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* << K_a for other acids in solution.

$$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Let's Try!

stronger! ✓ only acid to use in calculation

1. A solution contains 1.00 *M* HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 *M* HNO_2 ($K_a = 4.0 \times 10^{-4}$) Calculate the pH of the solution.

$$HNO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + NO^-_{2(aq)}$$

HNO_2	H_2O	H_3O^+	NO_2^-
5.00		∅	∅
−x		+x	+x
5.00−x		x	x

$K_a <<1$, x negligible

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

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

$$pH = -\log(0.045) = \boxed{1.35}$$

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_2SO_4

not present! — both present in solution!

- The ionization constants for H_2SO_4 are listed below:

$H_2SO_4 + H_2O \rightarrow HSO_4^- + H_3O^+$	K_{a1} = strong
$HSO_4^- + H_2O \rightleftharpoons SO_4^{2-} + H_3O^+$	$K_{a2} = 1.2 \times 10^{-2}$

- Because sulfuric acid is a strong acid in its first dissociation, use $[H_2SO_4]_{initial} = [HSO_4^-]_{equil} = [H_3O^+]_{equil}$
- 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 M. ☺

Let's Practice!

1. Sulfurous acid, H_2SO_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 H_2SO_3?

   a. $[H_2SO_3] < [SO_3^{2-}] = [HSO_3^-]$
   c. $[H_2SO_3] < [HSO_3^-] < [SO_3^{2-}]$
   (b.) $[SO_3^{2-}] < [HSO_3^-] << [H_2SO_3]$ weak!
   d. $[H_2SO_3] = [SO_3^{2-}] < [HSO_3^-]$

2. Which of the following ions will have the lowest concentration in a 0.50-molar solution of $H_2SO_4(aq)$?

   (a.) SO_4^{2-} b. HSO_4^- c. H_2SO_4 d. H_3O^+

3. Which of the following ions will have the greatest concentration in a 0.02-molar solution of $H_2SO_4(aq)$?

   a. SO_4^{2-} (b.) HSO_4^- c. H_2SO_4 d. OH^-

X 4. As the concentration of a weak acid increases, its percent dissociation ↓ and the pH ↓.

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

5. The acid dissociation constants of phosphoric acid (H_3PO_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

$$K_a = \frac{x^2}{[HA]} = \frac{x^2}{5} = 8E-3 \Rightarrow x = \sqrt{5(8E-3)}$$
$$= \sqrt{4E-2}$$
$$= 2E-1 \approx 1E-1 = [H_3O^+] \Rightarrow pH = 1$$

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

   a. HNO_3 [b. H_2SO_3 either c. CH_3COOH] d. $HClO_3$

$pH(1E-1) \neq 1 \Rightarrow$ 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°C, basic
   c. greater than 25°C, basic
   (b.) less than 25°C, neutral
   d. greater than 25°C, neutral

↑ pH = ↓[H⁺] = shifted left!

$$heat + H_2O \rightleftharpoons H^+ + OH^-$$