Calculate the pH of a 0.010 M solution of aspirin at 25 °C. The pKₐ of aspirin is 3.5 at this temperature.

As aspirin is a weak acid, [H₃O⁺] must be calculated using a reaction table:

<table>
<thead>
<tr>
<th></th>
<th>C₉H₈O₄(aq)</th>
<th>H₂O</th>
<th>H₃O⁺</th>
<th>C₉H₇O₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.010</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.010 -x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:

\[ K_a = \frac{[H_3O^+][C_9H_7O_4^-]}{[C_9H_8O_4(aq)]} = \frac{x^2}{0.010 - x} \]

As pKₐ = -log₁₀Kₐ, Kₐ = 10⁻³.₅ and is very small, 0.010 - x ~ 0.010 and hence:

\[ x^2 = 0.010 \times 10^{-3.5} \quad \text{or} \quad x = 1.8 \times 10^{-3} \text{ M} = [H_3O^+] \]

Hence, the pH is given by:

\[ pH = -\log_{10}[H_3O^+] = -\log_{10}(1.8 \times 10^{-3}) = 2.8 \]

\[ pH = 2.8 \]

Ammonia, NH₃, is a weak base in water. Write the equation for the acid/base reaction between aspirin and ammonia.

\[ C_9H_8O_4(aq) + NH_3(aq) \rightarrow C_9H_7O_4^-(aq) + NH_4^+(aq) \]

What is the expression for the equilibrium constant, K, for this reaction?

\[ K = \frac{[NH_4^+(aq)][C_9H_7O_4^-]}{[NH_3(aq)][C_9H_8O_4(aq)]} \]

Rewrite this expression in terms of the Kₐ of aspirin and the Kₐ of NH₄⁺. (Hint: multiply by [H⁺]/[H⁺] = 1) Hence calculate the value of K. The pKₐ of NH₄⁺ is 9.2.

For C₉H₈O₄, \( K_a \) (C₉H₈O₄) = \( \frac{[H_3O^+][C_9H_7O_4^-]}{[C_9H_8O_4(aq)]} \) = 10⁻³.₅

For NH₃, \( K_a \) (NH₄⁺) = \( \frac{[NH_3(aq)][H^+(aq)]}{[NH_4^+(aq)]} \) = 10⁻⁹.₂
\[
K = \frac{[\text{NH}_4^+(aq)][\text{C}_9\text{H}_7\text{O}_4^- (aq)]}{[\text{NH}_3(aq)][\text{C}_9\text{H}_8\text{O}_4(aq)]} = \frac{[\text{NH}_4^+(aq)]}{[\text{NH}_3(aq)][\text{H}^+(aq)]} \times \frac{[\text{H}^+(aq)][\text{C}_9\text{H}_7\text{O}_4^- (aq)]}{[\text{C}_9\text{H}_8\text{O}_4(aq)]}
\]

\[
K = (1 / K_a (\text{NH}_3)) \times K_a (\text{C}_9\text{H}_8\text{O}_4)
\]

\[
K = (1 / 10^{-9.2}) \times (10^{-3.5}) = 10^{5.7} = 5.0 \times 10^5
\]

Answer: \(5.0 \times 10^5\)

Would aspirin dissolve in a solution of ammonia? Explain your answer.

The equilibrium constant for the reaction of ammonia and aspirin is very large: aspirin will dissolve.
Solution A consists of a 0.050 M aqueous solution of benzoic acid, C₆H₅COOH, at 25 °C. Calculate the pH of Solution A. The pKₐ of benzoic acid is 4.20.

As benzoic acid is a weak acid, [H₃O⁺] must be calculated using a reaction table:

<table>
<thead>
<tr>
<th></th>
<th>C₆H₅COOH</th>
<th>←→</th>
<th>H⁺</th>
<th>C₆H₅COO⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.050</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.050 –x</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:

\[ K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{x^2}{0.050-x} \]

As pKₐ = -log₁₀Kₐ, Kₐ = 10⁻⁴.²⁰ and is very small, 0.050 – x ~ 0.050 and hence:

\[ x^2 = 0.050 \times 10^{-4.2} \quad \text{or} \quad x = 1.78 \times 10^{-3} \text{ M} = [H^+] \]

Hence, the pH is given by:

\[ \text{pH} = -\log_{10}[H^+] = -\log_{10}(1.78 \times 10^{-3}) = 2.75 \]

\[ \text{pH} = 2.75 \]

Other than water, what are the major species present in solution A?

\[ K_a \text{ is very small and the equilibrium lies almost completely to the left. The major species present are water and the undissociated acid: } C_6H_5COOH \]

Solution B consists of a 0.050 M aqueous solution of ammonia, NH₃, at 25 °C. Calculate the pH of Solution B. The pKₐ of NH₄⁺ is 9.24.

NH₃ is a weak base so [OH⁻] must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>NH₃</th>
<th>H₂O</th>
<th>←→</th>
<th>NH₄⁺</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.050</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-y</td>
<td>negligible</td>
<td></td>
<td>+y</td>
<td>+y</td>
</tr>
<tr>
<td>final</td>
<td>0.050 –y</td>
<td>large</td>
<td></td>
<td>y</td>
<td>y</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:
$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{y^2}{(0.050 - y)}$

For an acid and its conjugate base:

\[
pK_a + pK_b = 14.00
\]

\[
pK_b = 14.00 - 9.24 = 4.76
\]

As \( pK_b = 4.76 \), \( K_b = 10^{-4.76} \). \( K_b \) is very small so \( 0.050 - y \sim 0.050 \) and hence:

\[
y^2 = 0.050 \times 10^{-4.76} \text{ or } y = 9.32 \times 10^{-4} \text{ M} = [OH^-]
\]

Hence, the pOH is given by:

\[
pOH = -\log_{10}[OH^-] = \log_{10}[9.32 \times 10^{-4}] = 3.03
\]

Finally, \( pH + pOH = 14.00 \) so

\[
pH = 14.00 - 3.03 = 10.97
\]

\[
\text{pH} = 10.97
\]

Other than water, what are the major species present in solution B?

\[
K_b \text{ is very small and the equilibrium lies almost completely to the left. The major species present are water and the unprotonated weak base: } NH_3
\]

**THIS QUESTION CONTINUES ON THE NEXT PAGE.**
Write the equation for the reaction that occurs when benzoic acid reacts with ammonia?

\[ \text{C}_6\text{H}_5\text{COOH}(aq) + \text{NH}_3(aq) \rightarrow \text{C}_6\text{H}_5\text{COO}^-(aq) + \text{NH}_4^+(aq) \]

Write the expression for the equilibrium constant for the reaction of benzoic acid with ammonia?

\[ K = \frac{[\text{C}_6\text{H}_5\text{COO}^-](aq) [\text{NH}_4^+(aq)]}{[\text{C}_6\text{H}_5\text{COOH}(aq)][\text{NH}_3(aq)]} \]

What is the value of the equilibrium constant for the reaction of benzoic acid with ammonia?

