Chapter 10 - Monoprotic Acid-Base Equilibria Continued

Acid/Base Strength

Strong acids and bases COMPLETELY dissociates

\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]

_No reverse arrow as no HCl present in solution_

Weak acids and bases:

PARTIAL dissociation

**Acid:** \( \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \)

\[ K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \]

*acid dissociation constant*

**Base:** \( \text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH}^+ + \text{OH}^- \)

\[ K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} \]

*base hydrolysis constant*
How do you determine the pH of a weak acid or base solution?

Using the systematic treatment of equilibrium:

1. Reactions -
   
   \[ HA \leftrightarrow H^+ + A^- \]
   \[ \text{H}_2\text{O} \leftrightarrow H^+ + \text{OH}^- \]

2. Charge balance -
   \[ [H^+] = [A^-] + [\text{OH}^-] \]

3. Mass balance -
   \[ F = [A^-] + [HA] \]
   *Where F is the formal concentration (total moles of comp’d dissolved per liter)*

4. Equilibria -
   \[ K_a = [H^+] [A^-] / [HA] \]
   \[ K_w = [H^+] [\text{OH}^-] \]

5. # of unknowns and equations:  [HA], [A^-], [H^+], [OH^-] and 4 equations.

6. Solve
Assumptions (that come from chemical intuition):

• Assume that most of the \([H^+]\) is coming from the weak acid and not from the water dissociation. (so this \(HA \rightleftharpoons H^+ + A^-\) predominant over this \(H_2O \rightleftharpoons H^+ + OH^-\).)
• With this assumption, \([H^+] \approx [A^-]\).

So..

If we let \(x = [H^+] = [A^-]\), then \([HA] = F - x\) (Recall, \(F\) is the molarity of HA added to solution, so we subtract the molarity of HA that has dissociated to \(H^+\) and \(A^-\) to get the \([HA]\) in solution.)

\[
K_a = \frac{[H^+] [A^-]}{[HA]} = \frac{x^2}{(F - x)}
\]
Example:
What is the pH of a solution of 0.030 M formic acid?
$K_a = 1.80 \times 10^{-4}$ of formic acid.

\[
\begin{align*}
\text{HCO}_2\text{H} & \rightleftharpoons \text{HCO}_2^- + \text{H}^+ \\
\text{H}_2\text{O} & \rightleftharpoons \text{H}^+ + \text{OH}^-
\end{align*}
\]
Determining pH of weak base:

Similar for base

If we let $x = [\text{OH}^-] \approx [\text{BH}^+]$, then $[\text{B}] = F - x$ (Recall, $F$ is the molarity of $\text{B}$ added to solution, so we subtract the molarity of $\text{B}$ that has dissociated to $\text{OH}^-$ and $\text{BH}^+$ to get the $[\text{B}]$ in solution.)

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{(F - x)}$$

Example:

What is the pH of a 0.030 M Pyridine? $K_b = 1.7 \times 10^{-9}$
Fraction of Dissociation of acid or base:

For an acid -

\[ \alpha = \frac{[A^-]}{([A^-] + [HA])} = \frac{x}{(x + (F - x))} = \frac{x}{F} \]

where \( x = [A^-] = [H^+] \)

and \( F = \text{initial concentration of HA} \)

Or \( \alpha = \text{concentration of A}^- / \text{initial concentration of HA} \)

For a base -

\[ \alpha = \frac{[BH^+]}{([BH^+] + [B])} = \frac{x}{(x + (F - x))} = \frac{x}{F} \]

where \( x = [BH^+] = [OH] \)

\( F = \text{initial concentration of base} [B] \)
Buffer

• A buffer solution resists changes in pH when acids or bases are added or when dilution occurs.

• If buffering was not possible, we would have acid/base problems in biological systems, environmental systems, etc.
What is a buffer?

Acid Dissociation: \[ HA \Leftrightarrow H^+ + A^- \]

Base Hydrolysis: \[ A^- + H_2O \Leftrightarrow HA + OH^- \]

If we add both the acid (HA) and its conjugate base to the solution (A^-) to the solution, then…

- the added A^- or H^+, the acid reaction goes to the right:
  \[ HA \Leftrightarrow H^+ + A^- \]
- the added HA or OH-, the base reaction goes to the right:
  \[ A^- + H_2O \Leftrightarrow HA + OH^- \]

The net result is that neither the acid or the base will increase \( H^+ \) or \( OH^- \) content, so the pH (and pOH) will not change.
Henderson-Hasselbalch Equation
Describes the pH of a solution from the pK$_a$ and the ratio of the concentrations of the acid and its conjugate base.

\[ \text{pH} = \text{pK}_a + \log \left[ \frac{[A^-]}{[HA]} \right] \]

You can prepare a buffer with a base and its conjugate acid so…

For solution prepared from a weak base:

\[ \text{pH} = \text{pK}_a + \log \left[ \frac{[B]}{[BH^+]} \right] \]

However, most buffers are made from an acid and its conjugate base.
Things to notice about the Henderson-Hasselbalch Equation:

When the \([\text{base}] = [\text{acid}]\), then

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

\[
pH = pK_a + \log 1
\]

So… \(pH = pK_a\)

When the \([\text{base}] \neq [\text{acid}]\), then the \(pH \neq pK_a\)

<table>
<thead>
<tr>
<th>([\text{base}] / [\text{acid}])</th>
<th>(\log [\text{base}] / [\text{acid}])</th>
<th>(pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:1</td>
<td>(\log(100) = 2)</td>
<td>(pK_a + 2)</td>
</tr>
<tr>
<td>10:1</td>
<td>(\log(10) = 1)</td>
<td>(pK_a + 1)</td>
</tr>
<tr>
<td>1:10</td>
<td>(\log(0.1) = -1)</td>
<td>(pK_a - 1)</td>
</tr>
<tr>
<td>1:100</td>
<td>(\log(0.01) = -2)</td>
<td>(pK_a - 2)</td>
</tr>
</tbody>
</table>

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Buffer Capacity (\(\beta\))

Describes how well a solution resists changes in pH when a strong acid or strong base is added.

\[
\beta = \frac{dC_b}{dpH} \quad \text{for addition of base}
\]

\[
\beta = \frac{dC_a}{dpH} \quad \text{for addition of acid}
\]

In words:
The larger the buffer capacity, the higher the concentration of strong acid or strong base you can add without affecting the pH. The largest buffer capacity is when \(pH = pK_a\). So..

*Choose the acid or base for buffering that has a \(pK_a\) at or near the desired pH.*
Making a Buffer

1. Determine the desired pH.
2. Choose an acid or base with a $pK_a$ near the desired pH (See Table 10-2 for list of commonly used buffers).
3. Decide on the concentration (common concentration is 0.1M).
4. Make up solution using normal procedures except only add approximately $\frac{3}{4}$ the needed volume of water.
5. Use a strong acid or strong base to adjust the pH to the desired pH value (should be near the $pK_a$) value using a pH meter to determine the pH of the solution.
6. After the pH adjustment is made, then finish dilution of solution.

*This approach is better than calculating the amount of acid or base needed since activities, temperature, etc. can alter pH.*
Summary of Buffers

• Buffers are a mix of a weak acid and its conjugate base (typically).
• Buffers are best when the desired pH ≈ pK_a of the acid.
• Over a fairly large range of concentrations, the pH of a buffer is independent of concentration.
• A buffer resists changes in pH when an acid or base is added to solution (its purpose in the chemical world!).
• If a lot of acid or base is added, then the buffer will give way to pH changes (nothing is perfect).