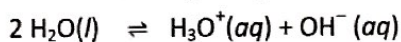


## Let's Mix it Up: Calculating pH of a Mixture of Weak Acids

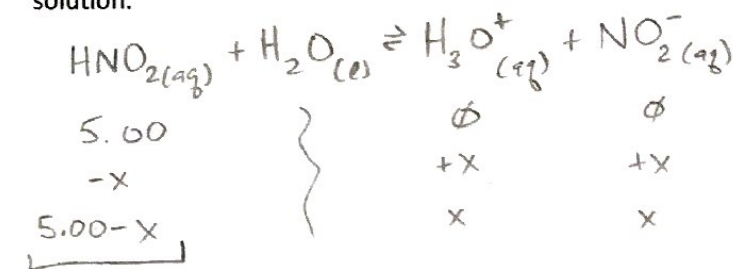
**Determination of the pH of a Mixture of Weak Acids:** Luckily, only the acid with the largest  $K_a$  will contribute an appreciable  $[H^+]$ . Determine the pH based on this acid and ignore all others!

- This is what we've been doing with the autoionization of water. Although hydronium ions are being produced through the equation below,  $K_w = 1 \times 10^{-14}$  which is *usually*  $\ll K_a$  for other acids in solution.



### Let's Try!

- A solution contains 1.00 M HCN ( $K_a = 6.2 \times 10^{-10}$ ) and 5.00 M HNO<sub>2</sub> ( $K_a = 4.0 \times 10^{-4}$ ). Calculate the pH of the solution.



$K_a \ll 1$ ,  $x$  negligible

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{5.00-x} \approx \frac{x^2}{5.00} = 4.0 \times 10^{-4}$$

$$x = [H_3O^+] = \sqrt{(5.00)(4.0 \times 10^{-4})} = 0.45 \text{ M}$$

$$pH = -\log(0.45) = \boxed{1.35}$$

### Determination of the pH of Polyprotic Acids:

- Acids with more than one ionizable hydrogen will ionize in steps, and each dissociation has its own  $K_a$  value.
- As the negative charge on the acid increases it becomes more difficult to remove the positively charged proton.
- As each  $H^+$  is removed, the remaining acid gets weaker and therefore has a smaller  $K_a$ .

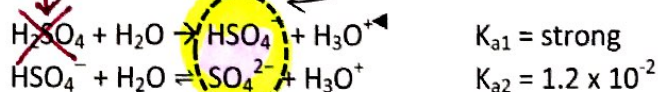
$$K_{a1} > K_{a2} > K_{a3}$$

Generally, the difference between  $K_a$  values is great enough so the second ionization doesn't affect the pH value!

**For most polyprotic pH problems, just do first ionization.**

### Exception: H<sub>2</sub>SO<sub>4</sub>

- The ionization constants for H<sub>2</sub>SO<sub>4</sub> are listed below:



- Because sulfuric acid is a strong acid in its first dissociation, use  $[H_2SO_4]_{\text{initial}} = [HSO_4^-]_{\text{equil}} = [H_3O^+]_{\text{equil}}$
- Because sulfuric acid is a weak acid in its second dissociation, the second dissociation will contribute a negligible amount for concentrations less than 1.0 M.
- Luckily, the AP test only considers quantitative calculations for  $[H_2SO_4] < 1.0 \text{ M}$ . ☺

stronger!  
only acid to use  
in calculation

## Let's Practice!

1. Sulfurous acid,  $\text{H}_2\text{SO}_3$ , is a diprotic acid with  $K_1 = 1.3 \times 10^{-2}$  and  $K_2 = 6.2 \times 10^{-8}$ . Which of the following best represents the relative concentrations of ions in a 2.0 M solution of  $\text{H}_2\text{SO}_3$ ?

- a.  $[\text{H}_2\text{SO}_3] < [\text{SO}_3^{2-}] = [\text{HSO}_3^-]$       c.  $[\text{H}_2\text{SO}_3] < [\text{HSO}_3^-] < [\text{SO}_3^{2-}]$   
 (b)  $[\text{SO}_3^{2-}] < [\text{HSO}_3^-] \ll [\text{H}_2\text{SO}_3]$       d.  $[\text{H}_2\text{SO}_3] = [\text{SO}_3^{2-}] < [\text{HSO}_3^-]$   
 Weak!

2. Which of the following ions will have the lowest concentration in a 0.50-molar solution of  $\text{H}_2\text{SO}_4(\text{aq})$ ?

- (a)  $\text{SO}_4^{2-}$       b.  $\text{HSO}_4^-$       c.  $\text{H}_2\text{SO}_4$       d.  $\text{H}_3\text{O}^+$

3. Which of the following ions will have the greatest concentration in a 0.02-molar solution of  $\text{H}_2\text{SO}_4(\text{aq})$ ?

- a.  $\text{SO}_4^{2-}$       (b)  $\text{HSO}_4^-$       c.  $\text{H}_2\text{SO}_4$       d.  $\text{OH}^-$

~~4.~~ As the concentration of a weak acid increases, its percent dissociation  $\downarrow$  and the pH  $\downarrow$ .

- a. increases, increases      c. increases, decreases  
 b. decreases, decreases      d. decreases, increases

5. The acid dissociation constants of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) are  $K_{a1} = 8 \times 10^{-3}$ ,  $K_{a2} = 6 \times 10^{-8}$  and  $K_{a3} = 4 \times 10^{-13}$  at 298 K. What is the pH of a 5.0 M aqueous solution of phosphoric acid?

- (a) 0.70      b. 1.7      c. 2.7      d. 3.7

$$K_a = \frac{x^2}{[\text{HA}]} = \frac{x^2}{5} = 8 \times 10^{-3} \Rightarrow x = \sqrt{5(8 \times 10^{-3})}$$

$$= \sqrt{4 \times 10^{-2}}$$

$$= 2 \times 10^{-1} \approx 1 \times 10^{-1} = [\text{H}_3\text{O}^+] \Rightarrow \text{pH} = 1$$

6. A 0.10 M acid solution has a pH of 2.00. The acid could be:

- a.  $\text{HNO}_3$       (b)  $\text{H}_2\text{SO}_3$  either      c.  $\text{CH}_3\text{COOH}$       d.  $\text{HClO}_3$

$$\text{pH}(1 \times 10^{-1}) \neq 1 \Rightarrow \text{weak acid!}$$

7. When a solution of pure water has a pH of 7.5, the temperature is \_\_\_\_\_ and the solution is \_\_\_\_\_.

- a. less than  $25^\circ\text{C}$ , basic      c. greater than  $25^\circ\text{C}$ , basic  
 (b) less than  $25^\circ\text{C}$ , neutral      d. greater than  $25^\circ\text{C}$ , neutral

$$\uparrow \text{pH} = \downarrow [\text{H}^+] = \text{shifted left!}$$

