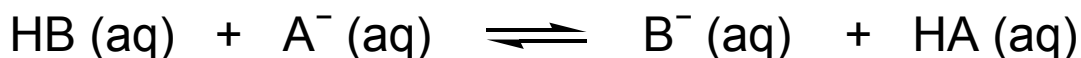


Weak Acids and Bases

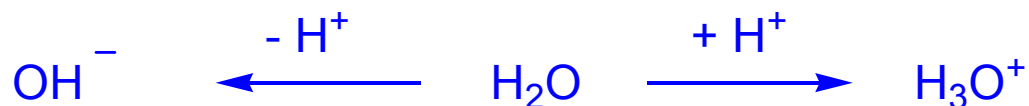
A. Introduction

- Recall strong acids and bases. These are compounds that ionize completely when dissolved in water.
 - HCl will ionize completely to H^+ and Cl^-
 - NaOH will ionize completely to Na^+ and OH^-
- Previously, we have defined acids and bases using the Arrhenius definition: in water, acids produce H^+ and bases produce OH^-
- However, the Bronsted-Lowry definition is better
 - An acid is an H^+ donor
 - A base is an H^+ acceptor
- Thus, in any acid-base reaction, the proton is transferred from the acid to the base.



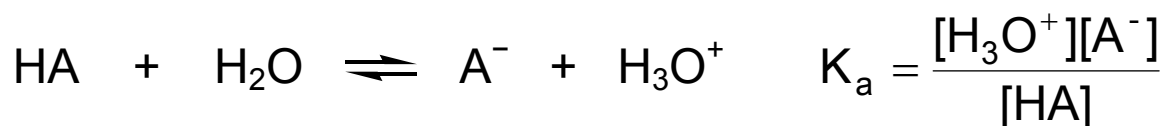
- When a proton is removed from an acid, the species formed is its conjugate base. Similarly, when a base gains a proton, the species formed is its conjugate acid. Examples:
 - Acid: CH_3COOH Conjugate Base: CH_3COO^-
 - Base: NH_3 Conjugate Acid: NH_4^+

- Some species, such as water, can either accept or donate a proton. These are referred to as **amphiprotic (amphoteric)**.



B. Weak Acids

- What is the difference between a strong acid and a weak acid? Weak ones are those that do NOT ionize completely in water. They are only partially ionized.
- Thus, we have an equilibrium described, by the acid dissociation constant K_a . Usually, less than about 1% of the acid is ionized.

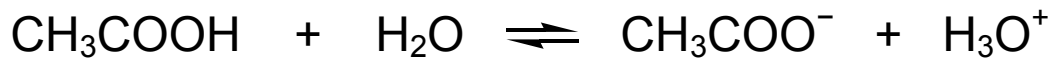


- Note that because the concentration of water is approximately constant, it is left out of the expression.
- We can also define $\text{p}K_a$ in a manner analogous to pH

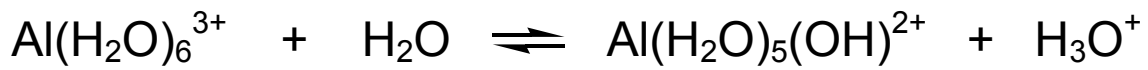
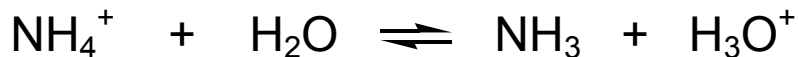
$$\text{p}K_a = -\log K_a$$

- Stronger acids are those that are more ionized. So, the stronger the acid, the HIGHER the K_a and the LOWER the $\text{p}K_a$ values.**

- There are two common forms of weak acids
 - Molecules that contain an ionizable hydrogen atom

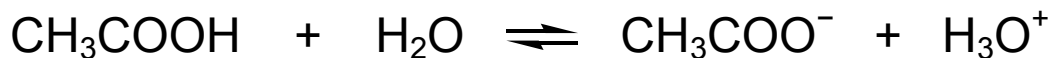


- Cations (positively charged species)

