

## Polyprotic Acids

## Homework

- Complete the AP practice test at the end of Chapter 14 Acid and Bases
- It is in between page 598-599

## Polyprotic Acids

- A polyprotic acid has more than one ionizable proton ( $H^+$ ).
- e.g.  $H_2SO_4$ ,  $H_2CO_3$ ,  $H_3AsO_4$
- Each successive  $K_a$  value get smaller ( $K_{a1} > K_{a2} > K_{a3}$ ). Therefore, the first dissociation step makes the most significant contribution to the equilibrium concentration of  $[H^+]$ .

- Sulfuric acid is unique in being a strong acid in its first dissociation step and a weak acid in its second step.

## LeChâtelier

- For 1.0 M or larger solutions of sulfuric acid, the large concentration of  $H_3O^+$  from the first dissociation step represses the second step, which can be neglected as a contributor of  $H_3O^+$  ions. For dilute solutions of sulfuric acid, the second step does make a significant contribution, ICE tables must be used to obtain the total  $H_3O^+$  concentration.

## Problem

- Calculate the pH of .50 M  $H_2SO_4$
- $H_2SO_4 \rightarrow HSO_4^- + H^+$   $K_a$  is very large
- $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$   $K_a = 1.2 \times 10^{-2}$
- The main difference from sulfuric acid from other problems will be the first step.
- 0.50 M  $H_2SO_4$  means .50 M  $H^+$  and .5 M  $HSO_4^-$  is formed.
- Now to the second dissociation

## Cont.

- $HSO_4^- \rightleftharpoons SO_4^{2-} + H^+$
- I .50 M .50 M
- C -x +x +x
- E .50 -x x .50 + x
- $K_a = x(.5+x) / (.5-x) = 1.2 \times 10^{-2}$
- $x = .011462$
- $[HSO_4^-] = .49$  M  $[SO_4^{2-}] = .011$  M
- $[H^+] = .51$  M **pH = .29**

## Problem

- Calculate the pH,  $[H^+]$ ,  $[HSO_4^-]$ ,  $[SO_4^{2-}]$  of .20 M  $H_2SO_4$
- Calculate the pH of a 5.0 M  $H_3PO_4$  solution and the equilibrium concentrations of the species  $H_3PO_4$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ , and  $PO_4^{3-}$ .  
 $K_{a1} = 7.5 \times 10^{-3}$   
 $K_{a2} = 6.2 \times 10^{-8}$   
 $K_{a3} = 4.8 \times 10^{-13}$

## Salts

## Salts and pH

- Salts are made of conjugate acids and bases.
- The conjugate acid/bases of strong acids or base will be neutral, excluding  $\text{H}_2\text{SO}_4$ .
- To be a strong acid or base, the conjugate base or acid must have no affinity for protons or hydroxide.
- That is to say it won't run the reverse reaction under **any** conditions.

## Salts of weak acids and bases

- Conjugate bases/acids of weak acids and bases will run the reverse reactions.
- Conjugate base of weak acids are weak bases**
- $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$
- $\text{F}^- + \text{H}_2\text{O} \rightleftharpoons \text{HF} + \text{OH}^-$
- Conjugate acids of weak bases are weak acids**
- $\text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
- $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$

## pH of salt

- Salts are made by joining the conjugate acids and bases
- Would potassium chlorite be acidic or basic?
- $\text{KClO}_2 \rightleftharpoons \text{K}^+ + \text{ClO}_2^-$
- Potassium is neutral ( $\text{KOH}$  = strong base), chlorite is basic ( $\text{HClO}_2$  = weak acid)
- Therefore it is basic

## Question

- Are these salts acidic or basic?
- $\text{NH}_4\text{Cl}$
- $\text{NaCH}_3\text{COO}$
- $\text{Ca}(\text{NO}_3)_2$

## What about salts of a weak acid and a weak bases...

- If you have  $\text{NH}_4\text{F}$ ...
- You have to look at the  $K_a$  value of  $\text{NH}_4^+$  and compare it to the  $K_b$  value of  $\text{F}^-$  to see which weak acid/base is stronger.
- The larger the K value the stronger the acid/base.

## $K_a$ and $K_b$

- The  $K_a$  and  $K_b$  of a weak acid and its conjugate base or a weak base and its conjugate acid are related and easily calculated from one another
- For a weak acid and its conjugate base or a weak base and its conjugate acid rel**
- $K_a \times K_b = K_w$

## Problem

- Calculate the  $K_a$  of  $\text{NH}_4\text{Cl}$  solution. The  $K_b$  value for  $\text{NH}_3$  is  $1.8 \times 10^{-5}$ .
- Calculate the  $K_b$  of  $\text{NaF}$  solution. The  $K_a$  value for  $\text{HF}$  is  $7.2 \times 10^{-4}$ .

## Hydrated metal ions

- Charged metals ions also produce an acidic solution.
- The metal itself does not act as a Bronsted-Lowry acid, but instead forms a hydrate that acts as a Bronsted-Lowry acid.
- Typically the higher the charge on the metal ion, stronger the acidity of the hydrated ion.
- $\text{Cu}^{2+} + 5 \text{H}_2\text{O} \rightarrow \text{Cu}(\text{H}_2\text{O})_5^{2+}$
- $\text{Cu}(\text{H}_2\text{O})_5^{2+} \rightleftharpoons \text{CuOH}(\text{H}_2\text{O})_4^+ + \text{H}^+$

## Acidity of hydrated metal ions

- $M$  = metal
- For  $M^{n+}$ , a small, highly charged ion,
- $M(\text{H}_2\text{O})_x^{n+} + \text{H}_2\text{O} \rightleftharpoons M(\text{H}_2\text{O})_{x-1}\text{OH}^{(n-1)+} + \text{H}_3\text{O}^+$
- Calculate the pH of a 0.010 M  $\text{AlCl}_3$  solution. The  $K_a$  value for  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  is  $1.4 \times 10^{-5}$ .