Multiplying the expression above by \([H^+] / [H^+]\) gives:

\[ K = \frac{[\text{C}_6\text{H}_5\text{COO}^-](aq) [\text{NH}_4^+(aq)]}{[\text{C}_6\text{H}_5\text{COOH}(aq)][\text{NH}_3(aq)]} \cdot \frac{[H^+(aq)]}{[H^+(aq)]} = \frac{[\text{H}^+(aq)][\text{C}_6\text{H}_5\text{COO}^-](aq) [\text{NH}_4^+(aq)]}{[\text{C}_6\text{H}_5\text{COOH}(aq)][\text{NH}_3(aq)][\text{H}^+(aq)]} \]

\[ = K_a \times \frac{K_b}{[\text{H}^+(aq)][\text{OH}^-](aq)} = \frac{K_a \times K_b}{K_w} \]

\[ = \frac{(10^{-4.20}) \times 10^{-4.76}}{10^{-14}} = 1.1 \times 10^5 \]

Answer: \(1.1 \times 10^5\)

What are the major species in the solution that results from dissolving equimolar amounts of benzoic acid and ammonia in water?

The equilibrium strongly favors products so the major species are:

\(\text{C}_6\text{H}_5\text{COO}^-(aq), \text{NH}_4^+(aq), \text{H}_2\text{O}(l)\)

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
What is the pH of a 0.1 M solution of ammonium chloride, given the $K_b$ for ammonia is $1.8 \times 10^{-5}$.

The ammonium ion, $\text{NH}_4^+$, is the conjugate acid of $\text{NH}_3$. The $K_a$ of a conjugate acid and base are related by:

$$K_a \times K_b = 10^{-14.00}$$

Hence,

$$K_a = \frac{10^{-14.00}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$\text{NH}_4^+$ is a weak acid so $[\text{H}_3\text{O}^+]$ must be calculated using the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>$\text{NH}_4^+$</th>
<th>$\text{H}_2\text{O}$</th>
<th>$\text{⇌}$</th>
<th>$\text{NH}_3$</th>
<th>$\text{H}_3\text{O}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.1</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.1 - x</td>
<td>large</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{(0.1-x)} = 5.6 \times 10^{-10}$$

As $K_a$ is very small, $0.1 - x \sim 0.1$ and hence:

$$x^2 = 0.1 \times 5.6 \times 10^{-10} \text{ or } x = 7.5 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = \log_{10}[7.5 \times 10^{-6}] = 5.1$$

$$\text{pH} = 5.1$$

What is the ratio of ammonia to ammonium ion in this solution?

From above, $[\text{NH}_3] = x \text{ M} = 7.5 \times 10^{-6} \text{ M}$ and $[\text{NH}_4^+] = (0.1 - x) \text{ M} = 0.1 \text{ M}$.

Hence:

$$[\text{NH}_3] / [\text{NH}_4^+] = 7 \times 10^{-5}$$

Answer: $7 \times 10^{-5}$
What is the pH of a solution which is 0.10 M in both acetic acid and sodium acetate? The $K_a$ for acetic acid is $1.8 \times 10^{-5}$.

By definition, $pK_a = -\log_{10}K_a$. Hence:

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Using the Henderson-Hasselbalch equation, $pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$

With $[\text{base}] = [\text{acetate}] = 0.10$ M and $[\text{acid}] = [\text{acetic acid}] = 0.10$ M, therefore:

$$pH = 4.74 + \log \frac{0.10}{0.10} = 4.74$$

Answer: 4.74

What is the final pH if 0.010 mol of HCl is added to 1.0 L of the above solution?

Using number of moles = concentration $\times$ volume, the number of moles of acetate and acetic acid originally present in 1.0 L of a 0.10 M solutions are:

$$n_{\text{acetate}} = 0.10 \text{ mol L}^{-1} \times 1.0 \text{ L} = 0.10 \text{ mol}$$
$$n_{\text{acetic acid}} = 0.10 \text{ mol L}^{-1} \times 1.0 \text{ L} = 0.10 \text{ mol}$$

The added $\text{H}_3\text{O}^+$ from HCl will react with the acetate to produce more acetic acid:

$$\text{acetate} + \text{H}_3\text{O}^+ \rightarrow \text{acetic acid} + \text{H}_2\text{O}$$

Hence, after addition of HCl, the amount of acetate will decrease and the amount of acetic acid will increase:

$$n_{\text{acetate}} = (0.10 - 0.010) \text{ mol} = 0.09 \text{ mol}$$
$$n_{\text{acetic acid}} = (0.10 + 0.010) \text{ mol} = 0.11 \text{ mol}$$

Using concentration = number of moles / volume, their concentrations will become:

$$[\text{acetate}] = 0.09 \text{ mol} / 1.0 \text{ L} = 0.09 \text{ M}$$
$$[\text{acetic acid}] = 0.11 \text{ mol} / 1.0 \text{ L} = 0.11 \text{ M}$$

Using the Henderson-Hasselbalch equation,

$$pH = 4.74 + \log \frac{0.09}{0.11} = 4.65$$

Answer: 4.65
The pKₐ of formic acid, HCO₂H, is 3.77. What is the pH of a 0.20 M solution of formic acid?

As formic acid is a weak acid, [H₃O⁺] must be calculated using a reaction table:

<table>
<thead>
<tr>
<th></th>
<th>HCO₂H</th>
<th>H₂O</th>
<th>H₂O⁺</th>
<th>HCO₂⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.20</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.20–x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:

\[ K_a = \frac{[H_3O^+][HCO_2^-]}{[HCO_2H]} = \frac{x^2}{0.20-x} \]

As pKₐ = -log₁₀Kₐ, Kₐ = 10⁻³.₇₇ and is very small, 0.20–x ~ 0.20 and hence:

\[ x^2 = 0.20 \times 10^{-3.77} \quad \text{or} \quad x = 5.8 \times 10^{-3} \text{M} = [H_3O^+] \]

Hence, the pH is given by:

\[ pH = -\log_{10}[H_3O^+] = -\log_{10}(5.8 \times 10^{-3}) = 2.23 \]

pH = 2.23

Give the equation for the reaction of formic acid with solid sodium hydroxide.

HCOOH(aq) + NaOH(s) → HCO₂⁻(aq) + Na⁺(aq) + H₂O(l)

Calculate the ratio of formate ion / formic acid required to give a buffer of pH 4.00.

Using the Henderson-Hasselbalch equation,

\[ pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} \]

\[ 4.00 = 3.77 + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} \]

So, \[ \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = 10^{0.23} = 1.70 \]

Answer: 1.70
What amount (in mol) of sodium hydroxide must be added to 100.0 mL of 0.20 M HCO₂H to prepare a solution buffered at pH 4.00?

If the concentration of OH⁻ which is added is \( x \) M then this will react with HCO₂H to produce HCO₂⁻ so that:

\[
[HCO₂H] = (0.20 - x) \text{ M and } [HCO₂⁻] = x \text{ M}
\]

From above, if pH = 4.00, then \( \frac{[HCO₂⁻]}{[HCO₂H]} = 1.70 \). Hence:

\[
\frac{x}{0.20-x} = 1.70 \quad \text{so } x = 0.13
\]

To achieve \( [\text{OH}^-(\text{aq})] = 0.13 \text{ mol L}^{-1} \) in 100.0 mL, the number of moles of NaOH that must be added is:

\[
\text{number of moles} = \text{concentration} \times \text{volume} \\
= 0.13 \text{ mol L}^{-1} \times 0.1000 \text{ L} = 0.013 \text{ mol}
\]

Answer: 0.013 mol
• Solution A consists of a 1.00 M aqueous solution of HOCl at 25 °C. The pKₐ of HOCl is 7.54. Calculate the pH of Solution A.

