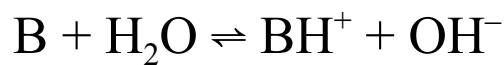


## Weak Base in Water

☞ For a solution of a weak base in water, the determination of all species concentrations follows analogously with the acid case; i.e., four equations in four unknowns to which simplifications can often be made.



$$\textcircled{1} \quad K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$\textcircled{2} \quad K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

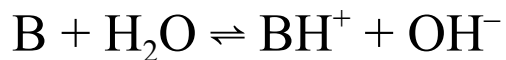
The **charge balance expression** is

$$\textcircled{3} \quad [OH^-] = [OH^-]_{\text{base}} + [OH^-]_{\text{water}} = [BH^+] + [H_3O^+]$$

The **mass balance expression** is

$$\textcircled{4} \quad [B] = C_B - [BH^+]$$

## Weak Base In Water Simplifying Assumptions



- ☞ Assumption I: If  $C_B \gg 10^{-7}$  M, assume virtually all  $OH^-$  comes from B. Thus,

$$[OH^-] \approx [HB^+]$$

- ☞ Assumption II: If  $C_B \gg K_b$  (usually 2 powers of 10 or more), assume B is negligibly hydrolyzed. Thus,

$$[B] \approx C_B$$

- ☞ If both assumptions can be made:

$$K_b = \frac{[OH^-][BH^+]}{[B]} = \frac{[OH^-]^2}{C_B}$$

and

$$[OH^-] = \sqrt{C_B K_b}$$

## Breakdown of Assumption II

- ☞ If  $C_B \approx K_b$  (usually within 2 powers of 10), assume B is *not* negligibly hydrolyzed. Thus,

$$[B] = C_B - [\text{OH}^-]$$

$$K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[B]} = \frac{[\text{OH}^-]^2}{C_B - [\text{OH}^-]}$$

$$[\text{OH}^-]^2 + K_b [\text{OH}^-] - K_b C_B = 0$$

- ☞ Solve the quadratic equation for  $[\text{OH}^-] = [\text{BH}^+]$

## **$K_a$ 's of Polyprotic Acids**

- We can define a  $K_a$  for each dissociation of a polyprotic acid.



- As is typical of polyprotic acids,  $K_1 > K_2 > K_3$ , etc.

## Determining $[\text{H}_3\text{O}^+]$ for a Polyprotic Acid

- All equilibria occur simultaneously, but  $K_1$  is usually so much greater than  $K_2$  and  $K_3$  that in a moderately concentrated solution we can assume that virtually all of the hydronium ion comes from the first step.

- ✓ Charge balance expression:

$$\begin{aligned}[\text{H}_3\text{O}^+] &= [\text{H}_3\text{O}^+]_1 + [\text{H}_3\text{O}^+]_2 + [\text{H}_3\text{O}^+]_3 + [\text{H}_3\text{O}^+]_{\text{water}} \\ &= [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}] + [\text{OH}^-] \\ &\approx [\text{H}_2\text{PO}_4^-] \quad \quad \quad \Rightarrow \text{Assumption I}\end{aligned}$$

- ✓ For calculations of a pure polyprotic acid in water (with no additional conjugate base) we only need to consider  $K_1$  to find  $[\text{H}_3\text{O}^+]$ .
- ✓ For polyprotic acids in general, this assumption is valid only if the successive  $K$ 's are widely separated; i.e.,  $K_1 \gg K_2 \gg K_3$ , etc.

## Simplifying Assumptions for a Polyprotic Acid, $H_nA$

- ☞ Assumption I: If  $C \gg 10^{-7}$  M, assume virtually all  $H_3O^+$  comes from the first dissociation. Thus, for  $H_nA$ ,

$$[H_3O^+] \approx [H_{(n-1)}A^-]$$

- ☞ Assumption II: If  $C \gg K_1$  (usually 2 powers of 10 or more), assume the acid is negligibly dissociated. Then, for  $H_nA$ ,

$$[H_nA] \approx C$$

- ☞ Breakdown of Assumption II: If  $C \approx K_1$  (usually within 2 powers of 10), assume the acid is *not* negligibly dissociated. Then, for  $H_nA$ ,

$$[H_nA] = C - [H_3O^+]$$

## Calculation Procedure for a Polyprotic Acid, $H_3A$ $K_1 \gg K_2 \gg K_3$

- ① Use  $K_1$  and Assumption I with or without Assumption II to calculate  $[H_3O^+] = [H_2A^-]$ .
- ②  $[HA^{2-}] \approx K_2$ .
- ③ Use  $K_3$  and the previously calculated values of  $[H_3O^+]$  and  $[HA^{2-}]$  to calculate  $[A^{3-}]$ .
- ④ Use  $K_w$  and the previously calculated value of  $[H_3O^+]$  to calculate  $[OH^-]$ .
- ⑤ Check Assumption I by substituting calculated values into the exact charge balance expression to verify

$$[H_3O^+] = [H_2A^-] + [HA^{2-}] + [A^{3-}] + [OH^-] \approx [H_2A^-]$$

- ⑥ If using Assumption II, check to make sure the error in the mass balance expression is acceptably small; i.e.,

$$[H_3A] = C - [H_3O^+] \approx C$$

$$\text{and } ([H_2A^-]/C) \times 100\% < 10\%$$