Polyprotic Acid/Base Equilibria

General considerations are the same as monoprotic acids/bases:

\[ H_2A = H^+ + HA^- \quad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} \]

\[ HA^- = H^+ + A^- \quad K_{a2} = \frac{[H^+][A^-]}{[HA^-]} \]

Let's look at this one species at a time, we'll use sulfurous acid (H₂SO₃) as a model compound:

\[ H_2SO_3 = H^+ + HSO_3^- \quad K_{a1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 1.23 \times 10^{-2} \]

\[ HSO_3^- = H^+ + SO_3^{2-} \quad K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.6 \times 10^{-8} \]

Polyprotic Acid/Base Equilibria...Chemistry!

\[ K_{a1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 1.23 \times 10^{-2} \quad K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.6 \times 10^{-8} \]

What is the pH of a solution prepared by dissolving 0.10 mol H₂SO₃ in 1.00 L water?

- What does the chemistry tell you?
- Look at the \( K_a \)'s, H₂SO₃ is a much stronger acid than HSO₃⁻; what does this mean??
Polyprotic Acid/Base Equilibria...Chemistry!

What is the pH of a solution prepared by dissolving 0.10 mol Na₂SO₃ in 1.00 L water?

- SO₃²⁻ is the dibasic (fully deprotonated) form of this weak acid, so let's look at Kᵢ's

\[
\begin{align*}
\text{SO}_3^{2-} + \text{H}_2\text{O} &= \text{OH}^- + \text{HSO}_3^- \\
\text{HSO}_3^- + \text{H}_2\text{O} &= \text{OH}^- + \text{H}_2\text{SO}_3
\end{align*}
\]

\[
K_{i1} = \frac{K_w}{K_{a2}} = 1.51 \times 10^{-7} \\
K_{i2} = \frac{K_w}{K_{a1}} = 8.13 \times 10^{-13}
\]

- Since SO₃²⁻ is a much stronger base than HSO₃⁻, we can solve a monoprotic base problem:

Amphiprotic Species

What is the pH of a solution prepared by dissolving 0.10 mol NaHSO₃ in 1.00 L water?

- HSO₃⁻ is the amphiprotic form of this weak acid, the problem is a little tougher.

\[
K_{a2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 6.6 \times 10^{-5}
\]

\[
K_{i2} = \frac{K_w}{K_{a1}} = 8.13 \times 10^{-13}
\]

- How do we approach this?
Amphiprotic Species

We need to take a more systematic approach! One starting point is a mass balance relationship called the "proton condition"

**proton condition**: The concentration of H⁺ is a result of the difference in concentration of the species that liberate H⁺ minus the concentrations of species that consume H⁺

Let's look at the proton condition for our system:

<table>
<thead>
<tr>
<th>Consume H⁺</th>
<th>Liberate H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO₃⁻ + H⁺ = H₂SO₃</td>
<td>HSO₃⁻ = SO₃²⁻ + H⁺</td>
</tr>
<tr>
<td>H₂O = H⁺ + OH⁻</td>
<td></td>
</tr>
</tbody>
</table>

So, the proton condition is:

\[ [H^+] = [SO_3^{2-}] + [OH^-] - [H_2SO_3] \]

We can substitute expressions for \([SO_3^{2-}],[OH^-]\) and \([H_2SO_3]\) from the appropriate equilibrium constant expressions to arrive at an expression in terms of \([H^+]\) and \([HSO_3^-]\).

\[
[H^+] = \frac{K_{a2} \cdot [HSO_3^-]}{[H^+]} + \frac{K_w}{[H^+] - \frac{[H^+] [HSO_3^-]}{K_{a1}}} \]

With the help of the god's of algebra we can come to this:

\[
[H^+] = \sqrt{\frac{K_{a2}K_{a2} [HSO_3^-] + K_{a1}K_w}{K_{a1} + [HSO_3^-]}}
\]

We still can't solve this completely (we don't know \([HSO_3^-])... What DO we know?

REMEMBER THIS IS CHEMISTRY!
Chemistry Can Be Helpful!

1. We know that HSO₃⁻ is acting as both an acid and a base in this case.
2. Every time an SO₃²⁻ is formed, a H⁺ is liberated. Every time a H₂SO₃ is formed OH⁻ is produced.
3. The H⁺ and OH⁻ can react to reform the original HSO₃⁻.
4. Therefore [HSO₃⁻] will not vary much from original concentration, F.

So, working under this assumption, the equation becomes:

\[ [H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} \]

We know all of these values, if we plug and chug, we discover that

\[ [H^+] = 2.69 \times 10^{-5} \text{M}, \text{ with } pH = 4.57 \]

Can we make things easier? Maybe!

Chemistry Can Be (more) Helpful!

\[ [H^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} \]

Two considerations:
1. If K_{a2}F >> K_{w}, the numerator in the fraction becomes K_{a1}K_{a2}F
2. If K_{a1} << F, the denominator becomes F

The result of these assumptions is a much simpler equation:

\[ [H^+] = \sqrt{\frac{K_{a1}K_{a2}F}{F}} = \sqrt{K_{a1}K_{a2}} \]

OR:

\[ pH = \frac{1}{2} (pK_{a1} + pK_{a2}) \]

Using this simplification, our problem becomes:

\[ pH = \frac{1}{2} (1.91 + 7.18) = 4.55 \]
Handling Polyprotic Acids/Bases
(Read text carefully)

As long as $K_a$’s aren’t too close (~1000x)

1. Treat fully protonated acid as a weak monoprotic acid

$$K_a = \frac{x^2}{F-x}$$

2. Treat fully deprotonated acid as weak monobasic base

3. Treat intermediate forms by looking at the $K_a$’s for the surrounding equilibria

$$[H^+] = \sqrt{\frac{K_{ax} K_{ax+1} F + K_{ax} K_w}{K_{ax} + F}}$$

Complete systematic approach will always work, but will require more effort.

Fraction of Dissociation

$$H_2A = H^+ + HA^-$$

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

$$HA^- = H^+ + A^-$$

$$K_{a2} = \frac{[H^+][A^-]}{[HA^-]}$$

Calculate $\alpha_{H_2A}$ as a function of pH.

$$\alpha_{H_2A} =$$

How do we get things in terms of $K$'s and $[H^+]$? Look at equilibrium expressions:

From $K_{a1}$:  
$$[HA] =$$

From $K_{a2}$:  
$$[A^{2-}] =$$

Combine Terms:
Fraction of Dissociation

\[ \alpha_{H_2A} = \frac{[H_2A]}{[H_2A] + K_{a1}[H_2A] + K_{a1}K_{a2}[H_2A]} \]

With some cancellation and manipulation:

\[ \alpha_{H_2A} = \frac{[H^+]^2}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \]

We can do the same treatment for HA\(^-\), and A\(^2^-\):

\[ \alpha_{HA^-} = \frac{K_{a1}[H^+]}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \]
\[ \alpha_{A^2^-} = \frac{K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \]

Is there a pattern emerging?

For triprotic acid, denominator becomes: