

Chapter 10 - Polyprotic Acid-Base Equilibria

Homework: Due Wednesday, February 25

Problems Chap 10: 10-2, 10-5, 10-11, 10-15, 10-17, 10-23, 10-24, 10-28, 10-36

Extra credit (5 pts) => 10-33

How do you recognize the acid or base groups?

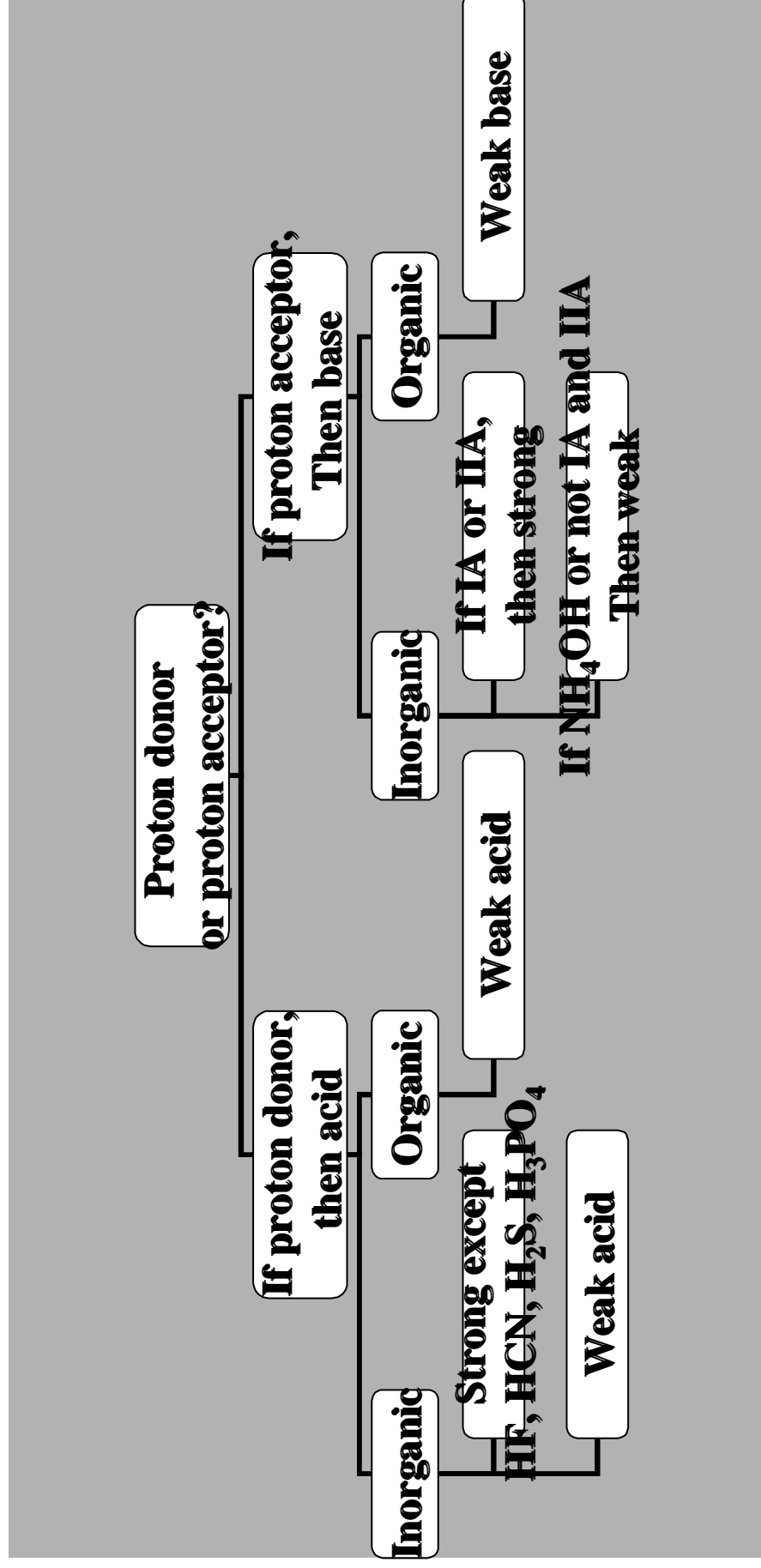
Weak acids:

- Look for the proton (H)
- Look for oxygen – typically the H associated with an oxygen is an acidic H (can be donated). For example -C-OH or $\text{-C} \begin{array}{c} \text{O} \\ \parallel \end{array}$ -OH
- NH_3^+ groups can also donate a proton, but tend to be less acidic than protons associated with oxygen groups.

