Worksheet 21 - Acid/Base Calculations

1. Start with 100.00 mL of a 0.10 M solution of acetic acid, CH₃COOH. It has a pH = 2.87 at 25°C. Calculate the $K_a$ of acetic acid at 25°C.

   a) Write the acid dissociation reaction.

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

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

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

   c) Write an ICE table for these experimental conditions.

   \[
   \begin{array}{ccc}
   & [\text{CH}_3\text{COOH}] & [\text{H}^+] & [\text{CH}_3\text{COO}^-] \\
   I & 0.10 & 0 & 0 \\
   C & -x & +x & +x \\
   E & 0.10-x & x & x \\
   \end{array}
   \]

   d) Solve for $[\text{H}^+]$ with the information in your table and equations. Then, calculate the value for $K_a$.

   \[
   K_a = \frac{x^2}{0.10-x} \\
   \]

   \[ \text{pH} = 2.87 \]

   \[ [\text{H}^+] = 10^{-2.87} \]

   \[ [\text{H}^+] = 1.35 \times 10^{-3} \]

   \[ K_a \approx \frac{(1.35 \times 10^{-3})^2}{0.10} = 1.82 \times 10^{-5} \]

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

   \[
   \frac{[\text{H}^+]_{\text{eq}}}{[\text{CH}_3\text{COOH}]} \times 100 = \frac{1.35 \times 10^{-3} \times 100}{0.10} = 1.35\% \approx 5\% \text{ approx in O.K.}
   \]
g) Now, add 900.00 mL of water to this system. Calculate the pH of a 0.010 M solution of acetic acid, using the same $K_a$.

\[
\frac{0.1 \text{ mol}}{1 \text{ L}} = 0.1 \text{ M}
\]

\[
1.82 \times 10^{-5} = \frac{x^2}{0.010}
\]

\[
x = 4.26 \times 10^{-4} = [H^+]
\]

\[
\text{pH} = 3.37
\]

h) Finally, calculate the % ionization. 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)

\[
\frac{4.26 \times 10^{-4}}{0.1} \times 100 = 4.26\%	ext{ ionization}
\]

At lower concentration, the ions side will move more. In a solution, the products will then cease.

2. What is the pH of a 0.0010 M solution of methyl amine, CH$_3$NH$_2$, with a $K_b = 4.4 \times 10^{-4}$?

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

\[
K_b = 4.4 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} \approx \frac{x^2}{0.001}
\]

\[
x = [\text{OH}^-] = 6.65 \times 10^{-4}
\]

\[
\frac{6.65 \times 10^{-4}}{100} = 6.65\%
\]

Solve for $x$.

\[
\text{Successive approximations:}
\]

\[
\begin{align*}
\text{X} & = 6.65 \times 10^{-4} \rightarrow 4.15 \times 10^{-4} \\
3.85 & \rightarrow 4.81 \\
5.20 & \rightarrow 4.78 \\
4.59 & \rightarrow 4.73 \\
4.88 & \rightarrow 4.73 \times 10^{-4} = [\text{OH}^-]
\end{align*}
\]

\[
\text{pH} = 3.32 \quad \text{pH} = 10.68
\]

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

\[
\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-
\]

\[
K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{4.2\% \times \frac{[\text{H}^+]}{0.10}}{0.10}
\]

\[
[\text{H}^+] = 4.2 \times 10^{-3}
\]

\[
K_a = \frac{(4.2 \times 10^{-3})^2}{1} = 1.76 \times 10^{-4}
\]
**Polyprotic acids** are those with more than one acidic proton. One example is arsenic acid, H₃AsO₄, a triprotic acid. It has three equilibrium expressions associated with its reaction with water:

\[
\begin{align*}
H₃AsO₄ + H₂O & \rightleftharpoons H₂AsO₄⁻ + H₃O⁺ & K_{a₁} = 5.0 \times 10^{-3} \\
H₂AsO₄⁻ + H₂O & \rightleftharpoons HAsO₄²⁻ + H₃O⁺ & K_{a₂} = 8.0 \times 10^{-5} \\
HAsO₄²⁻ + H₂O & \rightleftharpoons AsO₄³⁻ + H₃O⁺ & K_{a₃} = 6.0 \times 10^{-10}
\end{align*}
\]

It is a weak acid, whose ionization constants decrease markedly for the second and third dissociation reactions. The concentrations of each of the four species can be calculated as follows:

The value of \( K_{a₁} \) will be used to calculate the concentration of \( H₃AsO₄ \), \( H₂AsO₄⁻ \) and \( H⁺ \). These concentrations will **not** be affected by the other equilibria.

The value of \( K_{a₂} \) will be used to calculate the concentration of \( HAsO₄²⁻ \), using the previously calculated value of \( H₂AsO₄⁻ \) and \( H₃O⁺ \).

The value of \( K_{a₃} \) will be used to calculate the concentration of \( AsO₄³⁻ \), using the previously calculated value of \( HAsO₄²⁻ \) and the concentration of \( H₃O⁺ \), from \( K_{a₁} \).