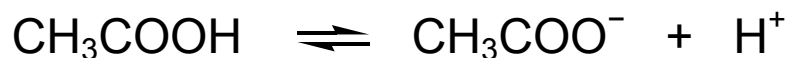


1. Weak acid calculations: monoprotic acids

- Suppose we dissolved 0.10 mol acetic acid ($K_a = 1.8 \times 10^{-5}$) in enough water to make a 1.0 L solution. Calculate the pH and the determine the percent dissociation of acetic acid.
- To be able to calculate the pH, we need to know the concentration of H^+ (same thing as H_3O^+) at equilibrium.



same as



- When the 0.10 M of acetic acid is mixed with water, some of it dissociates. Thus, the INITIAL concentration (conc_{ini}) of acetic acid is 0.10 M, and the conc AT EQUILIBRIUM will be lower by some unknown value x . The value of x is $[\text{H}^+]$.



- The K_a equation above is a quadratic equation that can be rearranged to the following

$$x^2 + (K_a)(x) - 0.1(K_a) = 0 \quad \text{where } x = [\text{H}^+]$$

- How do we solve this? Remember the quadratic formula? The quadratic ($ax^2 + bx + c$) has two roots:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

- Thus, x can be a positive or a negative value. Have you heard of a negative concentration??? No! So, only the positive value of x is correct.

$$x = \frac{-b + \sqrt{b^2 - 4ac}}{2a}$$

- Substituting the appropriate parameters, where $a = 1$, $b = K_a$, and c is a negative number ($-0.1K_a$), we get

$$x = \frac{-K_a + \sqrt{(K_a)^2 + 4(\text{conc}_{\text{ini}})K_a}}{2}$$

- Solving x using the K_a of acetic acid and $\text{conc}_{\text{ini}} = 0.1 \text{ M}$

$$x = \frac{-(1.8 \times 10^{-5}) + \sqrt{(1.8 \times 10^{-5})^2 + 4(0.1)(1.8 \times 10^{-5})}}{2}$$

$$x = 1.33 \times 10^{-3} \text{ M} = [\text{H}^+] = [\text{CH}_3\text{COO}^-]$$

Corresponds to pH value 2.88

- With this value of x , we can also determine the percentage of 0.1 M acetic acid that is dissociated.

$$\% \text{ dissociated} = \frac{\text{amount dissociated}}{\text{total amount}} \times 100\% = \frac{[x]}{[\text{conc}_{\text{ini}}]} \times 100\%$$

$$\% \text{ dissociated} = 1.3 \%$$

- So, only about 1% of acetic acid ionizes when in water.
- This has some important consequences:
 - $[\text{conc}_{\text{ini}}]$ is very close to $[\text{conc}_{\text{ini}} - x]$, and the difference between these two concentrations is “negligible”
 - We can only say that they are negligible if the amount of dissociation is less than 5%. This is generally the case if the original concentration conc_{ini} divided by K_a is > 100 .

- And why this important? With this assumption, we do NOT need to solve the quadratic formula!
- Going back to our example of 0.1 M acetic acid



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{HA}]} = \frac{[x][x]}{[\text{conc}_{\text{ini}}]}$$

$$1.8 \times 10^{-5} = \frac{[x]^2}{0.1}$$

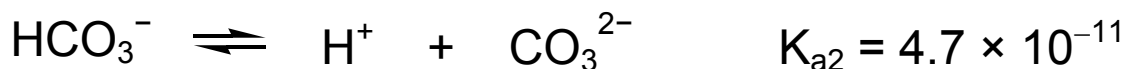
$$x = 1.34 \times 10^{-3} \text{ M}$$

- Compare this value to the one obtained with the quadratic, and you'll notice that they're very close to each other.
- Remember, you can only assume $[\text{conc}_{\text{ini}} - x] = [\text{conc}_{\text{ini}}]$ when conc_{ini} is at least 100-fold greater than K_a . Always check that this is true before making the assumption.
- Also note that for any given weak acid, the percentage of dissociation increases as the solution is diluted, even though $[\text{H}^+]$ decreases. *e.g.* for acetic acid
 - 1.00 M dissociation = 0.42 % pH 2.37
 - 0.01 M dissociation = 4.2 % pH 3.37
 - This is why the approximation only works when conc_{ini} is at least 100 times greater than K_a .

