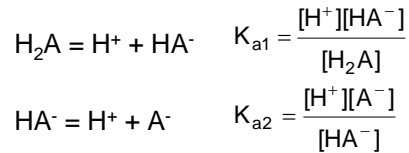
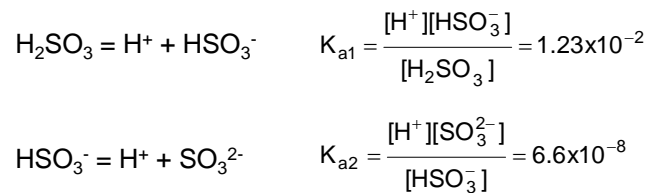


## Polyprotic Acid/Base Equilibria

General considerations are the same as monoprotic acids/bases:

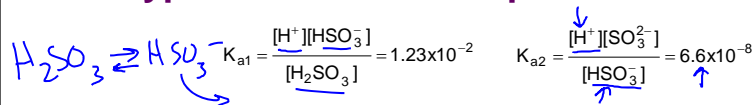


Lets look at this one species at a time, we'll use sulfurous acid ( $\text{H}_2\text{SO}_3$ ) as a model compound:



1

## Polyprotic Acid/Base Equilibria...Chemistry!



What is the pH of a solution prepared by dissolving 0.10 mol  $\text{H}_2\text{SO}_3$  in 1.00 L water?

- What does the chemistry tell you?
  - Look at the  $K_a$ 's,  $\text{H}_2\text{SO}_3$  is a much stronger acid than  $\text{HSO}_3^-$ , what does this mean?? *blc  $K_{a2}$  small +  $K_{a1}$  also sorta small,  $K_{a2} \ll K_{a1}$  don't expect much  $\text{SO}_3^{2-}$  and  $[\text{H}^+]$  from  $K_{a2}$  eg. insignificant*
- ∴ ignore  $K_{a2}$ , treat as "monoprotic" acid problem assume  $[\text{SO}_3^{2-}] \ll [\text{HSO}_3^-]$*

$$K_{a1} = \frac{x^2}{F-x} \quad [\text{H}^+] = x = 0.0295 \text{ M}, \text{ pH} = 1.53$$

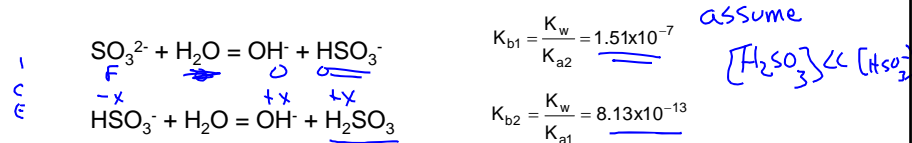
*∴  $[\text{SO}_3^{2-}] = 6.6 \times 10^{-8} \text{ M}$*

2

## Polyprotic Acid/Base Equilibria...Chemistry!

What is the pH of a solution prepared by dissolving 0.10 mol  $\text{Na}_2\text{SO}_3$  in 1.00 L water?

- $\text{SO}_3^{2-}$  is the dibasic (fully deprotonated) form of this weak acid, so let's look at  $K_b$ 's



- Since  $\text{SO}_3^{2-}$  is a much stronger base than  $\text{HSO}_3^-$ , we can solve a monoprotic base problem:

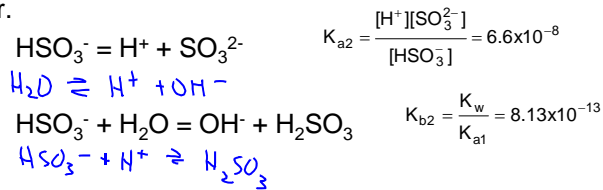
$$K_{b1} = \frac{x^2}{F-x} \quad x = [\text{OH}^-] = 1.24 \times 10^{-4} \text{ M} \\
 \text{pH} = 10.09$$

3

## Amphiprotic Species

What is the pH of a solution prepared by dissolving 0.10 mol  $\text{NaHSO}_3$  in 1.00 L water?

- $\text{HSO}_3^-$  is the *amphiprotic* form of this weak acid, the problem is a little tougher.



- How do we approach this?

