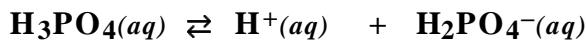


ALL work must be shown to receive full credit. Due 5:00 pm on Tuesday, November 6, 2001.

PS12.1. Calculate the pH of a 0.200 M H<sub>3</sub>PO<sub>4</sub>. Calculate the [PO<sub>4</sub><sup>3-</sup>] in the solution.



|             |          |                          |  |
|-------------|----------|--------------------------|--|
| initial     | .200     | 1 x 10 <sup>-7</sup>     | 0  |
| change      | -x       | +x                       | +x x = [H <sub>3</sub> PO <sub>4</sub> ] <sub>diss</sub> |
| equilibrium | .200 - x | 1 x 10 <sup>-7</sup> + x | 0 + x  |

$$K_a = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$7.53 \times 10^{-3} = \frac{x^2}{.200 - x}$$

$$7.53 \times 10^{-3} (0.200 - x) = x^2$$

$$x^2 + 7.53 \times 10^{-3}x - 1.51 \times 10^{-3} = 0$$

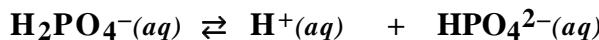
$$\text{solving the quadratic equation } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-7.53 \times 10^{-3} \pm \sqrt{(7.53 \times 10^{-3})^2 - 4(1)(-1.51 \times 10^{-3})}}{2(1)}$$

$$x = \frac{-7.53 \times 10^{-3} \pm 7.79 \times 10^{-2}}{2}$$

Use only the positive root

$$x = 3.52 \times 10^{-2} \text{ M} = [\text{H}^+] = [\text{H}_2\text{PO}_4^-]$$



|             |                             |                             |   |
|-------------|-----------------------------|-----------------------------|---|
| initial     | 3.52 x 10 <sup>-2</sup>     | 3.52 x 10 <sup>-2</sup>     | 0   |
| change      | -x                          | +x                          | +x x = [H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ] <sub>diss</sub> |
| equilibrium | 3.52 x 10 <sup>-2</sup> - x | 3.52 x 10 <sup>-2</sup> + x | 0 + x   |

$$K_a = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$6.2 \times 10^{-8} = \frac{3.52 \times 10^{-2} + x \cdot x}{3.52 \times 10^{-2} - x}$$

assume x << 3.52 x 10<sup>-2</sup>

$$6.2 \times 10^{-8} = \frac{3.52 \times 10^{-2} x}{3.52 \times 10^{-2}}$$

$$6.2 \times 10^{-8} \text{ M} = x = [\text{HPO}_4^{2-}],$$

$$\text{the } [\text{H}^+] = 3.52 \times 10^{-2} \text{ M} + 6.2 \times 10^{-8} \text{ M} = 3.52 \times 10^{-2} \text{ M}$$

|             |  |                           |         |
|-------------|--|---------------------------|---------|
|             | $\text{HPO}_4^{2-}(aq) \rightleftharpoons \text{H}^+(aq) + \text{PO}_4^{3-}(aq)$ |                           |         |
| initial     | $6.2 \times 10^{-8}$   | $3.52 \times 10^{-2}$     | 0       |
| change      | -x   | +x                        | +x      |
| equilibrium | $6.2 \times 10^{-8} - x$   | $3.52 \times 10^{-2} + x$ | $0 + x$ |

$$K_a = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$4.2 \times 10^{-13} = \frac{3.52 \times 10^{-2} + x \cdot x}{6.2 \times 10^{-8} - x}$$

assume  $x \ll 3.52 \times 10^{-2}$

$$4.2 \times 10^{-13} = \frac{3.52 \times 10^{-2}x}{6.2 \times 10^{-8}}$$

$$7.4 \times 10^{-19} \text{ M} = x$$

The  $[\text{H}^+]$  is still  $3.52 \times 10^{-2} \text{ M}$  so the  $\text{pH} = 1.45$ . The  $[\text{PO}_4^{3-}] = 7.4 \times 10^{-19} \text{ M}$ .

PS12.2. Predict the products of the following neutralization reactions.