As HOCl is a weak acid, \([H^+(aq)]\) must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>HOCl(aq)</th>
<th>(\rightleftharpoons)</th>
<th>OCl(^-)(aq)</th>
<th>H(^+)(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>1.00</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>(-x)</td>
<td></td>
<td>(+x)</td>
<td>(+x)</td>
</tr>
<tr>
<td>final</td>
<td>1.00 (-x)</td>
<td></td>
<td>(x)</td>
<td>(x)</td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[OCl^-] [H^+]}{[HOCl]} = \frac{x^2}{(1.00-x)}
\]

As \(pK_a = 7.54\), \(K_a = 10^{-7.54}\). \(K_a\) is very small so \(1.00 - x \approx 1.00\) and hence:

\[
x^2 = 1.00 \times 10^{-7.54} \quad \text{or} \quad x = 0.000170 \text{ M} = [H^+(aq)]
\]

Hence, the pH is given by:

\[
pH = -\log_{10}[H^+(aq)] = -\log_{10}[0.000170] = 3.77
\]

pH = 3.77

At 25 °C, 1.00 L of Solution B consists of 74.4 g of NaOCl dissolved in water. Calculate the pH of Solution B.

The molar mass of NaOCl is:

\[
\text{molar mass} = (22.99 \text{ (Na)} + 16.00 \text{ (O)} + 35.45 \text{ (Cl)}) \text{ g mol}^{-1} = 74.44 \text{ g mol}^{-1}
\]

The number of moles present in 74.4 g is therefore:

\[
\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{74.4 \text{ g}}{74.44 \text{ g mol}^{-1}} = 0.999 \text{ mol}
\]

If this is present in 1.00 L, then \([\text{OCl}^-] = 0.999 \text{ M}\).

As it is a weak base, \([\text{OH}^-]\) must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>OCl(^-)</th>
<th>H(_2)O</th>
<th>(\rightleftharpoons)</th>
<th>HOCl</th>
<th>OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.999</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>(-y)</td>
<td>negligible</td>
<td>+(y)</td>
<td>+(y)</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.999 (-y)</td>
<td>large</td>
<td></td>
<td>(y)</td>
<td>(y)</td>
</tr>
</tbody>
</table>
The equilibrium constant $K_b$ is given by:

$$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} = \frac{y^2}{(0.999 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 7.54 = 6.46$$

As $pK_b = 6.46$, $K_b = 10^{-6.46}$. $K_b$ is very small so $0.999 - y \sim 0.999$ and hence:

$$y^2 = 0.999 \times 10^{-6.46} \text{ or } y = 0.000589 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = \log_{10} [\text{OH}^-] = \log_{10} [0.000589] = 3.23$$

Finally, $\text{pH} + \text{pOH} = 14.00$ so

$$\text{pH} = 14.00 - 3.23 = 10.77$$

$pH = 10.77$

Solution B (0.40 L) is poured into Solution A (0.60 L). What amount of NaOH (in mol) must be added to give a solution, after equilibration, with a pH of 8.20?

The number of moles of HOCl in 0.60 L is:

$$\text{number of moles} = \text{concentration} \times \text{volume}$$

$$= (1.00 \text{ mol L}^{-1}) \times (0.60 \text{ L}) = 0.60 \text{ mol}$$

The number of moles of OCl$^-$ in 0.60 L is:

$$\text{number of moles} = \text{concentration} \times \text{volume}$$

$$= (0.999 \text{ mol L}^{-1}) \times (0.40 \text{ L}) = 0.40 \text{ mol}$$

The added NaOH will react with the HOCl to form more OCl$^-$:

$$\text{HOCl(aq)} + \text{OH}^-(aq) \rightarrow \text{OCl}^-(aq) + \text{H}_2\text{O(l)}$$

If $x$ mol of NaOH is added then this reaction will lead to:

$$\text{number of moles of HOCl} = (0.60 - x) \text{ mol}$$

$$\text{number of moles of OCl}^- = (0.40 + x) \text{ mol}$$

ANSWER CONTINUES ON THE NEXT PAGE
The solution has a volume of 1.00 L so:

\[ [\text{HOCl}] = (0.60 - x) \text{ M and } [\text{OCl}^-] = (0.40 + x) \text{ M} \]

Using the Henderson-Hasselbalch equation with pH = 8.20:

\[
\text{pH} = \text{p}K_a + \log \frac{[\text{OCl}^- \text{(aq)}]}{[\text{HOCl} \text{(aq)}]} = 7.54 + \log \frac{(0.40 + x)}{(0.60 - x)} = 8.20
\]

\[
\log \frac{(0.40 + x)}{(0.60 - x)} = 0.66 \text{ or } \frac{(0.40 + x)}{(0.60 - x)} = 10^{0.66} = 4.57
\]

Solving this gives \( x = 0.42 \text{ mol} \).

Answer: \( 0.42 \text{ mol} \)
Citric acid, \(C_6H_8O_7\), has three \(pK_a\) values: \(pK_{a1} = 3.13\), \(pK_{a2} = 4.76\) and \(pK_{a3} = 6.40\).

Explain, giving exact volumes and concentrations, how to make 1.0 L of a citrate-based buffer with pH 5.58.

The desired pH is equally close to \(pK_{a2}\) and \(pK_{a3}\) so the best buffer could use either of these equilibria. Using \(pK_{a3}\) corresponds to using the equilibrium:

\[
\text{HCit}^2-(aq) \rightleftharpoons H^+(aq) + \text{Cit}^3-(aq)
\]

Using the Henderson-Hasselbalch equation,

\[
\text{pH} = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = \text{pH} = 6.40 + \log\frac{[\text{Cit}^3-]}{[\text{HCit}^2-]}
\]

At pH = 5.58,

\[
\log\frac{[\text{Cit}^3-]}{[\text{HCit}^2-]} = (5.58 - 6.40) = -0.82
\]

\[
\frac{[\text{Cit}^3-]}{[\text{HCit}^2-]} = 0.15
\]

As 1.0 L of the buffer is required,

\[
[\text{Cit}^3-] = n_{\text{Cit}^3-} / 1.0 \text{ M}
\]

\[
[\text{HCit}^2-] = n_{\text{HCit}^2-} / 1.0 \text{ M}
\]

So,

\[
\frac{[\text{Cit}^3-]}{[\text{HCit}^2-]} = \frac{n_{\text{Cit}^3-}}{n_{\text{HCit}^2-}} = 0.15
\]

There are many ways to construct the buffer to achieve this ratio when the acid and base are mixed.

If the two solutions have the same initial concentrations, then the ratio of the volumes used is 0.15. The volumes add up to 1000 mL:

\[
\text{volume of HCit}^2- = x \text{ L} \quad \text{volume of Cit}^3- = 1.0 - x \text{ L}
\]

So,

\[
\frac{V_{\text{Cit}^3-}}{V_{\text{HCit}^2-}} = \frac{1.0-x}{x} = 0.15
\]

\[
x = 0.87
\]

Hence, 870 mL of HCit\(^2\) and 130 mL of Cit\(^3\) are used.
A 20.0 mL solution of nitrous acid (HNO₂, pKₐ = 3.15) was titrated to its equivalence point with 24.8 mL of 0.020 M NaOH. What is the concentration of the HNO₂ solution?