5. If we have a 5.0 M solution of \( H₃AsO₄ \), what are the concentrations of all of the species present?

a) First, calculate the following concentrations:

\[
\begin{align*}
[H₃AsO₄] & = 5.0 \text{ M} \\
[H₂AsO₄⁻] & = 0.158 \text{ M} \\
[H₃O⁺] & = 0.158 \text{ M}
\end{align*}
\]

\[
K_{a₁} = 5.0 \times 10^{-3} = \frac{[H₂AsO₄⁻][H⁺]}{[H₃AsO₄]} \implies \frac{5x^2}{5} \implies x = 1.58
\]

\[
\begin{align*}
[H₂AsO₄⁻] & = 5.0 \times 10^{-5} = 4.84 \\
[H₃AsO₄] & = 1.58 \\
[H⁺] & = 1.58
\end{align*}
\]

b) What is the pH of this solution?

\[
pH = -\log (1.58 \times 10^{-5}) = 0.80
\]
c) Calculate the \([\text{HAsO}_4^{2-}]\) by solving for \(K_{a2}\).

\[
K_{a2} = 8.0 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{HAsO}_4^{2-}]}{[\text{H}_2\text{AsO}_4^-]} \quad \text{Use } [\text{H}_2\text{AsO}_4^-] \text{ and } [\text{H}_3\text{O}^+] \text{ from part a)}
\]

\[
8.0 \times 10^{-8} = \frac{1.158 + x}{x} \quad \Rightarrow \quad 8.0 \times 10^{-8} = \frac{1.158}{1.158 - x} \quad \Rightarrow \quad x = 8.0 \times 10^{-8}
\]

\([\text{HAsO}_4^{2-}] = 8.0 \times 10^{-8}
\]

\text{d) } \text{pH} = 0.80

\text{e) Calculate the } [\text{AsO}_4^{3-}] \text{ by solving for } K_{a3}. \quad \text{Use } [\text{HAsO}_4^{2-}] \text{ from part c)}

\[
K_{a3} = 6.0 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{AsO}_4^{3-}]}{[\text{HAsO}_4^{2-}]} \quad \text{and } [\text{H}_3\text{O}^+] \text{ from part a)}
\]

\[
6.0 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{AsO}_4^{3-}]}{8.0 \times 10^{-8} - x} \quad \Rightarrow \quad (6.0 \times 10^{-10})(8.0 \times 10^{-8}) = 1.158x \quad \Rightarrow \quad x = 3.04 \times 10^{-16}
\]

\([\text{AsO}_4^{3-}] = 3.04 \times 10^{-16}
\]

\text{f) pH} = 0.80

\text{Only the first } K_a \text{ determines the pH since it is the strongest acid.}
6. Ascorbic acid, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ is a diprotic acid, with $K_{a1} = 1.0 \times 10^{-5}$ and $K_{a2} = 5.0 \times 10^{-12}$.

It is often abbreviated as $\text{H}_2\text{Asc}$. Using this abbreviation:

\begin{align*}
\text{HAsc} + \text{H}_2\text{O} & \rightleftharpoons \text{HAsc}^- + \text{H}_3\text{O}^+ \quad K_{a1} = 1.0 \times 10^{-5} \\
\text{HAsc}^- + \text{H}_2\text{O} & \rightleftharpoons \text{Asc}^{2-} + \text{H}_3\text{O}^+ \quad K_{a2} = 5.0 \times 10^{-12}
\end{align*}

a) Write out the equilibria of this acid with water.

b) Write all of the species that will exist in a $0.500$ M solution of this weak acid, and label them as acids, bases or both.

<table>
<thead>
<tr>
<th>species</th>
<th>acid/base</th>
<th>$[\text{species}]_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i) $\text{H}_2\text{Asc}$</td>
<td>acid</td>
<td>$0.500$</td>
</tr>
<tr>
<td>ii) $\text{HAsc}$</td>
<td>base</td>
<td>$2.24 \times 10^{-3}$</td>
</tr>
<tr>
<td>iii) $\text{Asc}^{2-}$</td>
<td>base</td>
<td>$5.0 \times 10^{-12}$</td>
</tr>
<tr>
<td>iv) $\text{H}_3\text{O}^+$</td>
<td>acid</td>
<td>$2.24 \times 10^{-3}$</td>
</tr>
<tr>
<td>v) $\text{H}_2\text{O}$</td>
<td>base</td>
<td>$55$ M</td>
</tr>
<tr>
<td>vi) $\text{OH}^-$</td>
<td>base</td>
<td>$4.46 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

b) Calculate the equilibrium concentrations of all of these species.
(Hint: water will still be $55.5$ M, one down, five to go)

\begin{align*}
1.0 \times 10^{-5} = \frac{x^2}{0.50} \\
5.0 \times 10^{-12} = \frac{(2.24 \times 10^{-3} + x)\chi}{2.2 + x \times 10^{-3} - \chi} \\
\chi = 5.0 \times 10^{-12} = [\text{Asc}^{2-}]
\end{align*}

\begin{align*}
[\text{H}^+][\text{OH}^-] = 1 \times 10^{-12} \\
(2.24 \times 10^{-3})[\text{OH}^-] = 1 \times 10^{-15} \\
[\text{OH}^-] = 4.46 \times 10^{-12}
\end{align*}