_a\) = 7.46). To make this buffer, we need to calculate the \[\text{[base]}/\text{[acid]}\] ratio.

\[ 7.00 = 7.46 + \log \left[ \frac{\text{[OCl}^-]}{\text{[HOCl]}^{-}} \right], \frac{\text{[OCl}^-]}{\text{[HOCl]}} = 10^{-0.46} = 0.35 \]

Any OCl\(^-\)/HOCl buffer in a concentration ratio of 0.35:1 will have a pH = 7.00. One possibility is [NaOCl] = 0.35 M and [HOCl] = 1.0 M.

The reaction \( \text{OH}^- + \text{CH}_3\text{NH}_3^+ \rightarrow \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \) goes to completion for solutions a, c, and d (no reaction occurs between the species in solution because both species are bases). After the \( \text{OH}^- \) reacts completely, there must be both CH\(_3\)NH\(_3^+\) and CH\(_3\)NH\(_2\) in solution for it to be a buffer. The important components of each solution (after the \( \text{OH}^- \) reacts completely) is/are:

a. 0.05 M CH\(_3\)NH\(_2\) (no CH\(_3\)NH\(_3^+\) remains, no buffer)

b. 0.05 M OH\(^-\) and 0.1 M CH\(_3\)NH\(_2\) (two bases present, no buffer)

c. 0.05 M OH\(^-\) and 0.05 M CH\(_3\)NH\(_2\) (too much OH\(^-\) added, no CH\(_3\)NH\(_3^+\) remains, no buffer)

d. 0.05 M CH\(_3\)NH\(_2\) and 0.05 CH\(_3\)NH\(_3^+\) (a buffer solution results)

Only the combination in mixture d results in a buffer. Note that the concentrations were halved from the initial values. This is because equal volumes of two solutions were added together, which halves the concentrations.

Added OH\(^-\) converts HC\(_2\)H\(_3\)O\(_2\) into C\(_2\)H\(_3\)O\(_2^-\): 
\[ \text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightarrow \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \]

From this reaction, the moles of C\(_2\)H\(_3\)O\(_2^-\) produced equal the moles of OH\(^-\) added. Also the total concentration of acetic acid plus acetate ion must equal 2.0 M (assuming no volume change on addition of NaOH). Summarizing for each solution:

\[ [\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}_2] = 2.0 \text{ M and } [\text{C}_2\text{H}_3\text{O}_2^-] \text{ produced } = [\text{OH}^-] \text{ added} \]

a. pH = pK\(_a\) + log \[\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\]; For pH = pK\(_a\), log \[\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\] = 0

Therefore, \[ [\text{C}_2\text{H}_3\text{O}_2^-] / [\text{HC}_2\text{H}_3\text{O}_2] = 1.0 \text{ and } [\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] \]

Because \[ [\text{C}_2\text{H}_3\text{O}_2^-] + [\text{HC}_2\text{H}_3\text{O}_2] = 2.0 \text{ M, } [\text{C}_2\text{H}_3\text{O}_2^-] = [\text{HC}_2\text{H}_3\text{O}_2] = 1.0 \text{ M = [OH}^-\text{] added} \]

To produce a 1.0 M C\(_2\)H\(_3\)O\(_2^-\) solution, we need to add 1.0 mol of NaOH to 1.0 L of the 2.0 M HC\(_2\)H\(_3\)O\(_2\) solution. The resultant solution will have pH = pK\(_a\) = 4.74.
b. 
\[ 4.00 = 4.74 + \log \left( \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \right) \] 
\[ \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{0.74} = 0.18 \]

\[ [C_2H_3O_2^-] = 0.18 \text{ [HC}_2\text{H}_3\text{O}_2] \text{ or } [HC_2H_3O_2] = 5.6 \text{ [C}_2\text{H}_3\text{O}_2^-] \]; Because \([C_2H_3O_2^-] + [HC_2H_3O_2] = 2.0 \text{ M}, then:\

\[ [C_2H_3O_2^-] + 5.6 \text{ [HC}_2\text{H}_3\text{O}_2] = 2.0 \text{ M, } [C_2H_3O_2^-] = 2.0 / 6.6 = 0.30 \text{ M } = [OH^-] \text{ added} \]

We need to add 0.30 mol of NaOH to 1.0 L of 2.0 M HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} solution to produce a buffer solution with pH = 4.00.

c. 
\[ 5.00 = 4.74 + \log \left( \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} \right) \] 
\[ \frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]} = 10^{0.26} = 1.8 \]

\[ 1.8 \text{ [HC}_2\text{H}_3\text{O}_2] = [C_2\text{H}_3\text{O}_2^-] \text{ or } [HC_2H_3O_2] = 0.56 \text{ [C}_2\text{H}_3\text{O}_2^-] \]; Because \([C_2H_3O_2^-] + [HC_2H_3O_2] = 2.0 \text{ M}, then:\

\[ 1.56 \text{ [C}_2\text{H}_3\text{O}_2^-] \text{ 2.0 M, } [C_2H_3O_2^-] = 1.3 \text{ M } = [OH^-] \text{ added} \]

We need to add 1.3 mol of NaOH to 1.0 L of 2.0 M HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} to produce a buffer solution with pH = 5.00.