Worksheet 19 – Weak Acids and Bases

Calculating the pH of a strong acid (base) is straightforward because all of the initial acid (base) dissociates completely. For a monoprotic acid, \([H_3O^+] = [\text{Acid}]_{\text{init}}\). For a monobasic base, \([OH^-] = [\text{Base}]_{\text{init}}\)

When weak acids (bases) are added to water, an equilibrium occurs. We can use ICE tables and the \(K_a\) (\(K_b\)) values of the acids (bases) to determine the extent of the reaction.

As an approximation, \([HA]_{\text{init}} = [HA]_{\text{eq}}\) for acids with very small \(K_a\) values. This approximation will not affect the calculated pH of a solution if the % ionization of the acid is less than 5%. We call this the **5% rule**. In situations where the 5% rule does not apply, you’ll need to use the quadratic formula to solve for \(x\) in the ICE table:

\[
ax^2 + bx + c = 0, \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

You’ll get two values of \(x\) (2 roots to the equation), but one of them will not make physical sense. Think about both values carefully and select the one that is appropriate.

1. Start with 100.00 mL of a 0.10 M solution of acetic acid, \(\text{CH}_3\text{COOH}\). It has a pH = 2.87 at 25ºC. Calculate the \(K_a\) of acetic acid at 25ºC.

   a) Write the acid dissociation reaction.

   \[
   \text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+
   \]

   b) Write an expression for \(K_a\) in terms of the reactants and products of this reaction.

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

   c) Write an ICE table for these experimental conditions.

   

<table>
<thead>
<tr>
<th></th>
<th>([\text{CH}_3\text{COOH}])</th>
<th>([\text{CH}_3\text{COO}^-])</th>
<th>([\text{H}_3\text{O}^+])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.10 – x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
d) Solve for $[\text{H}_3\text{O}^+]$ with the information in your table and equations. Then, calculate the value for $K_a$.

$$[\text{H}_3\text{O}^+] = 10^{-pH} = 10^{-2.87} = 1.35 \times 10^{-3} \text{ M} = x$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(1.35 \times 10^{-3})(1.35 \times 10^{-3})}{(9.865 \times 10^{-2})} = 1.85 \times 10^{-5}$$

e) Calculate the % ionization for 0.10 M acetic acid. Is the 5% approximation O.K.?

$$\frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{CH}_3\text{COOH}]_{\text{init}}} \times 100\% = \frac{(1.35 \times 10^{-3})}{0.10} \times 100\% = 1.35\%$$

This tells us that $[\text{CH}_3\text{COOH}]_{\text{eq}} \approx [\text{CH}_3\text{COOH}]_{\text{init}}$ because 1.35 % < 5%.

We could write the $[\text{CH}_3\text{COOH}]$ at equilibrium in our ICE table simply as $\sim 0.10$, and it would not make a significant impact on pH or $K_a$

f) Now, add 900.00 mL of water to this system (total volume is 1.00 L). Calculate the pH of a 0.010 M solution of acetic acid, using the same $K_a$.

\[
\begin{array}{ccc}
\text{Initial} & [\text{CH}_3\text{COOH}] & [\text{CH}_3\text{COO}^-] & [\text{H}_3\text{O}^+] \\
& 0.010 & 0 & 0 \\
\text{Change} & -x & +x & +x \\
\text{Equil.} & 0.010 – x & x & x \\
\end{array}
\]

$$K_a = 1.85 \times 10^{-5} = \frac{x^2}{0.010 – x} \approx \frac{x^2}{0.010}$$

$$x \approx 4.30 \times 10^{-4} = [\text{H}_3\text{O}^+]$$

$$pH = -\log(4.30 \times 10^{-4}) = 3.37$$

g) Calculate the % ionization of this reaction. Is it larger or smaller than in the 0.10 M solution? Explain this in terms of Le Chatelier's Principle. (Hint: think about the effects of volume changes on gaseous systems)

$$\% \text{ ionization} = \frac{(4.30 \times 10^{-4})}{0.010} \times 100\% = 4.30\%$$

This is a larger dissociation, but still less than 5%, so the approximation that “0.010 – x = 0.010” was okay. We increased the solution volume, so the reaction shifted to the side that had more moles (not counting the water, which doesn’t appear in the equilibrium expression). We could also calculate $Q$ to see that the reaction would shift to the right (towards the product side)
2. What is the pH of a 0.0010 M solution of methyl amine, CH₃NH₂, with a

\[ K_b = 4.4 \times 10^{-4} \]?