The number of moles of OH⁻ added at the equivalence point is:

\[
\text{number of moles} = \text{concentration} \times \text{volume} = (0.020 \text{ mol L}^{-1})(0.0248 \text{ L}) = 0.00050 \text{ mol}
\]

This must also be equal to the number of moles of HNO₂ present in 20.0 mL. Its concentration is therefore:

\[
\text{concentration} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.00050 \text{ mol}}{0.020 \text{ L}} = 0.025 \text{ M}
\]

Answer: 0.025 M

What was the pH at the start of the titration?

As HNO₂ is a weak acid, [H⁺(aq)] must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>HNO₂(aq)</th>
<th>(\rightleftharpoons)</th>
<th>NO₂⁻(aq)</th>
<th>H⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.025</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.025 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[\text{HNO}_2^-](\text{aq})[\text{H}^+](\text{aq})}{[\text{HNO}_2]} = \frac{x^2}{(0.025-x)}
\]

As \(pK_a = 3.15\), \(K_a = 10^{-3.15}\). \(K_a\) is very small so \(0.025 - x \approx 0.025\) and hence:

\[
x^2 = 0.025 \times 10^{-3.15} \quad \text{or} \quad x = 0.0042 \text{ M} = [\text{H}^+](\text{aq})
\]

Hence, the pH is given by:

\[
pH = -\log_{10}[\text{H}^+](\text{aq}) = -\log_{10}[0.0042] = 2.38
\]

\[\text{pH} = 2.38\]

ANSWER CONTINUES ON THE NEXT PAGE
What was the pH after (a) 12.4 mL and (b) 24.8 mL of the NaOH had been added?

When OH\(^-\) reacts with HNO\(_2\), the amount of HNO\(_2\) decreases and the amount of its conjugate base, NO\(_2^-\), increases.

(a) 12.4 mL represents the half equivalence point. When this much OH\(^-\) is added, the amount of HNO\(_2\) is reduced to half its initial value and an equal amount of NO\(_2^-\) is produced. With [HNO\(_2\)(aq)] = [NO\(_2^-\)(aq)], the Henderson-Hasselbalch equation gives the pH as:

\[
pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 3.15 + \log(1) = 3.15
\]

(b) 24.8 mL represents the equivalence point. When this much OH\(^-\) is added, the amount of HNO\(_2\) is reduced zero and all of the initial HNO\(_2\) is now present as NO\(_2^-\). From above, the amount of NO\(_2^-\) is therefore 0.00050 mol. The total volume is now (20.0 + 24.8) mL = 44.8 mL so:

\[
[\text{NO}_2^- (aq)] = (0.00050 \text{ mol}) / 0.0448 \text{ L} = 0.0112 \text{ M}
\]

As NO\(_2^-\) (aq) is a weak base, the pH must be calculated using a reaction table:

<table>
<thead>
<tr>
<th></th>
<th>NO(_2^-)(aq)</th>
<th>H(_2)O(l)</th>
<th>(\rightleftharpoons)</th>
<th>HNO(_2)(aq)</th>
<th>OH(^-)(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.0112</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-(y)</td>
<td>negligible</td>
<td>(+y)</td>
<td>(+y)</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.0112 (-y)</td>
<td>large</td>
<td>(y)</td>
<td>(y)</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_b\) is given by:

\[
K_b = \frac{[\text{HNO}_2(aq)][\text{OH}^-(aq)]}{[\text{NO}_2^- (aq)]} = \frac{y^2}{(0.0112-y)}
\]

For an acid and its conjugate base:

\[
pK_a + pK_b = 14.00
\]

\[
pK_b = 14.00 - 3.15 = 10.85
\]

As \(pK_b = 10.85\), \(K_b = 10^{-10.85}\). \(K_b\) is very small so \(0.0112 - y \approx 0.0112\) and hence:

\[
y^2 = 0.0112 \times 10^{-10.85} \text{ or } y = 0.000000397 \text{ M} = [\text{OH}^-]
\]

Hence, the pOH is given by:

\[
pOH = -\log_{10}[\text{OH}^-] = \log_{10}[0.000000397] = 6.40
\]

Finally, pH + pOH = 14.00 so pH = 14.00 \(- 6.40\) = 7.60

(a) 12.4 mL: \(pH = 3.15\)  
(b) 24.8 mL: \(pH = 7.60\)

ANSWER CONTINUES ON THE NEXT PAGE
Qualitatively, how would each of these three pH values be affected if 5 mL of water were added to the 20.00 mL of nitrous acid before beginning the titration?

The initial pH would increase slightly as the nitrous acid solution would be more dilute.

The pH at half-equivalence point would not change (as pH = pK_a).

The final pH would decrease slightly as the NO_2^- solution produced would also be more dilute.
Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using \([\text{Co(NH}_3\text{)}_5(\text{OH}_2)]^{3+}\) as an example.

Co\(^{3+}\) has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.

This weakens the O–H bond causing the complex to be acidic in aqueous solution.

Solution A consists of a 0.10 M aqueous solution of \([\text{Co(NH}_3\text{)}_5(\text{OH}_2)](\text{NO}_3)_3\) at 25 °C. Calculate the pH of Solution A. The \(pK_a\) of \([\text{Co(NH}_3\text{)}_5(\text{OH}_2)]^{3+}\) = 5.69.

As \([\text{Co(NH}_3\text{)}_5(\text{OH}_2)]^{3+}\) is a weak acid, \([\text{H}_3\text{O}^+]\) must be calculated using a reaction table (acid = \([\text{Co(NH}_3\text{)}_5(\text{OH}_2)]^{3+}\) and base = \([\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+}\)

\[
\begin{array}{c|c|c|c|c}
\text{acid} & \text{H}_2\text{O} & \text{H}_3\text{O}^+ & \text{base} \\
\hline
\text{initial} & 0.10 & \text{large} & 0 & 0 \\
\text{change} & -x & \text{negligible} & +x & +x \\
\text{final} & 0.10 - x & \text{large} & x & x \\
\end{array}
\]

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10 - x}
\]

As \(pK_a = -\log_{10}K_a\), \(K_a = 10^{-5.69}\) and is very small, 0.10 – \(x\) ~ 0.10 and hence:

\[x^2 = 0.10 \times 10^{-5.69}\] or \[x = 4.5 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]\]

Hence, the pH is given by:

\[\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(4.5 \times 10^{-4}) = 3.35\]

\[\text{pH} = 3.35\]

At 25 °C, 1.00 L of Solution B consists of 28.5 g of \([\text{Co(NH}_3\text{)}_5(\text{OH})](\text{NO}_3)_2\) dissolved in water. Calculate the pH of Solution B.

The molar mass of \([\text{Co(NH}_3\text{)}_5(\text{OH})](\text{NO}_3)_2\) is:

\[
\text{molar mass} = (58.93 \text{ (Co)}) + 7 \times 14.01 \text{ (N)} + 7 \times 16.00 \text{ (O)} + 16 \times 1.008 \text{ (H)} \text{ g mol}^{-1}
= 285.128 \text{ g mol}^{-1}
\]

The number of moles present in 28.5 g is therefore:

\[
\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{28.5 \text{ g}}{285.128 \text{ g mol}^{-1}} = 0.100 \text{ mol}
\]
If this is present in 1.00 L, then \([\text{base}] = 0.100 \text{ M}\).

