- Definitions
  - **Bronsted-lowry acid** is a proton donor.
  - **Bronsted-lowry base** is a proton acceptor.
  - **Conjugate base** is the species left over when an acid donates a proton.
  - **Conjugate acid** is the species left over when a base accepts a proton.

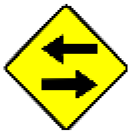
$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \Leftrightarrow \underset{\substack{\text{conjugate}\\\text{acid}}}{NH_4^+} + \underset{\substack{\text{conjugate}\\\text{base}}}{OH^-}$$

- Strong vs. weak
  - **Strong acids and bases** completely dissociate in water. Its essentially a one-way reaction.

$$\underset{\text{acid}}{HCl_{(aq)}} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + \underset{\text{conj. base}}{Cl^-_{(aq)}}$$

    - Strong acids:
      - HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4
    - Strong bases:
      - group I hydroxides
      - group II hydroxides
      - NH_2^-, O_2^-, H^-, R_3C^-
  - **Weak acids and bases** do not dissociate completely. Instead, an equilibrium is established in water between an acid, its conjugate base, and hydronium (for an acid) or a base, its conjugate acid, and hydroxide (for a base)

$$\underset{\text{base}}{(CH_3)_3N_{(aq)}} + H_2O_{(l)} \leftrightarrow \underset{\text{conj. acid}}{(CH_3)_3NH^+_{(aq)}} + OH^-_{(aq)}$$



- Identifying acids and bases
  - **Molecular acids** = H^+ + anion.

$$HCl,\ H_2S,\ HClO_3,\ H_3PO_4$$

  - **Carboxylic acids** have the functional group -COOH.

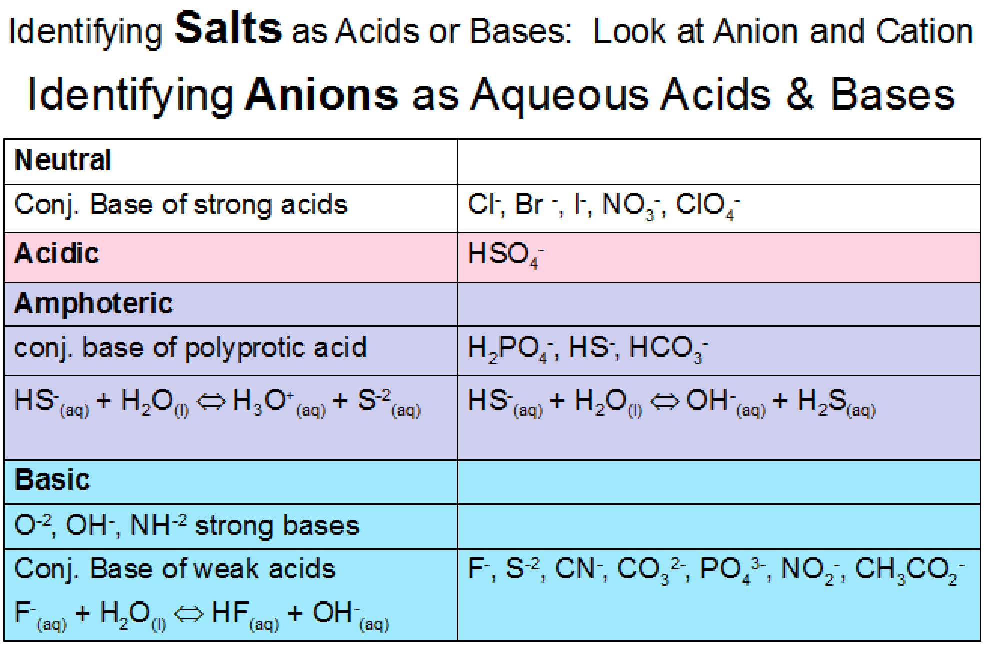
$$CH_3COOH_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

  - **Bases** tend to be hydroxides and amines.

$$NaOH,\ Ca(OH)_2\ \ NH_3,\ (CH_3)_3N$$
$$NH_{3(aq)} + H_2O_{(l)} \Leftrightarrow OH^-_{(aq)} + NH_4^+_{(aq)}$$

  - **Metallic oxides** are basic (i.e. Mg_2O).
  - **Molecular oxides** are acidic (i.e. CO_2).
  - Identifying salts as acids or bases:
    - (1) break up the salt into its cation and anion
    - (2) add “OH” to cation and “H” to anion
    - (3) check to see if the resulting acid or base is strong. If it is strong, then the anion/cation is neutral. If it is not strong, then use this following table to determine if the anion/cation is acidic or basic:

