Equilibrium IV: Polyprotic Acid-Base Equilibrium

1. Calculate the approximate pH of a solution prepared to be 0.0010 M malonic acid ($H_2C_3H_2O_4$, $K_1 = 1.5 \times 10^{-3}$, $K_2 = 2.0 \times 10^{-6}$).

Treat this problem like a monoprotic acid problem:

$$H_2mal + H_2O \rightleftarrows H_3O^+ + Hmal^-$$

$$K_1 = \frac{[H_3O^+][Hmal^-]}{[H_2mal]}$$

$$1.5\times10^{-3} = \frac{x^2}{0.0010 - x}$$ The simplifying assumption that $x<0.0010$ is not valid here

$$x = [H_3O^+] = 6.86\times10^{-4}\ \text{M} \qquad p\text{H} = 3.16$$

2. Calculate the concentration of all species in 0.10 M H_3PO_4.

$K_1 = 7.5 \times 10^{-3}$ $K_2 = 6.2 \times 10^{-8}$ $K_3 = 4.8 \times 10^{-13}$

$$H_3PO_4 + H_2O \rightleftarrows H_2PO_4^- + H_3O^+$$

$$K_1 = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} \qquad 7.5\times10^{-3} = \frac{x^2}{0.10 - x}$$

$$x = [H_2PO_4^-] = [H_3O^+] = 0.0239\ \text{M}$$

$$[H_3PO_4] = 0.10\ \text{M} - 0.0239\ \text{M} = 0.076\ \text{M}$$

$$H_2PO_4^- + H_2O \rightleftarrows HPO_4^{2-} + H_3O^+$$

$$K_2 = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]} \qquad 6.2\times10^{-8} = \frac{[HPO_4^{2-}](0.0239)}{(0.0239)}$$

$$[HPO_4^{2-}] = 6.2\times10^{-8}\ \text{M}$$

$$HPO_4^{2-} + H_2O \rightleftarrows PO_4^{3-} + H_3O^+$$

$$K_3 = \frac{[PO_4^{3-}][H_3O^+]}{[HPO_4^-]} \qquad 4.8\times10^{-13} = \frac{[PO_4^{3-}](0.0239)}{6.2\times10^{-8}}$$

$$[PO_4^{3-}] = 1.25\times10^{-18}\ \text{M}$$

$$[OH^-] = \frac{1.0\times10^{-14}}{0.0239} = 4.18\times10^{-13}\ \text{M}$$

3. Calculate the pH of the solution prepared to be 0.015 M sodium malonate ($Na_2C_3H_2O_4$)

Get K_{a_2} from problem 1. The first K_b reaction is the only significant mass action.

$$K_{b_1} = \frac{K_w}{K_{a_2}} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9}$$

$$mal^{2-} + H_2O \rightleftarrows Hmal^- + OH^-$$

$$K_{b_1} = \frac{[Hmal^-][OH^-]}{[mal^{2-}]} \qquad 5.0 \times 10^{-9} = \frac{x^2}{0.015 - x} \qquad x = [OH^-] = 8.66 \times 10^{-6} \text{ M}$$

$$pOH = 5.06 \qquad pH = 14 - 5.06 = 8.94$$