Weak bases:

- NH_3^+ , organic amines, and hydroxides other than group Ia (like NaOH or KOH as they are strong bases)
- organic amines contain amino group:
 $\text{R-NH}_2 + \text{H}^+ = \text{R-NH}_3^+$

Scheme for Identification of Acids and Bases



Salts

- There are four kinds of salts:
 - salts of weak acids and strong bases
example: sodium acetate
 - salts of weak bases and strong acids
example: trimethyl ammonium chloride
 - salts of strong acids and strong bases
example: sodium chloride
 - salts of weak acids and weak bases
example: trimethyl ammonium acetate

Identification of Salts

- Salts hydrolyze in water:

Salt + water = acid + base

Example: $\text{NaCl} + \text{HOH} \rightarrow \text{Na}^+ + \text{OH}^- + \text{H}^+ + \text{Cl}^-$

- Salts are obtained by reacting acids and bases:
Acid + Base = Salt + water

Identification of Salts

- Salts are classified based by their **parent acids** and **bases**
- Their parents are the acids and bases which were used in the reaction to form them

- Example: NaCl



So, parents are strong acid and strong base and NaCl is the salt of a strong acid and strong base

Polyprotic Acids/Bases

- Protons are always lost (acid) or gained (base) one at a time!
- Each donation of a proton (acid) or acceptance of a proton (base) is characterized by a unique K_a (or K_b) value.
- When you have a polyprotic acid or base in solution you can have many different species present; however, depending on the pH of the solution one or two species is usually dominant.

Polyprotic Acids



$$\mathbf{K_{a1} = \frac{[H^+][H_2A^-]}{[H_3A]}}$$



$$\mathbf{K_{a2} = \frac{[H^+][HA^{-2}]}{[H_2A^-]}}$$



$$\mathbf{K_{a3} = \frac{[H^+][A^{-3}]}{[HA^{-2}]}}$$

Polyprotic Bases



$$K_{b1} = \frac{[\text{OH}^{-}][\text{HA}^{-2}]}{[\text{A}^{-3}]} \quad K_{b1} = K_w/K_{a3}$$



$$K_{b2} = \frac{[\text{OH}^{-}][\text{H}_2\text{A}^{-2}]}{[\text{HA}^{-2}]} \quad K_{b2} = K_w/K_{a2}$$



$$K_{b3} = \frac{[\text{OH}^{-}][\text{H}_3\text{A}]}{[\text{H}_2\text{A}^{-}]} \quad K_{b3} = K_w/K_{a1}$$

For most polyprotic acids, the K_a values are fairly different indicating that there must be fairly large pH changes (2 or more pH units) to dissociate the proton (H^+) from the molecule.

So for a diprotic acid (H_2A)...

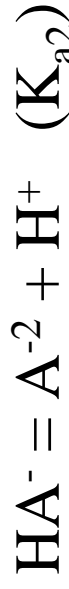
At **acidic** pH values ($pH < pK_{a1}$), mainly the acidic form of the molecule (H_2A) is present.



At **basic** pH values ($pH > pK_{a2}$), mainly the basic form of the molecule (A^{-2}) is present.



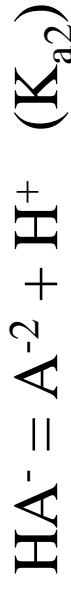
At **intermediate** pH values ($pK_{a1} < pH < pK_{a2}$), the intermediate form of the molecule (HA^-) is present.