- Example: Nitrous acid has a K_a of 6.0×10^{-4} . Calculate the concentration of the acid if the pH is 3.65.
 - Realize the concentration refers to both the dissociated and the undissociated forms. *i.e.* calculate conc_{ini}

2. Weak acid calculations: polyprotic acids

- Polyprotic acids are those that contain more than one ionizable atom.
- These acids dissociate in steps, with each successive step being less likely (lower K_a) than the one before. This is because it is much harder to move a proton from an ion that is already negatively charged. *e.g.* carbonic acid



- The K_a of each successive ionization is typically at least 100-fold smaller than the previous.
- Calculations are therefore easy, because virtually all of the H^+ in solution comes from the first ionization. So, we only need to consider the first K_a value!
- What is the pH of a 0.0010 M solution of carbonic acid?

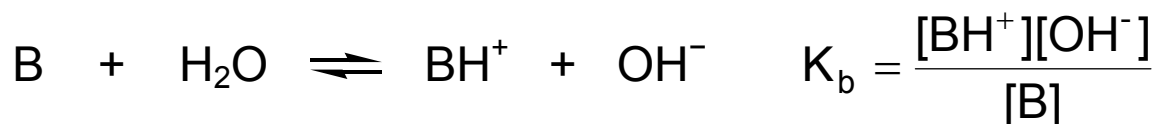
- Interestingly, what is $[\text{CO}_3^{2-}]$ in the 0.0010 M solution?

- So, for any weak diprotic acid H_2A
 - $[\text{H}^+]$ is calculated from K_{a1} only
 - The conc of $\text{A}^{2-} =$

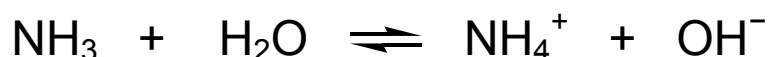
- For practice, do Dec 2004 #39 at home.

C. Weak Bases

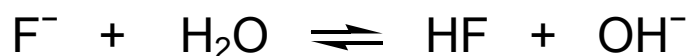
- Like weak acids, weak bases are those that do not ionize completely. We can write K_b (base dissociation constant) for weak bases, and we say that the base **hydrolyzes** water.



- We also define $pK_b = -\log K_b$
 - A stronger base has a larger K_b and a smaller pK_b
- There are two common forms of weak bases
 - Ammonia and related compounds



- Anions



This reaction resembles the reverse of the dissociation of the acid HF, and it is because the fluoride ion is the conjugate base of the weak acid HF. (In this reaction, fluoride is the base and HF is the conjugate acid).

- Consequently, there is a relationship between K_a and K_b for a given conjugate acid-base pair.

- Consider
 - $\text{HB} \rightleftharpoons \text{H}^+ + \text{B}^-$ K_a of species HB
 - $\text{B}^- + \text{H}_2\text{O} \rightleftharpoons \text{BH} + \text{OH}^-$ K_b of species B^-
- If we add these together, we get the K_W we've seen before!
 - $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ K_W
- When we add equations, we multiple K values. *i.e.*

$(K_a \text{ of HB}) \times (K_b \text{ of B}^-) = K_W = 10^{-14}$ or $\text{p}K_a + \text{p}K_b = 14$
- This relationship also suggests that
 - Strong acids have weak conjugate bases
 - HCl is a very strong acid, so Cl^- is a very weak base.
 - Cl^- will NOT react with water to form HCl and OH^-
 - Weak acids have strong conjugate bases
 - $\text{CH}_3\text{CH}_2\text{OH}$ (ethanol) is a very weak acid
 - $\text{CH}_3\text{CH}_2\text{O}^-$ (ethoxide) is a very strong base and will react with water to form ethanol and OH^-

Acid	Acid Strength	$\text{p}K_a$	Conj Base	Base Strength	$\text{p}K_b$
HF	stronger	3.14	F^-	weaker	10.86
CH_3COOH	↓	4.74	CH_3COO^-	↓	9.26
HCN	weaker	9.40	CN^-	stronger	4.60

1. Weak base calculations: monobasic compounds

- Monobasic compounds are those that accept a single H. Their calculations are no different than those of monoprotic weak acids, except we are now working with hydroxide.
- Example: Dec 2004 #33. What is the pH of a 0.0185 M solution of potassium benzoate, C_6H_5COOK ? The K_a for benzoic acid, C_6H_5COOH , is 6.3×10^{-5} .