As it is a weak base, \([\text{OH}^-]\) must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>base</th>
<th>(\text{H}_2\text{O})</th>
<th>(\rightleftharpoons)</th>
<th>acid</th>
<th>(\text{OH}^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.100</td>
<td>large</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-(y)</td>
<td>negligible</td>
<td>+(y)</td>
<td>+(y)</td>
<td>+(y)</td>
</tr>
<tr>
<td>final</td>
<td>0.100 – (y)</td>
<td>large</td>
<td>(y)</td>
<td>(y)</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_b\) is given by:

\[
K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100 - y)}
\]

For an acid and its conjugate base:

\[
pK_a + pK_b = 14.00
\]

\[
pK_b = 14.00 - 5.69 = 8.31
\]

As \(pK_b = 8.31\), \(K_b = 10^{-8.31}\). \(K_b\) is very small so \(0.100 - y \approx 0.100\) and hence:

\[
y^2 = 0.100 \times 10^{-8.31} \text{ or } y = 2.21 \times 10^{-5} \text{ M} = [\text{OH}^-]
\]

Hence, the \(p\text{OH}\) is given by:

\[
p\text{OH} = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65
\]

Finally, \(p\text{H} + p\text{OH} = 14.00\) so

\[
p\text{H} = 14.00 - 4.65 = 9.35
\]

\[
p\text{H} = 9.35
\]

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a \(p\text{H} = 7.00\).

The ratio of acid to conjugate base needed can be calculated using the Henderson-Hasselbalch equation, \(p\text{H} = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}\):

\[
7.00 = 5.69 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4
\]

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As \(V_{\text{acid}} + V_{\text{base}} = 1.0 \text{ L}\) and \(V_{\text{base}} / V_{\text{acid}} = 20.4\):

\[
V_{\text{acid}} = 0.047 \text{ L} \text{ and } V_{\text{base}} = 0.953 \text{ L}
\]
• Solution A consists of a 0.020 M aqueous solution of propionic acid, C$_3$H$_6$O$_2$, at 25 °C. Calculate the pH of Solution A. The pK$_a$ of propionic acid is 4.87.

As C$_3$H$_6$O$_2$ is a weak acid, [H$^+$] must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>C$_3$H$_6$O$_2$</th>
<th>$\rightleftharpoons$</th>
<th>C$_3$H$_5$O$_2^-$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.020</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-$x$</td>
<td>$+$x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.020 -$x$</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant $K_a$ is given by:

$$K_a = \frac{[C_3H_5O_2^-][H^+]}{[C_3H_6O_2]} = \frac{x^2}{(0.020-x)}$$

As pK$_a$ = 4.87, $K_a = 10^{-4.87}$. $K_a$ is very small so 0.020 -$x$ ~ 0.020 and hence:

$$x^2 = 0.020 \times 10^{-4.87} \quad \text{or} \quad x = 0.000519 \text{ M} = [\text{H}^-]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}^+] = -\log_{10}[0.000519] = 3.28$$

Answer: pH = 3.28

At 25 °C, 1.00 L of Solution B consists of 2.24 g of potassium propionate (KC$_3$H$_5$O$_2$) dissolved in water. Calculate the pH of Solution B.

The molar mass of KC$_3$H$_5$O$_2$ is:

molar mass = (39.10 (K) + 3×12.01 (C) + 5×1.008 (H) + 2×16.00 (O)) g mol$^{-1}$

= 112.17 g mol$^{-1}$

Thus, 2.24 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{2.24 \text{ g}}{112.17 \text{ g mol}^{-1}} = 0.0200 \text{ mol}$$

If this is dissolved in 1.0 L, [C$_3$H$_5$O$_2^-$]$_{\text{initial}}$ = 0.0200 M.

As C$_3$H$_6$O$_2^-$ is a weak base, [C$_3$H$_5$O$_2^-$] must be calculated by considering the equilibrium:
The equilibrium constant $K_b$ is given by:

$$K_b = \frac{[C_3H_6O_2][OH^-]}{[C_3H_5O_2^{-}]} = \frac{y^2}{(0.0200 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 4.87 = 9.13$$

As $pK_b = 9.13$, $K_b = 10^{-9.13}$. $K_b$ is very small so $0.0200 - y \sim 0.0200$ and hence:

$$y^2 = 0.0200 \times 10^{-9.13} \text{ or } y = 0.000000385 \text{ M} = [OH^-]$$

Hence, the $pOH$ is given by:

$$pOH = -\log_{10}[OH^-] = \log_{10}[0.000000385] = 5.41$$

Finally, $pH + pOH = 14.00$ so

$$pH = 14.00 - 5.41 = 8.59$$

Answer: $pH = 8.59$

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Combining the two solutions will double the overall volume, to 2.00 L. As a result, the concentration of both the acid and base will halve: $[acid] = 0.010$ M and $[base] = 0.0100$ M.

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[base]}{[acid]} = 4.87 + \log\frac{0.0100}{0.010} = 4.87$$

Answer: $pH = 4.87$

If you wanted to adjust the pH of Solution C to be exactly equal to 5.00, which component in the mixture would you need to increase in concentration?

More base is needed: add $KC_3H_5O_2$
Solution A consists of a 0.020 M aqueous solution of aspirin (acetylsalicylic acid, C₉H₈O₄) at 25 °C. Calculate the pH of Solution A. The pKₐ of aspirin is 3.52.

As C₉H₈O₄ is a weak acid, [H⁺] must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>C₉H₈O₄</th>
<th>C₉H₇O₄⁻</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.020</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.020 – x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant Kₐ is given by:

$$K_a = \frac{[C_9H_7O_4^-][H^+]}{[C_9H_8O_4]} = \frac{x^2}{(0.020 – x)}$$

As pKₐ = 3.52, Kₐ = 10⁻³.₅₂. Kₐ is very small so 0.020 – x ~ 0.020 and hence:

$$x^2 = 0.020 \times 10^{-3.52} \quad \text{or} \quad x = 0.00246 \ M = [H^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H^+] = -\log_{10}[0.00246] = 2.61$$

Answer: 2.61

At 25 °C, 1.00 L of Solution B consists of 4.04 g of sodium acetylsalicylate (NaC₉H₇O₄) dissolved in water. Calculate the pH of Solution B.

The molar mass of NaC₉H₇O₄ is:

$$\text{molar mass} = (22.99 \ (\text{Na}) + 9 \times 12.01 \ (\text{C}) + 7 \times 1.008 \ (\text{H}) + 4 \times 16.00 \ (\text{O})) \ \text{g mol}^{-1}$$

$$= 202.136 \ \text{g mol}^{-1}$$

Thus, 4.04 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{4.04 \ \text{g}}{202.136 \ \text{g mol}^{-1}} = 0.0200 \ \text{mol}$$

If this is dissolved in 1.0 L, [C₉H₇O₄⁻]_{initial} = 0.0200 M.

