Chapter 14 Part 4

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Polyprotic Acids and Bases

Polyprotic Acids

- Polyprotic acids are acids capable of loosing two or more protons (H^+)
- Ex.
  H_2CO_3 is diprotic and H_3PO_4 is triprotic

Polyprotic Bases

- Polyprotic bases are bases capable of accepting two or more protons (H^+)
- Ex. CO_3^{2-} is a diprotic base and PO_4^{3-} is a triprotic base

Stepwise Ionizations

- The ionization steps of the diprotic acid H_2CO_3 are as follows

$$H_2CO_3 + H_2O \leftrightharpoons HCO_3^{\,-} + H_3O^+$$

$$HCO_3^{\,-} + H_2O \leftrightharpoons CO_3^{\,2-} + H_3O^+$$

Stepwise Ionizations

- The ionization steps of the diprotic acid H_2CO_3 are as follows

$$H_2CO_3 + H_2O \leftrightharpoons HCO_3^{\,-} + H_3O^+$$

$$K_{a_1} = \frac{[HCO_3^{\,-}][H_3O^+]}{[H_2CO_3]}$$

$$HCO_3^{\,-} + H_2O \leftrightharpoons CO_3^{\,2-} + H_3O^+$$

$$K_{a_2} = \frac{[CO_3^{\,2-}][H_3O^+]}{[HCO_3^{\,-}]}$$

Stepwise Ionizations

- The ionization steps of the diprotic base SO_3^{2-} are as follows

$$SO_3^{2-} + H_2O \leftrightharpoons HSO_3^{-} + OH^{-}$$

$$HSO_3^{-} + H_2O \leftrightharpoons H_2SO_3 + OH^{-}$$

Stepwise Ionizations

- The ionization steps of the diprotic base $SO_3{}^{2-}$ are as follows

$$SO_3{}^{2-} + H_2O \leftrightharpoons HSO_3{}^{-} + OH^{-}$$

$$K_{b_1} = \frac{[HSO_3{}^{-}][OH^{-}]}{[SO_3{}^{2-}]}$$

$$HSO_3{}^{-} + H_2O \leftrightharpoons H_2SO_3 + OH^{-}$$

$$K_{b_2} = \frac{[H_2SO_3][OH^{-}]}{[HSO_3{}^{-}]}$$

Polyprotic acids

Consider a H_3PO_4 solution (A) Show the stepwise hydrolysis of H_3PO_4. (B) Write K_a expressions for K_{a_1}, K_{a_2}, and K_{a_3}. (C) Find the values of pK_{a_1}, pK_{a_2}, and pK_{a_3} if $K_{a_1} = 7.1 \times 10^{-3}$, $K_{a_2} = 6.3 \times 10^{-8}$, and $K_{a_3} = 4.2 \times 10^{-13}$.

Polyprotic bases

Consider a K_3AsO_4 solution (A) Show the stepwise hydrolysis of $AsO_4{}^{3-}$. (B) Write K_b expressions for K_{b_1}, K_{b_2}, and K_{b_3}. (C) Find the values of pK_{b_1}, pK_{b_2}, and pK_{b_3} if $K_{b_1} = 2.0 \times 10^{-3}, K_{b_2} = 5.9 \times 10^{-8}$, and $K_{b_3} = 1.8 \times 10^{-12}$.

Calculating ion concentrations in polyprotic acids

For a 3.0 M H_3PO_4 solution, (A) calculate $[H_3O^+]$, $[H_2PO_4^-]$, $[HPO_4^{2-}]$, and $[PO_4^{3-}]$. $K_{a_1} = 7.1 \times 10^{-3}$. $K_{a_2} = 6.3 \times 10^{-8}$. $K_{a_3} = 4.2 \times 10^{-13}$. (B) Calculate the pH of the solution.

A new approximation for polyprotic acids

- The following approximation may only be implemented for the second ionization step
- Approximation: If the second ionization constant, K_{a_2}, of a weak polyprotic acid is 5% or less of the first ionization constant, K_{a_1}, the concentration of the dissociated products of the K_{a_2} reaction are equal to K_{a_2}.
- The approximation works by assuming that only the first deionization substantially deionizes and thus the deionized products of the subsequent ionizations have a negligible impact on the hydronium ion concentration.

Calculating ion concentrations in polyprotic bases

For a 4.0 M Na_3AsO_4 solution, (A) calculate $[OH^-]$, $[HAsO_4{}^{2-}]$, $[H_2AsO_4{}^-]$, and $[H_3AsO_4]$. $K_{b_1} = 2.0 \times 10^{-3}$, $K_{b_2} = 5.9 \times 10^{-8}$, and $K_{b_3} = 1.8 \times 10^{-12}$. (B) Calculate the pH of the solution.

Ionization constants of polyprotic acids

Identify the most typical ranking of K_a values for polyprotic acids.

A. $K_{a1} = K_{a2} = K_{a3}$
B. $K_{a1} > K_{a2} > K_{a3}$
C. $K_{a1} < K_{a2} < K_{a3}$
D. $K_{a1} = K_{a2} < K_{a3}$

Using the polyprotic acid assumption

Identify the best method for calculating the pH of a diprotic acid solution when $K_{a1} >> K_{a2}$.

A. add the pH values from each ionization
B. calculate pH only from the first ionization
C. calculate pH only from the second ionization
D. assume $pH = pK_{a1}$
E. assume $pH = pK_{a2}$