Systematic

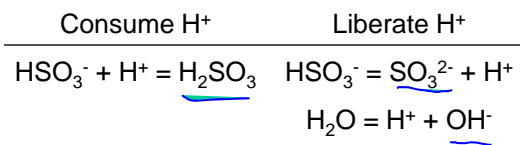
4

## 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:

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

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

## Amphiprotic Species

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

$[H_2SO_3] = \frac{[H^+][HSO_3^-]}{K_{a1}}$       $[SO_3^{2-}] = \frac{K_{a2}[HSO_3^-]}{[H^+]}$

$[H^+] = [SO_3^{2-}] + [OH^-] - [H_2SO_3]$   
 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  $[HSO_3^-]$ .

$K_w = [OH^-][H^+]$   
 $[OH^-] = \frac{K_w}{[H^+]}$

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

- 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!

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## Chemistry Can Be Helpful!

1. We know that  $\text{HSO}_3^-$  is acting as both an acid and a base in this case
2. Every time an  $\text{SO}_3^{2-}$  is formed, a  $\text{H}^+$  is liberated. Every time a  $\text{H}_2\text{SO}_3$  is formed  $\text{OH}^-$  is produced.
3. The  $\text{H}^+$  and  $\text{OH}^-$  can react to reform the original  $\text{HSO}_3^-$  (more favorable)
4. Therefore  $[\text{HSO}_3^-]$  will not vary much from original concentration, F.

So, working under this assumption, the equation becomes:

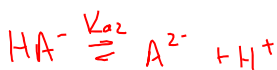
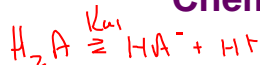
$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}}$$

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!

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## Chemistry Can Be (more) Helpful!



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

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

as  $K_{a1} \downarrow$ , strength of  $\text{H}_2\text{A}$  as acid  $\downarrow$

The result of these assumptions is a much simpler equation:

$$K_{a1} = 1.2 \times 10^{-2} \\ = 0.012$$

$$F = 0.10 \text{M}$$

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

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

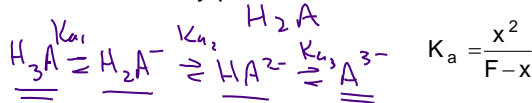
Using this simplification, our problem becomes:  $\text{pH} = \frac{1}{2}(1.91 + 7.18) = 4.55$

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## 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



2. Treat fully deprotonated acid as weak monobasic base

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

amphiprotic

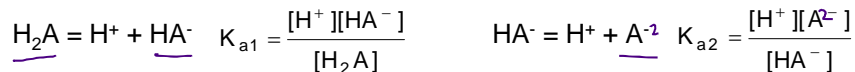
$$[\text{H}^+] = \sqrt{\frac{K_{ax} K_{ax+1} F + K_{ax} K_w}{K_{ax} + F}}$$

$$\Rightarrow \text{pH} = \frac{\text{p}K_a + \text{p}K_{a+1}}{2}$$

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

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## Fraction of Dissociation



Calculate  $\alpha_{\text{H}_2\text{A}}$  as a function of pH.

$$\alpha_{\text{H}_2\text{A}} = \frac{[\text{H}_2\text{A}]}{[\text{H}_2\text{A}] + [\text{HA}^-] + [\text{A}^{2-}]}$$

$\propto \text{HA}^-$ ,  $\propto \text{A}^{2-}$

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

From  $K_{a1}$ :  $[\text{HA}^-] = \frac{K_{a1}[\text{H}_2\text{A}]}{[\text{H}^+]}$

From  $K_{a2}$ :  $[\text{A}^{2-}] = \frac{K_{a2}[\text{HA}^-]}{[\text{H}^+]}$

Combine Terms:  $[\text{A}^{2-}] = \frac{K_{a1} K_{a2} [\text{H}_2\text{A}]}{[\text{H}^+]^2}$

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## Fraction of Dissociation

$$\alpha_{H_2A} + \alpha_{HA^-} + \alpha_{A^{2-}} = 1$$

$$\alpha_{H_2A} = \frac{[H_2A]}{[H_2A] + \frac{K_{a1}[H_2A]}{[H^+]} + \frac{K_{a1}K_{a2}[H_2A]}{[H^+]^2}} = \frac{[H_2A]}{[H_2A] \left( 1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} \right)}$$

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  $A^{2-}$ .

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

Is there a pattern emerging?

For triprotic acid, denominator becomes:

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Monoprotic

$$\alpha_{A^-} = \frac{K_a}{[H^+] + K_a} \quad \alpha_{HA} = \frac{[H^+]}{[H^+] + K_a}$$

Triprotic  $\alpha$   $H_3A$   $K_{a1}, K_{a2}, K_{a3}$   
 $H_3A, H_2A^-, HA^{2-}, A^{3-}$

$$\alpha_{H_3A} = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}}$$

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