As C₉H₇O₄⁻ is a weak base, [C₉H₇O₄⁻] must be calculated by considering the equilibrium:

ANSWER CONTINUES ON THE NEXT PAGE
The equilibrium constant $K_b$ is given by:

$$K_b = \frac{[C_9H_8O_4][OH^-]}{[C_9H_7O_4^-]} = \frac{y^2}{(0.0200 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 3.52 = 10.48$$

As $pK_b = 10.48$, $K_b = 10^{10.48}$. $K_b$ is very small so $0.0200 - y \sim 0.0200$ and hence:

$$y^2 = 0.0200 \times 10^{-10.48} \quad \text{or} \quad y = 0.000000814 \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[OH^-] = \log_{10}[0.000000814] = 6.09$$

Finally, $pH + pOH = 14.00$ so

$$pH = 14.00 - 6.09 = 7.91$$

Answer: 7.91

Solution B (200.0 mL) is mixed with Solution A (400.0 mL) and water (200.0 mL) to give Solution C. Calculate the pH of Solution C after equilibration at 25 °C.

400.0 mL of solution A (the acid) contains:

$$\text{number of moles} = \text{concentration} \times \text{volume} = (0.0200 \text{ mol L}^{-1}) \times (0.4000 \text{ L}) = 0.00800 \text{ mol}$$

200.0 mL of solution B (the base) contains:

$$\text{number of moles} = \text{concentration} \times \text{volume} = (0.0200 \text{ mol L}^{-1}) \times (0.2000 \text{ L}) = 0.00400 \text{ mol}$$

The final solution has a total volume of $(200.0 + 400.0 + 200.0)$ mL $= 800.0$ mL.

The concentrations of acid and base in the final solution are:
concentration of acid = \( \frac{\text{number of moles}}{\text{volume}} = \frac{0.00800 \text{ mol}}{0.8000 \text{ L}} = 0.0100 \text{ M} \)

concentration of base = \( \frac{\text{number of moles}}{\text{volume}} = \frac{0.00400 \text{ mol}}{0.8000 \text{ L}} = 0.00500 \text{ M} \)

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation:

\[
\text{pH} = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.52 + \log\left(\frac{0.00500}{0.0100}\right) = 3.22
\]

Answer: 3.22

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

To lower the pH, more acid is required: solution A
- Calculate the pH of a 0.20 M solution of potassium fluoride. The $pK_a$ of HF is 3.17.

As $F^-$ is a weak base, $[OH^-]$ must be calculated by considering the equilibrium:

<table>
<thead>
<tr>
<th></th>
<th>$F^-$</th>
<th>$H_2O$</th>
<th>$\rightleftharpoons$</th>
<th>$OH^-$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.20</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>$-x$</td>
<td>negligible</td>
<td></td>
<td>$+x$</td>
<td>$+x$</td>
</tr>
<tr>
<td>final</td>
<td>0.20 $-x$</td>
<td>large</td>
<td></td>
<td>$x$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

The equilibrium constant $K_b$ is given by:

$$K_b = \frac{[OH^-][HF]}{[F^-]} = \frac{x^2}{0.20 - x}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 3.17 = 10.83$$

As $pK_b = 10.83, K_b = 10^{-10.83}$. $K_b$ is very small so $0.20 - x \sim 0.20$ and hence:

$$x^2 = 0.20 \times 10^{-10.83} \quad \text{or} \quad x = 0.0000017 \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = -\log_{10}[0.0000017] = 5.76$$

Finally, $pH + pOH = 14.00$ so

$$pH = 14.00 - 5.76 = 8.24$$

Answer: $pH = 8.24$

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the $pK_a$ of iodic acid, $HIO_3$, is 0.79, how many moles of sodium iodate, $NaIO_3$, would need to be added to this solution to raise its pH to 2.00?

Using $pH = -\log_{10}[H^+(aq)]$,

$$[H^+(aq)]_{\text{initial}} = 10^{-1.22} = 0.060 \text{ M}$$

$$[H^+(aq)]_{\text{final}} = 10^{-2.00} = 0.010 \text{ M}$$
The change of \((0.060 - 0.010 \text{ M}) = 0.050 \text{ M}\) occurs due to the reaction with \(\text{IO}_3^- (\text{aq})\) to produce \(\text{HIO}_3(\text{aq})\). If \([\text{IO}_3^- (\text{aq})] = x\), the reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>(\text{H}^+ (\text{aq})) +</th>
<th>(\text{IO}_3^- (\text{aq}))</th>
<th>(\text{HIO}_3(\text{aq}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.060</td>
<td>(x)</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-0.050</td>
<td>-0.050</td>
<td>+0.050</td>
</tr>
<tr>
<td>final</td>
<td>0.010</td>
<td>(x - 0.050)</td>
<td>0.050</td>
</tr>
</tbody>
</table>

As \(pK_a = 0.79 = -\log_{10} K_a\):

\[
K_a = \frac{[\text{H}^+ (\text{aq})][\text{IO}_3^- (\text{aq})]}{[\text{HIO}_3(\text{aq})]} = \frac{(0.010)(x - 0.050)}{0.050} = 10^{-0.79}
\]

Thus, \(x = 0.86 \text{ M} = [\text{IO}_3^- (\text{aq})]_{\text{initial}}\). This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:

\[
\text{number of moles} = \text{concentration} \times \text{volume} = (0.86 \text{ M}) \times (0.3000 \text{ L}) = 0.26 \text{ mol}
\]

Answer: 0.26 mol
Buffers made of mixtures of $H_2PO_4^-$ and $HPO_4^{2-}$ are used to control the pH of soft drinks. What is the pH of a 350 mL drink containing 6.0 g of $NaH_2PO_4$ and 4.0 g of $Na_2HPO_4$?

For phosphoric acid, $H_3PO_4$, $pK_{a1} = 2.15$, $pK_{a2} = 7.20$ and $pK_{a3} = 12.38$.

The formula masses of $NaH_2PO_4$ and $Na_2HPO_4$ are:

\[
M(\text{NaH}_2\text{PO}_4) = (22.99 \text{ (Na)} + 2\times1.008 \text{ (H)} + 30.97 \text{ (P)} + 4\times16.00 \text{ (O)}) \text{ g mol}^{-1} = 119.976 \text{ g mol}^{-1}
\]

\[
M(\text{Na}_2\text{HPO}_4) = (2\times22.99 \text{ (Na)} + 1.008 \text{ (H)} + 30.97 \text{ (P)} + 4\times16.00 \text{ (O)}) \text{ g mol}^{-1} = 141.958 \text{ g mol}^{-1}
\]

Hence, the number of moles of each present are:

\[
n(\text{NaH}_2\text{PO}_4) = \frac{\text{mass}}{\text{formula mass}} = \frac{6.0 \text{ g}}{119.976 \text{ g mol}^{-1}} = 0.050 \text{ mol}
\]

\[
n(\text{Na}_2\text{HPO}_4) = \frac{4.0}{141.958} \text{ g mol}^{-1} = 0.028 \text{ mol}
\]

As both are present in the same solution, the ratio of their concentrations is the same as the ratio of these amounts. There is no need to calculate the concentrations, although it does not change the answer.