2. Weak base calculations: polybasic compounds

- Treat compounds that can accept more than one proton just like polyprotic acids. Only the first ionization is significant!
- Example: calculate the pH of a 0.150 M solution of Na_2CO_3

$$K_b \text{ of } \text{CO}_3^{2-} = 2.08 \times 10^{-4}$$

$$K_b \text{ of } \text{HCO}_3^- = 2.38 \times 10^{-8}$$

D. Hydrolysis of Salts of Weak Acids and Bases

- Salts of weak acids and bases would respectively contain the corresponding conjugate bases and conjugate acids. As we saw earlier, these can potentially act as bases or acids. Thus, a salt may change the pH of water when they are dissolved
- However, many salts do not change the pH of water, *e.g.* NaCl. This is because both the cation and the anion act as spectator ions, so they will not affect the pH.
 - Some spectator anions are Cl^- , Br^- , I^- , NO_3^- , SO_4^{2-} , etc. These are all conjugate bases of strong acids!!! On the contrary, conjugate bases of weak acids (*e.g.* F^- , CO_3^{2-} , CH_3COO^-) will act as bases and raise the pH.
 - Some spectator cations are Li^+ , Na^+ , Ca^{2+} , etc. Likewise, conjugate acids of weak bases (*e.g.* NH_4^+) will act as acids and lower the pH.
- Determine if the water solutions of following salts are acidic, basic, or neutral.
 - NH_4I
 - KClO_4
 - CH_3COONa

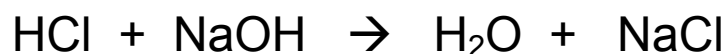
- Example: Calculate the pH and % hydrolysis for 0.10 M solutions of (a) KF and (b) KCN

- Example: Calculate the pH and % hydrolysis for 0.10 M NH_4Cl . (K_b of $\text{NH}_3 = 1.8 \times 10^{-5}$)

Type of Salt	Examples	Ions That React with Water	pH of Solution
Cation from strong base; anion from strong acid	NaCl , KNO_3 , BaI_2	None	~ 7
Cation from weak base; anion from strong acid	NH_4Cl , NH_4NO_3 , $[(\text{CH}_3)_3\text{NH}]\text{Cl}$	Cation	< 7
Small, highly charged cation; anion from strong acid	AlCl_3 , $\text{Cr}(\text{NO}_3)_3$, $\text{Fe}(\text{ClO}_4)_3$	Hydrated cation	< 7
Cation from strong base; anion from weak acid	NaCN , KF , Na_2CO_3	Anion	> 7

E. Equivalence Point of a Titration

- This is the point where the stoichiometric quantities of acid and base, as determined by the equation, have been mixed. *i.e.* all the acid and base have neutralized
- NOTE: the pH of the solution at the equivalence point is NOT always neutral!!!!
- In a strong acid + strong base titration, such as HCl and NaOH, the pH at the EP is indeed neutral. This is because neither Na^+ nor Cl^- is the conjugate of a weak species, so they are just spectator ions.



1. Strong base + weak acid titration

- Suppose we titrate CH_3COOH (weak acid) and NaOH (strong base). At EP, we'll have sodium acetate (salt of weak acid).



- However, as discussed earlier, acetate hydrolyzes.



- So, even at equivalence point, the pH of the solution will be basic and thus greater than 7. If we wish to know the exact pH at EP, we need to determine the concentration.

- Example: Calculate the pH of a solution formed by the reaction of 100 mL of 1.0 M NaOH with 100 mL of 1.0 M CH₃COOH ($K_a = 1.8 \times 10^{-5}$).

2. Strong acid + weak base titration

- Suppose we titrate NH_3 (weak base) and HCl (strong acid). At EP, we'll have ammonium chloride (salt of weak base).



- NH_4Cl ionizes to NH_4^+ and Cl^- , and the former is acidic.



- Therefore, at the equivalence point, the solution will be acidic and the pH will be less than 7.
- Example: Calculate pH at the EP of the titration of 0.175 M CH_3NH_2 and 0.250 M HNO_3 . (K_b for $\text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}$)