- a)  $\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(aq)$
- b)  $2\text{HNO}_3(aq) + \text{Ba}(\text{OH})_2(aq) \rightarrow \text{Ba}(\text{NO}_3)_2(aq) + 2\text{H}_2\text{O}(aq)$
- c)  $2\text{NaOH}(aq) + \text{H}_2\text{CO}_3(aq) \rightarrow \text{Na}_2\text{CO}_3(aq) + 2\text{H}_2\text{O}(aq)$
- d)  $2\text{NH}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightarrow (\text{NH}_4)_2\text{SO}_4(aq)$
- e)  $\text{HC}_6\text{H}_5\text{O}(aq) + \text{NaOH}(aq) \rightarrow \text{NaC}_6\text{H}_5\text{O}(aq) + \text{H}_2\text{O}(aq)$
- f)  $\text{HCN}(aq) + \text{KOH}(aq) \rightarrow \text{KCN}(aq) + \text{H}_2\text{O}(aq)$

PS12.3. Given a solution containing the following ions (neglect the counter-ion for the moment), write a reaction (with water) and indicate whether the ion acts as an acid or as a base.

- a)  $\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$
- b)  $\text{ClO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HClO}_2(aq) + \text{OH}^-(aq)$
- c)  $\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HNO}_2(aq) + \text{OH}^-(aq)$
- d)  $\text{NH}_4^+(aq) \rightleftharpoons \text{NH}_3(aq) + \text{H}^+(aq)$
- e)  $\text{CH}_3\text{NH}_3^+(aq) \rightleftharpoons \text{CH}_3\text{NH}_2(aq) + \text{H}^+(aq)$
- f)  $\text{C}_2\text{H}_5\text{NH}_3^+(aq) \rightleftharpoons \text{C}_2\text{H}_5\text{NH}_2(aq) + \text{H}^+(aq)$

- PS12.4. Can you make any generalizations about the acid-base character of the ions in Problem #12.3? If so, state them.

**Generally anions act as bases reacting with water to form  $[OH^-]$ . Cations act as acids reacting with water to form  $[H^+]$ .**

- PS12.5. Indicate an acid and a base which could react, in a neutralization reaction, to form each of the following salts. In some cases water will be present as another product.

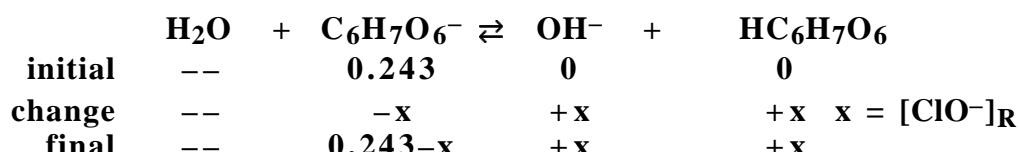
- $NaOH(aq) + HC_6H_7O_6(aq) \rightarrow NaC_6H_7O_6(aq) + H_2O(l)$
- $KOH(aq) + HClO(aq) \rightarrow KClO(aq) + H_2O(l)$
- $(CH_3)_2NH(aq) + HNO_3(aq) \rightarrow (CH_3)_2NH_2NO_3(aq)$
- $NH_3(aq) + HBr(aq) \rightarrow NH_4Br(aq)$
- $KOH(aq) + HCl(aq) \rightarrow KCl(aq) + H_2O(l)$
- $2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$

- PS12.6. If each salt in Problem 12.5 is added to water, indicate whether the resulting solution is acidic, basic or neutral.

- $NaC_6H_7O_6(aq) \rightarrow Na^+(aq) + C_6H_7O_6^-(aq)$   
 $C_6H_7O_6^-(aq) + H_2O(l) \rightleftharpoons HC_6H_7O_6(aq) + OH^-(aq)$  **basic**
- $KClO(aq) \rightarrow K^+(aq) + ClO^-(aq)$   
 $ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$  **basic**
- $(CH_3)_2NH_2NO_3(aq) \rightarrow (CH_3)_2NH_2^+(aq) + NO_3^-(aq)$   
 $(CH_3)_2NH_2^+(aq) \rightleftharpoons (CH_3)_2NH_2(aq) + H^+(aq)$  **acidic**
- $NH_4Br(aq) \rightarrow NH_4^+(aq) + Br^-(aq)$   
 $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$  **acidic**
- $KCl(aq) \rightarrow K^+(aq) + Cl^-(aq)$  **neutral**
- $(NH_4)_2SO_4(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$   
 $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$  **acidic**

