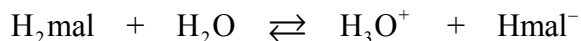


## Equilibrium IV: Polyprotic Acid-Base Equilibrium

1. Calculate the approximate pH of a solution prepared to be 0.0010 M malonic acid ( $\text{H}_2\text{C}_3\text{H}_2\text{O}_4$ ,  $K_1 = 1.5 \times 10^{-3}$ ,  $K_2 = 2.0 \times 10^{-6}$ ).

Treat this problem like a monoprotic acid problem:



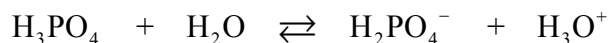
$$K_1 = \frac{[\text{H}_3\text{O}^+][\text{Hmal}^-]}{[\text{H}_2\text{mal}]}$$

$$1.5 \times 10^{-3} = \frac{x^2}{0.0010 - x} \quad \text{The simplifying assumption that } x < 0.0010 \text{ is not valid here}$$

$$x = [\text{H}_3\text{O}^+] = 6.86 \times 10^{-4} \text{ M} \quad \text{pH} = 3.16$$

2. Calculate the concentration of all species in 0.10 M  $\text{H}_3\text{PO}_4$ .

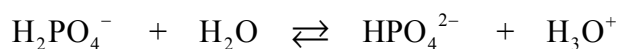
$$K_1 = 7.5 \times 10^{-3} \quad K_2 = 6.2 \times 10^{-8} \quad K_3 = 4.8 \times 10^{-13}$$



$$K_1 = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} \quad 7.5 \times 10^{-3} = \frac{x^2}{0.10 - x}$$

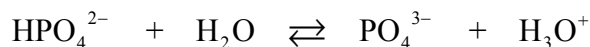
$$x = [\text{H}_2\text{PO}_4^-] = [\text{H}_3\text{O}^+] = 0.0239 \text{ M}$$

$$[\text{H}_3\text{PO}_4] = 0.10 \text{ M} - 0.0239 \text{ M} = 0.076 \text{ M}$$



$$K_2 = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} \quad 6.2 \times 10^{-8} = \frac{[\text{HPO}_4^{2-}](0.0239)}{(0.0239)}$$

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



$$K_3 = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} \quad 4.8 \times 10^{-13} = \frac{[\text{PO}_4^{3-}](0.0239)}{6.2 \times 10^{-8}}$$

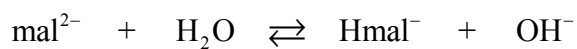
$$[\text{PO}_4^{3-}] = 1.25 \times 10^{-18} \text{ M}$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{0.0239} = 4.18 \times 10^{-13} \text{ M}$$

3. Calculate the pH of the solution prepared to be 0.015 M sodium malonate ( $\text{Na}_2\text{C}_3\text{H}_2\text{O}_4$ )

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

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



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

$$p\text{OH} = 5.06 \quad p\text{H} = 14 - 5.06 = 8.94$$