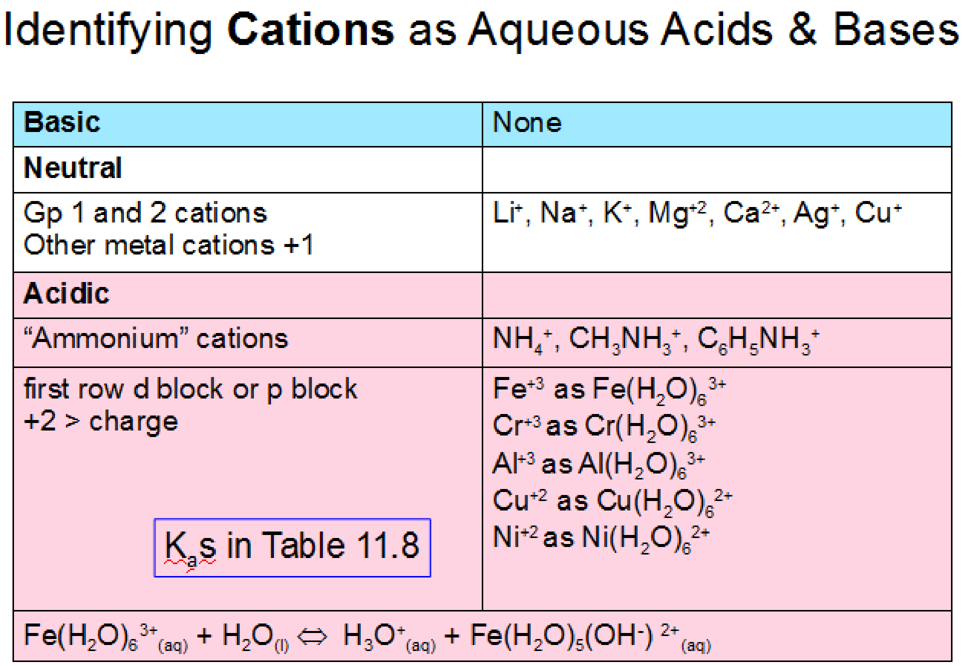
- anions:
    - acidic = HSO_4^-
    - basic = all other weak acids
- cations:
    - neutral = group I and II cations and other +1 metal cations
    - acidic = NH_4^+, first row d block or p block with at least +2 charge.



Identifying **Salts** as Acids or Bases: Look at Anion and Cation

Identifying **Anions** as Aqueous Acids & Bases

Neutral	
Conj. Base of strong acids	Cl^-, Br^-, I^-, NO_3^-, ClO_4^-
Acidic	HSO_4^-
Amphoteric	
conj. base of polyprotic acid	$H_2PO_4^-$, HS^-, HCO_3^-
$HS^-_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + S^{-2}_{(aq)}$	$HS^-_{(aq)} + H_2O_{(l)} \Leftrightarrow OH^-_{(aq)} + H_2S_{(aq)}$
Basic	
O^{-2}, OH^-, NH^{-2} strong bases	
Conj. Base of weak acids $F^-_{(aq)} + H_2O_{(l)} \Leftrightarrow HF_{(aq)} + OH^-_{(aq)}$	F^-, S^{-2}, CN^-, CO_3^{2-}, PO_4^{3-}, NO_2^-, $CH_3CO_2^-$