AND



At intermediate pH values ($\text{p}K_{\text{a}1} < \text{pH} < \text{p}K_{\text{a}2}$),



AND



If $[\text{HA}^-] \approx \text{F}$, then

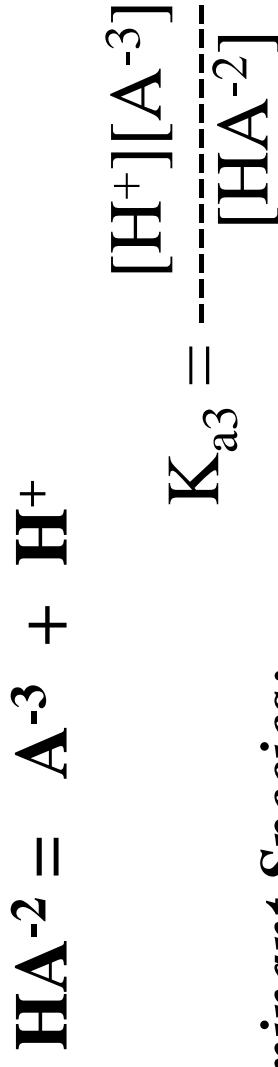
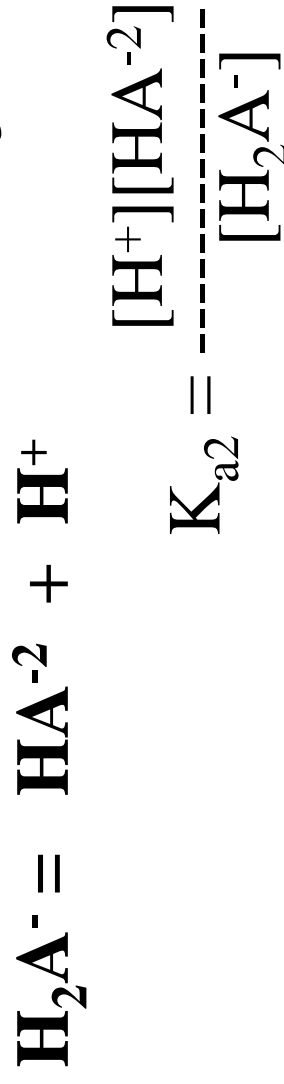
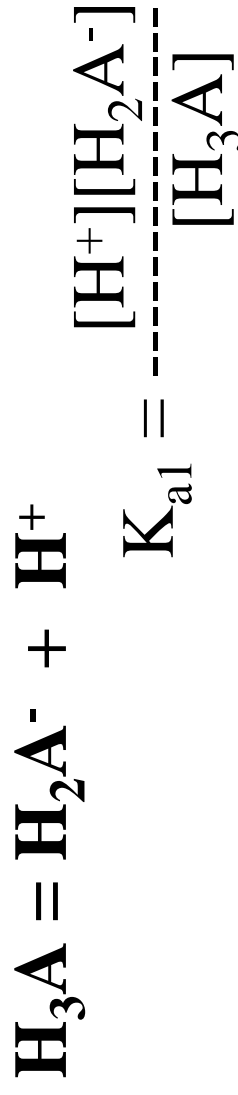
$$K_{\text{a}2} = [\text{A}^{2-}] [\text{H}^+] / [\text{HA}^-] \quad \text{so} \quad [\text{A}^{2-}] = K_{\text{a}2} [\text{HA}^-] / [\text{H}^+]$$

$$\begin{aligned} K_{\text{b}2} &= [\text{H}_2\text{A}] [\text{OH}^-] / [\text{HA}^-] \quad \text{so} \quad [\text{H}_2\text{A}] = K_{\text{b}2} [\text{HA}^-] / [\text{OH}^-] \\ &= (K_{\text{w}}/K_{\text{a}1}) [\text{HA}^-] / (K_{\text{w}}/[\text{H}^+]) \\ &= [\text{H}^+] [\text{HA}^-] / K_{\text{a}1} \end{aligned}$$