The relevant equilibrium for this buffer is

\[
H_2PO_4(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)
\]

This corresponds to the second ionization of $H_3PO_4$ so $pK_{a2}$ is used with the base acid being $H_2PO_4^-$ (from $NaH_2PO_4$) and the base being $HPO_4^{2-}$ (from $Na_2HPO_4$). The pH can be calculated using the Henderson-Hasselbalch equation:

\[
pH = pK_{a2} + \log([\text{base}]/[\text{acid}])
= pK_{a2} + \log([HPO_4^{2-}]/[H_2PO_4^-]) = 7.20 + \log(0.028/0.050) = 6.95
\]

Briefly describe how this buffer system functions. Use equations where appropriate.

The buffer contains an acid ($H_2PO_4^-$) and its conjugate base ($HPO_4^{2-}$) and is able to resist changes in pH when $H^+$ or $OH^-$ is added.

If $H^+$ is added, the base reacts with it to remove it according to the equilibrium:

\[
HPO_4^{2-}(aq) + H^+(aq) \rightleftharpoons H_2PO_4(aq)
\]
If $\text{OH}^-$ is added, the acid reacts with it to remove it according to the equilibrium:

$$
\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l)
$$

As long the amounts of the acid and base present are not exceeded, the changes in pH will be small.

Is this buffer better able to resist changes in pH following the addition of acid or of base? Explain your answer.

Maximum buffering occurs when equal amounts of base and acid are present. This buffer has less base than acid present. As a result, it is less able to resist cope with the addition of $\text{H}^+$.

Larger changes in pH result from the addition of acid.
Solution A consists of a 0.20 M aqueous solution of formic acid, HCOOH, at 25 °C. Calculate the pH of Solution A. The pKₐ of HCOOH is 3.75.

The reaction table is:

<table>
<thead>
<tr>
<th></th>
<th>HCOOH(aq)</th>
<th>H₂O(l)</th>
<th>⇌</th>
<th>HCOO⁻(aq)</th>
<th>H₃O⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0.20</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.20-x</td>
<td>large</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

As $pK_a = -\log_{10}(K_a) = 3.75$, $K_a = 10^{-3.75}$ and:

$$K_a = \frac{[HCOO^-](aq)[H_3O^+](aq)}{[HCOOH(aq)]} = \frac{(x)(x)}{(0.20 - x)} = \frac{x^2}{(0.20 - x)} = 10^{-3.75}$$

As $K_a$ is very small, $x$ is tiny and $0.20 - x \sim x$. Hence,

$$K_a \sim \frac{x^2}{(0.20)} = 10^{-3.75}$$

or $x^2 = (0.20) \times (10^{-3.75})$ so $x = [H_3O^+(aq)] = 6.0 \times 10^{-4}$ M

As $pH = -\log_{10}([H_3O^+](aq))$:

$$pH = -\log_{10}(6.0 \times 10^{-4}) = 2.22$$

Answer: 2.22

ANSWER CONTINUES ON NEXT PAGE
At 25 °C, 1.00 L of Solution B consists of 13.6 g of sodium formate, NaHCO₂, dissolved in water. Calculate the pH of Solution B.

The molar mass of NaHCO₂ is

\[
(22.99 \text{ (Na)}) + (1.008 \text{ (H)}) + (12.01 \text{ (C)}) + (2 \times 16.00 \text{ (O)}) = 68.008
\]

The solution thus contains

\[
\frac{\text{mass}}{\text{molar mass}} = \frac{13.6}{68.008} = 0.200 \text{ mol}
\]

As this is dissolved in 1.00 L, the concentration is 0.200 M. The reaction table is now:

<table>
<thead>
<tr>
<th></th>
<th>HCOO⁻(aq)</th>
<th>H₂O(l)</th>
<th>⇌</th>
<th>HCOOH(aq)</th>
<th>OH⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>start</td>
<td>0.200</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-y</td>
<td>-y</td>
<td>+y</td>
<td>+y</td>
<td></td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.200-y</td>
<td>large</td>
<td></td>
<td>y</td>
<td>y</td>
</tr>
</tbody>
</table>

As pKₐ + pKₐ = 14.00, pKₐ = 14.00 - 3.75 = 10.25, Kₐ = 10⁻¹⁰.²⁵ and:

\[
Kₐ = \frac{[\text{HCOOH(aq)}][\text{OH}⁻(aq)]}{[\text{HCOO}⁻(aq)]} = \frac{(y)(y)}{(0.200 - y)} = \frac{y²}{(0.200 - y)} = 10⁻¹⁰.²⁵
\]

Again Kₐ is very small, y is tiny and 0.200 – y ~ y. Hence, \( y² = (0.200) \times (10⁻¹⁰.²⁵) \)

so \( y = [\text{OH}⁻(aq)] = 3.35 \times 10⁻⁶ \text{ M} \) and \( \text{pOH} = -\log₁₀([\text{OH}⁻(aq)]) = 5.47 \)

As pH + pOH = 14.00, pH = 14.00 – 5.47 = 8.52

Answer: 8.52

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

After mixing solution A (1.00 L) and solution B (1.00 L), the total volume is 2.00 L. This halves the concentration of the both the acid and the base.

\[
[\text{acid}] = \frac{0.200}{2} = 0.10 \text{ M and } [\text{base}] = \frac{0.200}{2} = 0.100 \text{ M}
\]

Solution C contains a weak acid (HCOOH) and its conjugate base (HCOO⁻). It is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation can be used:

\[
\text{pH} = \text{pKₐ} + \log₁₀ \left( \frac{[\text{base}]}{[\text{acid}]} \right) = 3.75 + \log₁₀ \left( \frac{0.100}{0.10} \right) = 3.75
\]

Answer: 3.75

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration? [HCOOH] would be increased (the acid)
• Buffer systems are frequently used in chemistry. What is a buffer system and how does it function? Use equations where appropriate.

Buffer systems resist changes in pH: a buffer will maintain a relatively constant pH when acid or base is added.

They consist of mixtures of a weak acid (HA) and its conjugate base (A⁻) in high concentration.

If acid is added, the system can respond by removing it using A⁻:

$$\text{H}^+(aq) + \text{A}^-(aq) \rightarrow \text{HA}(aq)$$

If base is added, the system can respond by removing it using HA:

$$\text{OH}^-(aq) + \text{HA}(aq) \rightarrow \text{H}_2\text{O}(l) + \text{A}^-(aq)$$

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 4.00? The $K_a$ of acetic acid is $1.8 \times 10^{-5}$ M.

The pH of a buffer system made from a mixture of the weak acid (HA) and its conjugate base (A⁻) is described by the equation:

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-(aq)]}{[\text{HA}(aq)]} \right)$$

For acetic acid, $K_a = 1.8 \times 10^{-5}$ or $\text{p}K_a = -\log(K_a) = 4.74$. To obtain pH = 4.00:

$$4.00 = 4.74 + \log \left( \frac{[\text{A}^-(aq)]}{[\text{HA}(aq)]} \right) \text{ and so } \frac{[\text{A}^-(aq)]}{[\text{HA}(aq)]} = 10^{-0.74} = 0.18$$

Alternatively, $\frac{[\text{HA}(aq)]}{[\text{A}^-(aq)]} = \frac{1}{0.18} = 5.56$

Answer: 5.56: 1
Solution A consists of a 0.25 M aqueous solution of hydrazoic acid, HN₃, at 25 °C. Calculate the pH of Solution A. The pKₐ of HN₃ is 4.63.