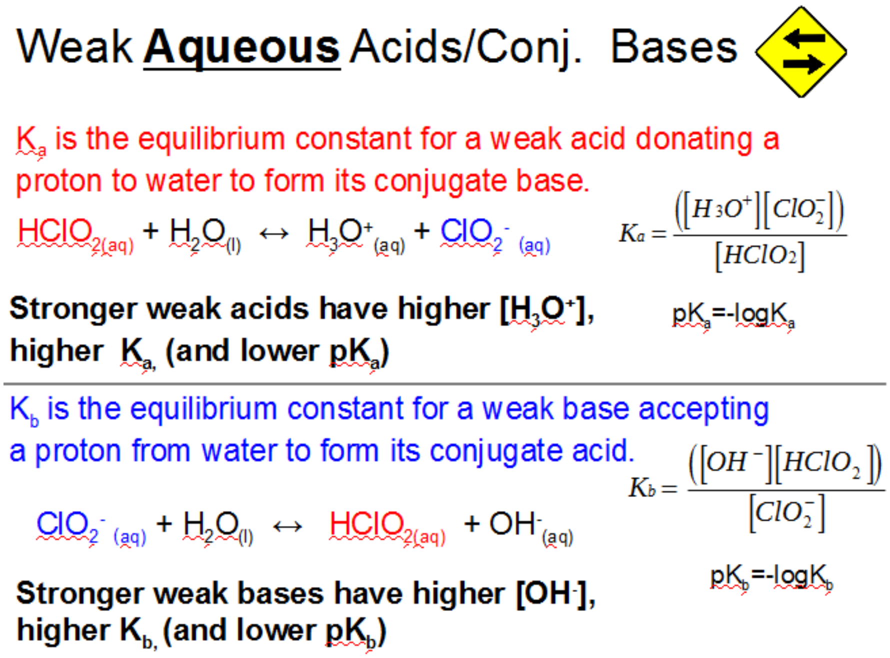


Identifying **Cations** as Aqueous Acids & Bases

Basic	None
Neutral	
Gp 1 and 2 cations Other metal cations +1	Li^+, Na^+, K^+, Mg^{+2}, Ca^{2+}, Ag^+, Cu^+
Acidic	
"Ammonium" cations	NH_4^+, $CH_3NH_3^+$, $C_6H_5NH_3^+$
first row d block or p block +2 > charge K_as in Table 11.8	Fe^{+3} as $Fe(H_2O)_6^{3+}$ Cr^{+3} as $Cr(H_2O)_6^{3+}$ Al^{+3} as $Al(H_2O)_6^{3+}$ Cu^{+2} as $Cu(H_2O)_6^{2+}$ Ni^{+2} as $Ni(H_2O)_6^{2+}$
$Fe(H_2O)_6^{3+}{}_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + Fe(H_2O)_5(OH^-)^{2+}{}_{(aq)}$	

- For binary acids, the more polar the bond, the stronger the acid. However, the more polarizable the atom bound to H leads to the stronger acid.
- The more electronegative atom bound in the molecule but not directly to H, the stronger the acid.
- Resonance of the conjugate base increases acidity.
- For oxoacids, the more oxygens bound to the central atom, the more acidic it is.
- For carboxylic acids, the greater the electronegativity of the groups attached to COOH, the stronger the acid.

- pH/pOH
    - Formulas:
        - $pH = -\log[H_3O^+]$
        - $pOH = -\log[OH^-]$
        - pH + pOH = 14
    - A difference of 1 pH/pOH unit is a difference in concentration of a factor by 10!!!!
    - **<u>DAT math formulas to estimate logs</u>**:
        - $-\log(m*10^{-n}) \approx n-1.10-m$
        - $\log(m*10^{-n}) \approx (-n)+1.10-m$
        - $\ln(x) \approx 2.3(\log(x))$
        - $\log(m*10^{n}) \approx n.1+m$
- K_a, K_b
    - K_a is the equilibrium constant for an acid dissociating in water to form its conjugate base.
    - K_b is the equilibrium constant for base dissociating in water to form its conjugate acid.
    - Stronger acids have higher K_a values and smaller K_b values.
    - Stronger bases have higher K_b values and smaller K_a values.



Weak **<u>Aqueous</u>** Acids/Conj. Bases

K_a is the equilibrium constant for a weak acid donating a proton to water to form its conjugate base.

$HClO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + ClO_2^-{}_{(aq)}$

$$K_a = \frac{([H_3O^+][ClO_2^-])}{[HClO_2]}$$

Stronger weak acids have higher $[H_3O^+]$, higher K_a (and lower pK_a)

$pK_a = -\log K_a$

K_b is the equilibrium constant for a weak base accepting a proton from water to form its conjugate acid.

$ClO_2^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow HClO_{2(aq)} + OH^-_{(aq)}$

$$K_b = \frac{([OH^-][HClO_2])}{[ClO_2^-]}$$

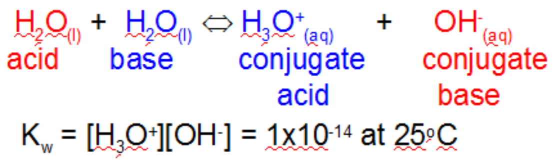
$pK_b = -\log K_b$

Stronger weak bases have higher $[OH^-]$, higher K_b, (and lower pK_b)

-
    - K_a and K_b can be converted using a logarithmic scale to pK_a and pK_b:

$$pKa = -\log(K_a) \qquad pKb = -\log(K_b)$$

-
    -
        - Stronger acids have lower pK_a and higher pK_b values.
        - Stronger bases have higher pK_a and lower pK_b values.
- The special case of water
    - Water is **amphiprotic**, meaning it can act as an acid or base.
    - At 25°C, there is $1*10^{-7}$ M H_3O^+ and $1*10^{-7}$ M OH^-.
    - The equilibrium constant the describes this association is K_w.