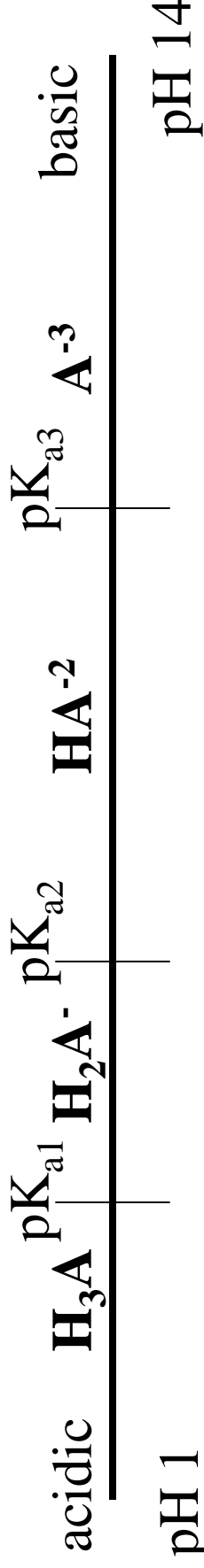
$$[\text{H}^+] = \sqrt{K_{\text{a}1} K_{\text{a}2} \text{F} + K_{\text{a}1} K_{\text{w}} / (K_{\text{a}1} + \text{F})} \quad (\text{see Harris pp. 207-208 for derivation of } [\text{H}^+] \text{ equation})$$

NOTE: $\text{pH} \approx 1/2 (\text{p}K_{\text{a}1} + \text{p}K_{\text{a}2})$

Polyprotic Acid



Dominant Species:

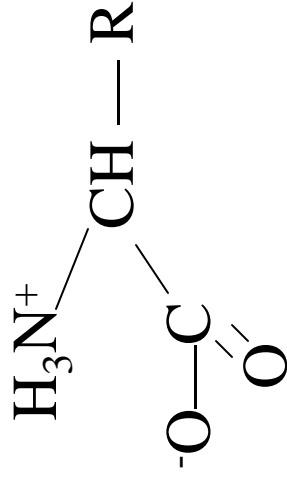


Find the pH and the concentrations of H_2SO_3 (sulfurous acid), HSO_3^- , and SO_3^{2-} in each solution ($\text{pK}_{\text{a}1} = 1.91$, $\text{pK}_{\text{a}2} = 7.18$):

- a) 0.050 M H_2SO_3
- b) 0.050 M NaHSO_3
- c) 0.050 M Na_2SO_3

Zwitterion – Molecule with both positive and negative charges

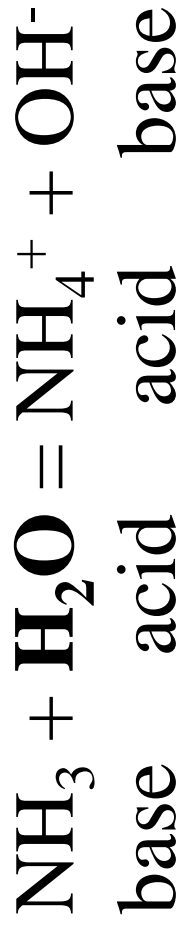
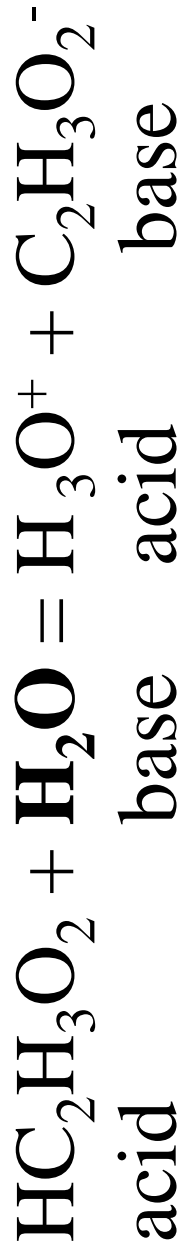
Amino acid:



At acid pH (low pH), both the ammonium and carboxyl groups are protonated. At basic pH (high pH), neither the ammonium or the carboxyl groups are protonated. At intermediate pH values, an amino acid exists as the zwitterion (the carboxyl group donates a proton (acidic) and the ammonium group accepts a proton (basic)).

Amphoterism

- Some compounds can function as both acids or bases depending on the situation e.g., H_2O . They are said to be amphiprotic.



- Amphiprotic molecules are typically the intermediate of a polyprotic acid or base

Titration of Polyprotic Base with Strong Acid

Titration of 2 mm of Na_2CO_3 with 0.1 M HCl

