21 - POLYPROTIC ACIDS & BASES

CHEM 251 SDSU

POLYPROTIC K_A & K_B VALUES

$$H_3A \underset{K_{b3}}{\overset{K_{a1}}{\rightleftharpoons}} H_2A^- \underset{K_{b2}}{\overset{K_{a2}}{\rightleftharpoons}} HA^{2-} \underset{K_{b1}}{\overset{K_{a3}}{\rightleftharpoons}} A^{3-}$$

The K_a and K_b values are numbered in order of the strength of the equilibrium to act as an acid or base. The lower the number the further the reaction shifts to the products.

K_{a1} good acid; K_{b3} bad base

K_{a3} bad acid; K_{b1} good base

PH OF ACIDS/BASES

- The pH of a weak acid or a weak base solution is dependent on the pK_a of that particular acid/base and its concentration in the solution.

- When an acid/base has more than one pK_a (polyprotic), the pH is dependent on the prominent form(s) of the acid/base in the solution.

- At its simplest, the polyprotic acid can be treated as a monoprotic acid/base if a solution is prepared directly from the full protonated, or fully deprotonated form.

PH OF A POLYPROTIC SOLUTION

The pH of a solution will depend on the primary form of the acid (base) present

$$H_3A \overset{K_{a1}}{\rightleftharpoons} H_2A^- \overset{K_{a2}}{\rightleftharpoons} HA^{2-} \overset{K_{a3}}{\rightleftharpoons} A^{3-}$$

Species:	Relevant Reactions:	Equilibria:
H_3A	$H_3A \rightleftharpoons H_2A^- + H^+$	K_{a1}
NaH_2A	$H_3A + OH^- \rightleftharpoons H_2A^- \rightleftharpoons HA^{2-} + H^+$	K_{a1} & K_{a2}
K_2HA	$H_2A^- + OH^- \rightleftharpoons HA^{2-} \rightleftharpoons A^{3-} + H^+$	K_{a2} & K_{a3}
Li_3A	$HA^{2-} + OH^- \rightleftharpoons A^{3-} + H_2O$	K_{a3}

PROBLEMS

What is the pH of a 36 mM solution of:

- **Carbonic acid (H_2CO_3)?**
- Sodium carbonate (Na_2CO_3)?
- Sodium bicarbonate ($NaHCO_3$)?

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^-$$

$36mM\ H_2CO_3$ treat like a weak monoprotic acid (HA)

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]} = 4.46\times10^{-7} \quad \left[HA\right] = 0.036 - x \quad \left[H^+\right] = \left[A^-\right] = x$$

$$4.46\times10^{-7} = \frac{(x)(x)}{0.036 - x} \quad 1.6056\times10^{-8} - 4.46\times10^{-7}(x) = x^2$$

$$0 = x^2 + 4.46\times10^{-7}(x) - 1.6056\times10^{-8}$$

$$x = \left[H^+\right] = 1.26\times10^{-4}\,M \quad pH = -\log\left(1.26\times10^{-4}\right) = 3.90$$

PROBLEMS

What is the pH of a 36 mM solution of:

- Carbonic acid (H_2CO_3)?
- **Sodium carbonate (Na_2CO_3)?**
- Sodium bicarbonate ($NaHCO_3$)?

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^-$$

$36mM\ Na_2CO_3$ treat like a weak monoprotic base (A^{2-})

$$CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^- \quad K_w = K_{a_2} \times K_{b_1} \quad K_{b_1} = \frac{K_w}{K_{a_2}} = \frac{1\times10^{-14}}{4.69\times10^{-11}} = 2.13\times10^{-4}$$

$$K_{b_1} = \frac{\left[HA^-\right]\left[OH^-\right]}{\left[A^{2-}\right]} = 2.13\times10^{-4} \quad \left[A^{2-}\right] = 0.036 - x \quad \left[HA^-\right] = \left[OH^-\right] = x$$

$$2.13\times10^{-4} = \frac{(x)(x)}{0.036 - x} \quad 7.668\times10^{-6} - 2.13\times10^{-4}(x) = x^2$$

$$0 = x^2 + 2.13\times10^{-4}(x) - 7.668\times10^{-6}$$

$$x = \left[OH^-\right] = 2.66\times10^{-3}M \quad pOH = -\log\left(2.66\times10^{-3}\right) = 2.57$$

$$pH = 14 - pOH \quad pH = 14 - 2.57 = 11.43$$

PROBLEMS

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- Carbonic acid (H_2CO_3)?
- Sodium carbonate (Na_2CO_3)?
- **Sodium bicarbonate ($NaHCO_3$)?**

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \quad and \quad HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$

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

$$F = 0.036M \quad K_{a1} = 4.46\times10^{-7} \quad K_{a2} = 4.69\times10^{-11}$$

$$[H^+] = \sqrt{\frac{(4.46\times10^{-7})(4.69\times10^{-11})(0.036) + (4.46\times10^{-7})(1\times10^{-14})}{(4.46\times10^{-7}) + (0.036)}}$$

$$[H^+] = 4.59\times10^{-9}M \quad pH = -\log(4.59\times10^{-9}) = 8.34$$