Polyprotic Acid/Base Equilibria

General considerations are the same as monoprotic acids/bases:

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

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

Lets look at this one species at a time, we'll use sulfurous acid (H_2SO_3) as a model compound:

$H_2SO_3 = H^+ + HSO_3^-$ $\quad K_{a1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 1.23x10^{-2}$

$HSO_3^- = H^+ + SO_3^{2-}$ $\quad K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.6x10^{-8}$

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Polyprotic Acid/Base Equilibria…Chemistry!

$K_{a1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 1.23x10^{-2}$ $\quad K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.6x10^{-8}$

What is the pH of a solution prepared by dissolving 0.10 mol H_2SO_3 in 1.00 L water?

- What does the chemistry tell you?
- Look at the K_a's, H_2SO_3 is a much stronger acid than HSO_3^-, what does this mean??

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Polyprotic Acid/Base Equilibria…Chemistry!

What is the pH of a solution prepared by dissolving 0.10 mol Na_2SO_3 in 1.00 L water?

- SO_3^{2-} is the dibasic (fully deprotonated) form of this weak acid, so let's look at K_b's

$SO_3^{2-} + H_2O = OH^- + HSO_3^-$ $$K_{b1} = \frac{K_w}{K_{a2}} = 1.51x10^{-7}$$

$HSO_3^- + H_2O = OH^- + H_2SO_3$ $$K_{b2} = \frac{K_w}{K_{a1}} = 8.13x10^{-13}$$

- Since SO_3^{2-} is a much stronger base than HSO_3^-, we can solve a monoprotic base problem:

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Amphiprotic Species

What is the pH of a solution prepared by dissolving 0.10 mol $NaHSO_3$ in 1.00 L water?

- HSO_3^- is the *amphiprotic* form of this weak acid, the problem is a little tougher.

$HSO_3^- = H^+ + SO_3^{2-}$ $$K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3]} = 6.6x10^{-8}$$

$HSO_3^- + H_2O = OH^- + H_2SO_3$ $$K_{b2} = \frac{K_w}{K_{a1}} = 8.13x10^{-13}$$

- How do we approach this?

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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^+

Lets look at the proton condition for our system:

Consume H^+	Liberate H^+
$HSO_3^- + H^+ = H_2SO_3$	$HSO_3^- = SO_3^{2-} + H^+$
	$H_2O = H^+ + OH^-$

So, the proton condition is:

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

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Amphiprotic Species

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

- 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 $[HSO_3^-]$.

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

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

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

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

REMEMBER THIS IS CHEMISTRY!

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Chemistry Can Be Helpful!

1. We know that HSO_3^- is acting as both an acid and a base in this case
2. Every time an SO_3^{2-} is formed, a H^+ is liberated. Every time a H_2SO_3 is formed OH^- is produced.
3. The H^+ and OH^- can react to reform the original HSO_3^-
4. Therefore $[HSO_3^-]$ 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
$[H^+] = 2.69 \times 10^{-5}M$, with pH = 4.57

Can we make things easier? Maybe!

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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: $pH = \frac{1}{2}(1.91 + 7.18) = 4.55$

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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.

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Fraction of Dissociation

$H_2A = H^+ + HA^-$ $\quad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$ $\qquad HA^- = H^+ + A^-$ $\quad K_{a2} = \frac{[H^+][A^-]}{[HA^-]}$

Calculate α_{H2A} as a function of pH.

α_{H2A} =

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:

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Fraction of Dissociation

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

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-}.

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

Is there a pattern emerging?

For triprotic acid, denominator becomes:

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