CHEM1102 Worksheet 9: Weak Acids and Titrations

Model 1: A Solution Containing a Weak Acid

As a **weak acid** is *significantly* less than 100% dissociated in water, an equilibrium must be considered:

\[
\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq) \quad K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{A}^-(aq)]}{[\text{HA}(aq)]}
\]

Calculating the pH requires that the equilibrium value of \([\text{H}_3\text{O}^+(aq)]\) be first calculated. To do this, the ‘ICE’ approach covered in CHEM1101 can be followed. Consider a 2.0 M solution of CH₃COOH:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COOH (aq)</th>
<th>H₂O(l)</th>
<th>CH₃COO⁻(aq)</th>
<th>H₃O⁺(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>2.00</td>
<td>large</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>equilibrium</td>
<td>2.00 - x</td>
<td>large</td>
<td>+x</td>
<td>+x</td>
</tr>
</tbody>
</table>

As hardly any weak acid dissociates, \(x\) is *very* small and so \(2.00 - x \approx 2.00\). Using this approximation, the equilibrium constant can then be written down as:

\[
K_a = \frac{[\text{CH}_3\text{COO}^- (aq)][\text{H}_3\text{O}^+ (aq)]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{2.00-x} \approx \frac{x^2}{2.00} \quad \text{and so} \quad x = [\text{H}_3\text{O}^+(aq)] = \sqrt{K_a \times 2.00}
\]

After working out \([\text{H}_3\text{O}^+(aq)]\), the pH and percentage dissociation of the weak acid can be calculated:

\[
\text{pH} = -\log[\text{H}_3\text{O}^+(aq)] \quad \text{and} \quad \% \text{ dissociation} = \frac{[\text{H}_3\text{O}^+(aq)]}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\
\]

**Critical thinking questions**

1. What are the initial and final concentrations of CH₃COOH in the ICE table above? How are they related when the small \(x\) approximation is used?

2. Using your answer to Q1, write down a formula for \(x\) for any dilute weak acid.

3. Calculate the pH and percentage dissociation of the acetic acid as it is diluted \((K_a = 10^{-4.76})\).

   (a) 2.00 M \hspace{2cm} \text{pH} = \hspace{2cm} \text{pH} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \\
   (b) 1.00 M \hspace{2cm} \text{pH} = \hspace{2cm} \text{pH} = \hspace{2cm} \text{pH} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \\
   (c) 0.500 M \hspace{2cm} \text{pH} = \hspace{2cm} \text{pH} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \\
   (d) 0.250 M \hspace{2cm} \text{pH} = \hspace{2cm} \text{pH} = \hspace{2cm} \text{pH} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} \% \text{ dissociation} = \hspace{2cm} 
Model 2: Addition of a Strong Base to a Weak Acid

In Model 1, you used an “ICE” approach to work out the pH of a solution containing a weak acid. For example, you worked out that a 0.500 M solution of CH₃COOH(aq) has a pH of 2.531.

If a strong base, such as NaOH, is added to this solution, it will react with the weak acid.

\[
\text{CH}_3\text{COOH(aq)} + \text{OH}^-(aq) \rightarrow \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O(aq)}
\]

As long as the amount of OH\(^-(aq)\) added is less than the amount of CH₃COOH(aq) present, the solution will contain both CH₃COO\(^-(aq)\) and left over CH₃COOH(aq). A solution like this containing both a weak acid and its conjugate base is a buffer and its pH is given by the Henderson-Hasselbalch equation:

\[
pH = pK_a + \log \left[ \frac{[\text{base}]}{[\text{acid}]} \right] = pK_a + \log \left[ \frac{[\text{CH}_3\text{COO}^- (aq)]}{[\text{CH}_3\text{COOH} (aq)]]} \right]
\]

Critical thinking questions

1. If 0.100 mol of NaOH(s) is added to a 1.00 L solution of 0.500 M CH₃COOH, it will react to form a solution which is 0.100 M in CH₃COO\(^-(aq)\) and 0.400 M CH₃COOH(aq). What is the pH of this solution? (pK\(_a\) (CH₃COOH) = 4.76).

2. Complete the table below showing the concentrations of CH₃COOH(aq) and CH₃COO\(^-(aq)\) and the pH of the solution as more NaOH(s) is added to this solution.

<table>
<thead>
<tr>
<th>Amount of NaOH(s) added (mol)</th>
<th>0.000</th>
<th>0.100</th>
<th>0.200</th>
<th>0.300</th>
<th>0.400</th>
<th>0.500</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CH₃COOH(aq)] (M)</td>
<td>0.500</td>
<td>0.400</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CH₃COO(^-(aq))] (M)</td>
<td>0.000</td>
<td>0.100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>2.531</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. To react completely with the original CH₃COOH, 0.500 mol of NaOH must be added. What is the pH of the solution when exactly half this amount is added?

4. How can you obtain the value for pK\(_a\) for an acid?
Model 3: Neutralizing a Weak Acid

Model 2 describes the pH changes as a strong base is added to a solution containing a weak acid. The strong base reacts with the weak acid leading to a solution containing the conjugate base of the weak acid and any left over acid. The *equivalence* point occurs when enough base has been added so that there is no acid left.

At this point, the solution contains the conjugate base and essentially none of the original acid.

The conjugate base will then set up its own equilibrium:

\[
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^- (aq)
\]

\[K_b = \frac{[\text{CH}_3\text{COO}^- (aq)][\text{OH}^- (aq)]}{[\text{CH}_3\text{COOH}(aq)]}\]

From the chemical equation:

\[[\text{CH}_3\text{COOH}(aq)]_{\text{equilibrium}} = [\text{OH}^- (aq)]_{\text{equilibrium}}\]

As hardly any base reacts, \[[\text{CH}_3\text{COO}^- (aq)]_{\text{equilibrium}} \approx [\text{CH}_3\text{COO}^- (aq)]_{\text{initial}}\] and so:

\[K_b = \frac{[\text{OH}^- (aq)]^2}{[\text{CH}_3\text{COO}^- (aq)]_{\text{initial}}} \quad \text{and} \quad [\text{OH}^- (aq)] = \sqrt{K_b \times [\text{CH}_3\text{COO}^- (aq)]_{\text{initial}}}\]

After working out \([\text{OH}^- (aq)]\), the pOH can be calculated:

\[\text{pOH} = -\log[\text{OH}^- (aq)]\]

Finally, the pH can then be calculated using \(\text{pH} = 14.00 - \text{pOH}\).

**Critical thinking questions**

1. To react completely with the original \(\text{CH}_3\text{COOH}\) in Q5, 0.500 mol of \(\text{NaOH}\) must be added. What will be \([\text{CH}_3\text{COO}^- (aq)]\) when this occurs?

2. Calculate the pH of the solution the reaction produced in Q1.  
   (*Hint*: remember that \(pK_a + pK_b = 14.00\) or \(K_a \times K_b = 10^{-14.00}\))

3. Correct your entry in the final column of the table in Model 1 if required!

4. What is the pH at the equivalence point of the titration of a *strong* acid with a strong base?

5. Is the pH at the equivalence point of the titration of a *weak* acid with a strong base less than or higher than 7?
• 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.

Answer:

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.

Answer:

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.

Answer:

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?