As pKₐ = -log(Kₐ) = 4.63, Kₐ = 10^{-4.63} = 2.34 \times 10^{-5}. The reaction table is:

<table>
<thead>
<tr>
<th>t = 0</th>
<th>HN₃(aq)</th>
<th>H⁺(aq)</th>
<th>N₃⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>equilibrium</td>
<td>0.25 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Hence, Kₐ = \frac{[H⁺(aq)][N₃⁻(aq)]}{[HN₃]} = \frac{(x)(x)}{(0.25-x)} = 2.34 \times 10^{-5}

As Kₐ is very small, very little HN₃ dissociates and x is tiny so (0.25 - x) ~ 0.25

Hence, \frac{x^2}{(0.25)} = 2.34 \times 10^{-5} \quad \text{or} \quad x = [H⁺(aq)] = 2.42 \times 10^{-3} \text{ M}

As pH = -log[H⁺(aq)]:

pH = -log(2.42 \times 10^{-3}) = 2.62

Answer: 2.62

(ANSWER CONTINUES ON THE NEXT PAGE)
At 25 °C, 1.00 L of Solution B consists of 13.0 g of sodium azide (NaN₃) dissolved in water. Calculate the pH of Solution B.

The relevant reaction is now: \( \text{N}_3^-(aq) + H_2O(l) \rightleftharpoons \text{HN}_3(aq) + \text{OH}^-(aq) \)

As \( \text{N}_3^- \) is the conjugate base of \( \text{HN}_3 \), the equilibrium constant for this reaction is \( K_b \) where \( pK_a + pK_b = 14.00 \).

Hence, using \( pK_a \) from above:

\[
pK_b = 14.00 - 4.63 = 9.37 \text{ or } K_b = 10^{-9.37} = 4.27 \times 10^{-10}.
\]

The molar mass of NaN₃ is \((22.99 \text{ (Na)}) + (3 \times 14.01 \text{ (N)}) = 65.02\). The number of moles in 13.0 g is therefore:

\[
\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{13.0}{65.02} = 0.200 \text{ mol}
\]

As this is dissolved in 1.00 L, \([\text{N}_3^-(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.200}{1.00} = 0.200 \text{ M}\)

The relevant reaction table is now:

<table>
<thead>
<tr>
<th></th>
<th>( \text{N}_3^-(aq) )</th>
<th>H₂O(l)</th>
<th>( \rightleftharpoons )</th>
<th>( \text{HN}_3(aq) )</th>
<th>( \text{OH}^-(aq) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t = 0 )</td>
<td>0.200</td>
<td></td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{equilibrium} )</td>
<td>0.200 − x</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \( K_b = \frac{[\text{NH}_3(aq)][\text{OH}^-(aq)]}{[\text{N}_3^-(aq)]} = \frac{(x)(x)}{(0.200-x)} = \frac{x^2}{(0.200-x)} \)

\( K_b \) is small so the amount of \( \text{N}_3^-(aq) \) which is protonated is tiny and hence \( 0.200 - x \approx 0.200 \).

Hence, \( \frac{x^2}{(0.200)} \approx 4.27 \times 10^{-10} \) or \( x = [\text{OH}^-(aq)] = 9.24 \times 10^{-6} \text{ M} \)

As \( pOH = -\log[\text{OH}(aq)] = -\log(9.24 \times 10^{-6}) = 5.03 \)

As \( pH + pOH = 14 \):

\[
pH = 14 - 5.03 = 8.97
\]

Answer: 8.97
Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Solution C is a buffer system as it contains both a weak acid (HN\textsubscript{3}) and its conjugate base (N\textsubscript{3}\textsuperscript{-}(aq)). The pH can be obtained from the Henderson-Hasselbalch equation:

\[
\text{pH} = \text{pK}_a + \log \frac{[A^- (aq)]}{[HA(aq)]}
\]

Using pK\textsubscript{a} = 4.63, [HA(aq)] = [HN\textsubscript{3}(aq)] = 0.25 M and [A\textsuperscript{-}(aq)] = [N\textsubscript{3}\textsuperscript{-}(aq)] = 0.200 M:

\[
\text{pH} = (4.63) + \log \frac{0.200}{0.25} = 4.53
\]

Answer: 4.53

If you wanted to adjust the pH of Solution C to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?

To lower the pH, the acid concentration (HN\textsubscript{3}) is increased.
Calculate the pH of a 0.200 M solution of acetic acid, CH\(_3\)COOH, at 25 °C. (The pK\(_a\) of acetic acid is 4.76).

As acetic acid is a weak acid, \([\text{H}_3\text{O}^+]\) must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>CH(_3)COOH</th>
<th>H(_2)O</th>
<th>(\text{H}_3\text{O}^+)</th>
<th>CH(_3)COO(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.200</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>final</td>
<td>0.200 - x</td>
<td>large</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.2 - x}
\]

As pK\(_a\) = 4.76 = −log\(_{10}\)K\(_a\) so \(K_a = 10^{-4.76}\). As \(K_a\) is very small, 0.200 − x \(\approx\) 0.200 and hence:

\[
x^2 = 0.200 \times 10^{-4.76} \quad \text{or} \quad x = 0.0019 \text{ M} = [\text{H}_3\text{O}^+]
\]

Hence, the pH is given by:

\[
\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}[0.0019] = 2.73
\]

\[
\text{pH} = 2.73
\]

Solid sodium acetate, NaCH\(_3\)CO\(_2\), (0.15 mol) was dissolved in 0.500 L of 0.200 M acetic acid and the volume made up to 750 mL with water. What is the pH of the resulting solution?

The solution contains a weak acid (acetic acid) and its conjugate base (acetate). 0.15 mol of acetate is present in 750 mL so its concentration is:

\[
[\text{base}] = \frac{(0.15 \text{ mol})}{(0.750 \text{ L})} = 0.20 \text{ M}
\]

500 mL of 0.200 M acid contains (0.5 L) \(\times\) (0.200 M) = 0.100 mol. The concentration of the acid in 750 mL is therefore:

\[
[\text{acid}] = \frac{(0.100 \text{ mol})}{(0.750 \text{ L})} = 0.133 \text{ M}
\]

The Henderson-Hasselbalch equation can be used for this buffer:

\[
\text{pH} = pK_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}ight) = 4.76 + \log_{10}\left(\frac{0.20}{0.133}\right) = 4.94
\]

\[
\text{pH} = 4.94
\]

**ANSWER CONTINUES ON THE NEXT PAGE**
How much more NaCH₃CO₂ needs to be dissolved in the above solution to give a final pH of 5.00?

A pH of 5.00 will be obtained when:

$$\text{pH} = 4.76 + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 5.00 \text{ or } \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 0.24$$

Hence,

$$\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 10^{0.24} = 1.74 \text{ or } [\text{base}] = 1.74 \times [\text{acid}] = 1.74 \times 0.133 = 0.232 \text{ M}$$

The number of moles of base in 750 mL is therefore $(0.232 \text{ M}) \times (0.750 \text{ L}) = 0.174 \text{ mol}$.

As 0.15 mol was added originally, an additional $(0.17 - 0.15) = 0.02 \text{ mol}$ is required.

Answer: 0.02 mol