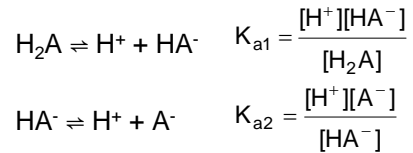
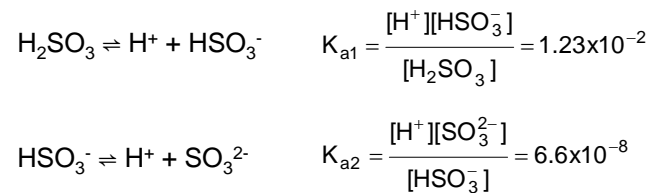


Polyprotic Acid/Base Equilibria

General considerations are the same as monoprotic acids/bases:



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



1

Polyprotic Acid/Base Equilibria...Chemistry!

$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} = 1.23 \times 10^{-2} \quad K_{a2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = 6.6 \times 10^{-8}$$

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

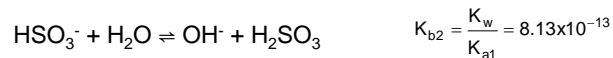
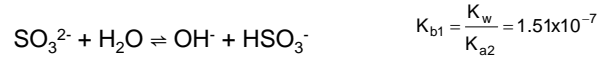
- What does the chemistry tell you?
- Look at the K_a 's, H_2SO_3 is a much stronger acid than HSO_3^- , what does this mean??

2

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



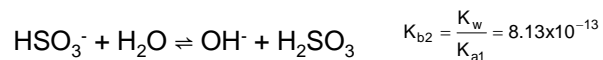
- Since SO_3^{2-} is a much stronger base than HSO_3^- , we can solve a monoprotic base problem:

3

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.



- How do we approach this?

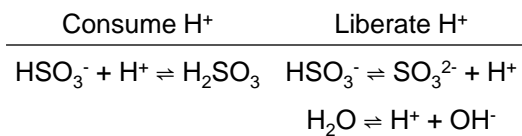
4

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:



So, the proton condition is:

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

5

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 $[HSO_3^-]$.

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

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

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

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

REMEMBER THIS IS CHEMISTRY!

6

Chemistry Can Be Helpful!

1. We know that HSO_3^- is acting as both a weak acid and a weak base in this case
2. Since the K's for each process are small (they are weak), neither reaction proceeds very far towards products.
3. Therefore $[\text{HSO}_3^-]$ will not vary much from original concentration, F.

So, working under this assumption, the equation becomes:

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

We know all of these values, if we plug and chug, we discover that
 $[\text{H}^+] = 2.69 \times 10^{-5} \text{M}$, with $\text{pH} = 4.57$

Can we make things easier? Maybe!

7

Chemistry Can Be (more) Helpful!

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

Two considerations:

1. If $K_{a2}F \gg K_w$, the numerator in the fraction becomes $K_{a1}K_{a2}F$
2. If $K_{a1} \ll F$, the denominator becomes F

The result of these assumptions is a much simpler equation:

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

$$\text{OR: } \text{pH} = \frac{1}{2}(\text{p}K_{a1} + \text{p}K_{a2})$$

Using this simplification, our problem becomes: $\text{pH} = \frac{1}{2}(1.91 + 7.18) = 4.55$

8

Handling Polyprotic Acids/Bases (Read text carefully)

As long as K_a 's aren't too close ($\sim 1000x$)

1. Treat fully protonated acid as a weak monoprotic acid

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

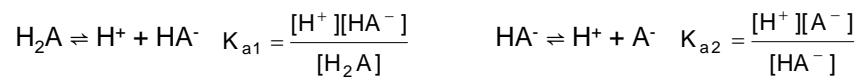
2. Treat fully deprotonated acid as weak monobasic base
3. Treat intermediate forms by looking at the K_a 's for the surrounding equilibria

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

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

9

Fraction of Dissociation



Calculate α_{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:

10

Fraction of Dissociation

$$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}_2\text{A}]}{[\text{H}_2\text{A}] + \frac{K_{\text{a}1}[\text{H}_2\text{A}]}{[\text{H}^+]} + \frac{K_{\text{a}1}K_{\text{a}2}[\text{H}_2\text{A}]}{[\text{H}^+]^2}}$$

With some cancellation and manipulation:

$$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2}}$$

We can do the same treatment for HA^- , and A^{2-} .

$$\alpha_{\text{HA}^-} = \frac{K_{\text{a}1}[\text{H}^+]}{[\text{H}^+]^2 + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2}} \quad \alpha_{\text{A}^{2-}} = \frac{K_{\text{a}1}K_{\text{a}2}}{[\text{H}^+]^2 + K_{\text{a}1}[\text{H}^+] + K_{\text{a}1}K_{\text{a}2}}$$

Is there a pattern emerging?

For triprotic acid, denominator becomes: