

Chapter 14 Part 4

Dr. Turner

Polyprotic Acids and Bases

Polyprotic Acids

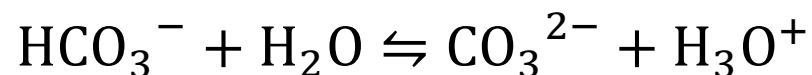
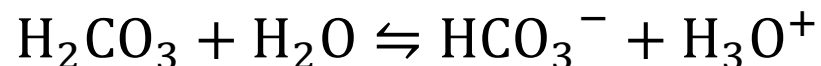
- Polyprotic acids are acids capable of losing two or more protons (H^+)
- Ex. H_2CO_3 is diprotic and H_3PO_4 is triprotic

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

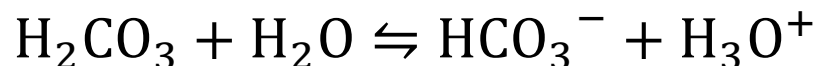
Stepwise Ionizations

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

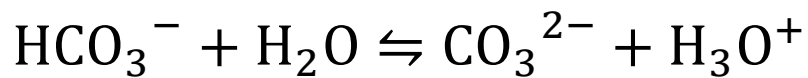


Stepwise Ionizations

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



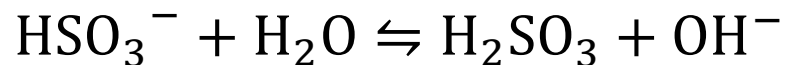
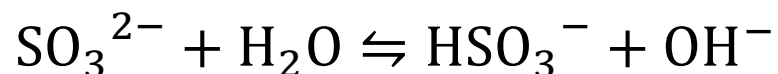
$$K_{a_1} = \frac{[\text{HCO}_3^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{CO}_3]}$$



$$K_{a_2} = \frac{[\text{CO}_3^{2-}][\text{H}_3\text{O}^+]}{[\text{HCO}_3^-]}$$

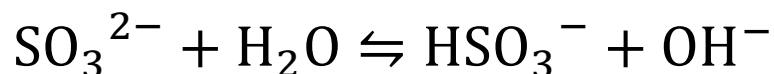
Stepwise Ionizations

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

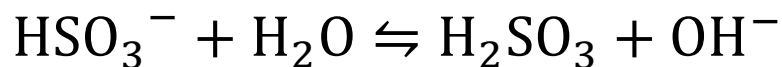


Stepwise Ionizations

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



$$K_{b_1} = \frac{[\text{HSO}_3^-][\text{OH}^-]}{[\text{SO}_3^{2-}]}$$



$$K_{b_2} = \frac{[\text{H}_2\text{SO}_3][\text{OH}^-]}{[\text{HSO}_3^-]}$$

Polyprotic acids

Consider a H_3PO_4 solution (A) Show the stepwise hydrolysis of H_3PO_4 . (B) Write K_a expressions for K_{a1} , K_{a2} , and K_{a3} . (C) Find the values of $\text{p}K_{a1}$, $\text{p}K_{a2}$, and $\text{p}K_{a3}$ if $K_{a1} = 7.1 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$, and $K_{a3} = 4.2 \times 10^{-13}$.

Polyprotic bases

Consider a K_3AsO_4 solution (A) Show the stepwise hydrolysis of AsO_4^{3-} . (B) Write K_b expressions for K_{b1} , K_{b2} , and K_{b3} . (C) Find the values of $\text{p}K_{b1}$, $\text{p}K_{b2}$, and $\text{p}K_{b3}$ if $K_{b1} = 2.0 \times 10^{-3}$, $K_{b2} = 5.9 \times 10^{-8}$, and $K_{b3} = 1.8 \times 10^{-12}$.

Calculating ion concentrations in polyprotic acids

For a 3.0 M H_3PO_4 solution, (A) calculate $[\text{H}_3\text{O}^+]$, $[\text{H}_2\text{PO}_4^-]$, $[\text{HPO}_4^{2-}]$, and $[\text{PO}_4^{3-}]$. $K_{a1} = 7.1 \times 10^{-3}$. $K_{a2} = 6.3 \times 10^{-8}$. $K_{a3} = 4.2 \times 10^{-13}$. (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_{a2} , of a weak polyprotic acid is 5% or less of the first ionization constant, K_{a1} , the concentration of the dissociated products of the K_{a2} reaction are equal to K_{a2} .
- 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 $[\text{OH}^-]$, $[\text{HAsO}_4^{2-}]$, $[\text{H}_2\text{AsO}_4^-]$, and $[\text{H}_3\text{AsO}_4]$. $K_{b1} = 2.0 \times 10^{-3}$, $K_{b2} = 5.9 \times 10^{-8}$, and $K_{b3} = 1.8 \times 10^{-12}$. (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 $K_{a1} \gg K_{a2}$.

- 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 $\text{pH} = \text{p}K_{a1}$
- E. assume $\text{pH} = \text{p}K_{a2}$