(Does the 5% rule apply here?)

Follow the same general steps that were used in problem #1, but consider how starting with a base will change the process.

We write the reaction of a base with water to product a conjugate acid and hydroxide:

\[ \text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+ + \text{OH}^- \]

\[ K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} \]

<table>
<thead>
<tr>
<th>[ [\text{CH}_3\text{NH}_2] ]</th>
<th>[ [\text{CH}_3\text{NH}_3^+] ]</th>
<th>[ [\text{OH}^-] ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.0010</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>+x</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.0010 – x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_b = 4.4 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} \approx \frac{x^2}{0.0010} \]

\[ x \approx 6.6 \times 10^{-4} \]

\[ \% \text{ ionization} = \frac{(6.6 \times 10^{-4})}{0.0010} \times 100\% = 66\% \]

The % ionization for this reaction is 66%, so the 5% rule definitely does NOT apply. We need to solve for the actual value of \( x \) (not an approximation) using the quadratic equation:

\[ K_b = 4.4 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{x^2}{0.0010 - x} \]

\[ 4.4 \times 10^{-4}(0.0010 - x) = x^2 \]

\[ x^2 + 4.4 \times 10^{-4}x - 4.4 \times 10^{-7} = 0 \]

For equations of the form \( ax^2 + bx + c = 0 \),

\[ x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\[ x = \frac{-4.4 \times 10^{-4} \pm \sqrt{(4.4 \times 10^{-4})^2 - 4(1)(-4.4 \times 10^{-7})}}{2(1)} \]

\[ x = 4.8 \times 10^{-4} \text{ and } x = -9.2 \times 10^{-4} \]
Equilibrium concentrations can never be less than 0, so we pick the first root, \( x = 4.8 \times 10^{-4} \), and then solve for the pOH before calculating the pH.

\[ x = 4.8 \times 10^{-4} = [OH^-] \]
\[ pOH = -\log(4.8 \times 10^{-4}) = 3.3 \]
\[ pH = 14 - 3.3 = 10.7 \]

3. A 0.1 M solution of a monoprotic acid, HA, is 4.2 % ionized. What is the \( K_a \)?

\[ HA + H_2O \rightleftharpoons A^- + H_3O^+ \]

<table>
<thead>
<tr>
<th></th>
<th>[HA]</th>
<th>[A(^-)]</th>
<th>[H(_3)O(^+)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-( x )</td>
<td>+( x )</td>
<td>+( x )</td>
</tr>
<tr>
<td>Equil.</td>
<td>0.1 – ( x )</td>
<td>( x )</td>
<td>( x )</td>
</tr>
</tbody>
</table>

\[ \text{% ionization} = \frac{x}{0.1} \times 100\% = 4.2\% \]
\[ x = 4.2 \times 10^{-3} \]

The 5% rule can be used here because the % ionization is less than 5%:

\[ K_a = \frac{[A^-][H_3O^+]}{[HA]} \approx \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} \approx \frac{(4.2 \times 10^{-3})^2}{0.10} \approx 1.76 \times 10^{-4} \]

How does the actual \( K_a \) value compare to the one determined using the 5% rule?

\[ K_a = \frac{x^2}{0.10 - x} \approx \frac{(4.2 \times 10^{-3})^2}{0.10 - 4.2 \times 10^{-3}} = 1.84 \times 10^{-4} \]

Both values round to 1.8x10\(^{-4}\), so the approximation does not have a significant affect on the calculated \( K_a \) value.