- PS12.7. Calculate the pH of the following salt solutions

- a) 0.243 M  $NaC_6H_7O_6$



$$K_b = \frac{1 \times 10^{-14}}{8 \times 10^{-5}} = \frac{[HC_6H_7O_6][OH^-]}{[C_6H_7O_6^-]}$$

$$1.25 \times 10^{-10} = \frac{x[x]}{[0.243-x]} \quad x \ll 0.243$$

$$5.5 \times 10^{-6} = x = [OH^-]$$

$$pOH = 5.26 \quad pH = 8.74$$

b) 0.319 M C<sub>5</sub>H<sub>5</sub>NHClO<sub>4</sub>

|             |   |                      |                |   |                                 |
|-------------|---|----------------------|----------------|---|---------------------------------|
|             | C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup> | $\rightleftharpoons$ | H <sup>+</sup> | + | C <sub>5</sub> H <sub>5</sub> N |
| initial     | 0.319   |                      | 0              |   | 0                               |
| change      | -x  |                      | +x             |   | +x                              |
| equilibrium | 0.319-x                                       |                      | +x             |   | +x                              |

$$K_a = \frac{1 \times 10^{-14}}{1.7 \times 10^{-9}} = \frac{[C_5H_5N][H^+]}{[C_5H_5NH^+]}$$

$$5.88 \times 10^{-6} = \frac{x[x]}{[0.319 - x]} \quad x \ll 0.319$$

$$1.37 \times 10^{-3} M = x = [H^+]$$

$$pH = 2.86$$

c) 0.0345 M KCl

$$pH = 7.00$$

d) 0.572 M KC<sub>3</sub>H<sub>5</sub>O<sub>2</sub>

|         |                  |   |   |                      |                 |   |   |
|---------|------------------|---|---|----------------------|-----------------|---|---|
|         | H <sub>2</sub> O | + | C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup> | $\rightleftharpoons$ | OH <sup>-</sup> | + | HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> |
| initial | --               |   | 0.572   |                      | 0               |   | 0   |
| change  | --               |   | -x  |                      | +x              |   | +x  |
| final   | --               |   | 0.572-x   |                      | +x              |   | +x  |

$$K_b = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

$$5.56 \times 10^{-10} = \frac{x[x]}{[0.572 - x]} \quad x \ll 0.572$$

$$1.78 \times 10^{-5} = x = [OH^-]$$

$$pH = 9.25$$

e) 1.00 M NaHSO<sub>4</sub>

|         |          |                               |   |                |   |                               |
|---------|----------|-------------------------------|---|----------------|---|-------------------------------|
|         | H        | SO <sub>4</sub> <sup>2-</sup> | ↔ | H <sup>+</sup> | + | SO <sub>4</sub> <sup>2-</sup> |
| initial | 1.00     |                               |   | 0              |   | 0                             |
| change  | -x       |                               |   | +x             |   | +x                            |
| final   | 1.00 - x |                               |   | +x             |   | +x                            |

$$K_a = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$1.2 \times 10^{-2} = \frac{[x][x]}{[1.00 - x]}$$

$$1.2 \times 10^{-2}(1.00 - x) = x^2$$

$$x^2 + 1.2 \times 10^{-2}x - 1.2 \times 10^{-2} = 0$$

solving the quadratic equation  $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$x = \frac{-1.2 \times 10^{-2} \pm \sqrt{(1.2 \times 10^{-2})^2 - 4(1)(-1.2 \times 10^{-2})}}{2(1)}$$

$$x = \frac{-1.2 \times 10^{-2} \pm 0.219}{2}$$

Use only the positive root

$$\begin{aligned} x &= 0.104 \text{ M} = [H^+] \\ \text{pH} &= 0.983 \end{aligned}$$

PS12.8. In the series of oxyacids, XOH, OXOH, and O<sub>2</sub>XOH, list the acids in order of increasing acid strength. Justify your answer.



As the number of oxygen atoms bonded to the central atom, X, increases, the more electron density is removed from the O-H bond. The smaller electron density decreases the strength of the O-H bond resulting in a larger ionization of the proton, increasing the acidity of the substance.