$H_2O_{(l)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$

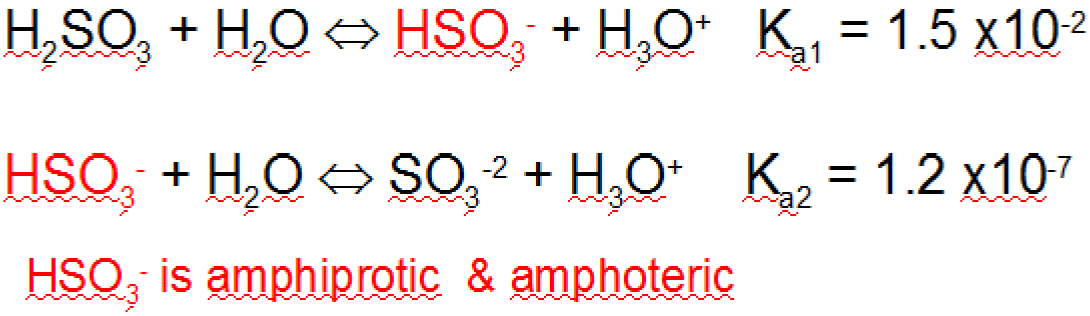
acid base conjugate acid conjugate base

$K_w = [H_3O^+][OH^-] = 1\times10^{-14}$ at $25^\circ C$

  - The autionization of water is an endothermic reaction. As the temperature increases, the pH and the pOH decreases. Why?
    - Increasing the temperature shifts the reaction to the right, meaning that there will be an increase in [H+] and [OH-]. Therefore
  - A special and important relationship arises from K_w:

$$K_w = K_a * K_b \quad \text{and at 25°C:} \quad 1*10^{-14} = K_a * K_b$$

- Polyprotic acids
  - Some acids have multiple protons that can be removed from it. These acids are **polyprotic acids**.
  - Polyprotic acids have multiple K_a values, one for each proton.
    - The easiest proton to remove from the polyprotic acid is the first proton. This proton has the highest K_a value and the lowest pK_a value.
    - After removing the first proton, every successive proton is harder to remove. As a result, the K_a value increases and the pKa value increases of every successive proton.
  - If an acid has already lost one proton but not all of them, then it tends to be amphoteric.

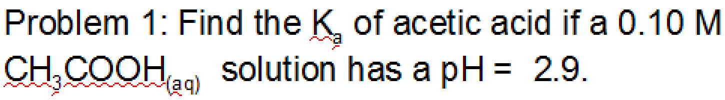


$$H_2SO_3 + H_2O \Leftrightarrow HSO_3^- + H_3O^+ \quad K_{a1} = 1.5 \text{ x}10^{-2}$$

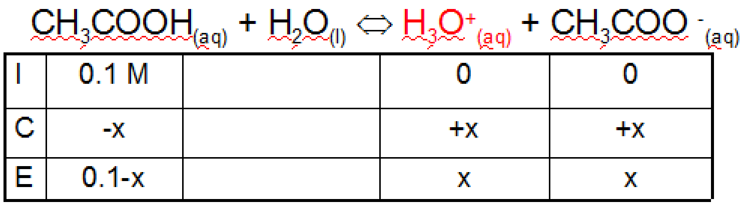
$$HSO_3^- + H_2O \Leftrightarrow SO_3^{-2} + H_3O^+ \quad K_{a2} = 1.2 \text{ x}10^{-7}$$

HSO_3^- is amphiprotic & amphoteric

- Problem solving: How to find pH of weak acids and bases
  - Example problem (<u>note that the numbers will be easier to work with on the DAT</u>):



Problem 1: Find the K_a of acetic acid if a 0.10 M $CH_3COOH_{(aq)}$ solution has a pH = 2.9.



$CH_3COOH_{(aq)} + H_2O_{(l)} \Leftrightarrow H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$

I	0.1 M		0	0
C	-x		+x	+x
E	0.1-x		x	x

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$pH = -\log[H_3O^+] = 2.9$$

$$[H_3O^+] = 10^{-2.9} = 1.26x10^{-3} = x$$

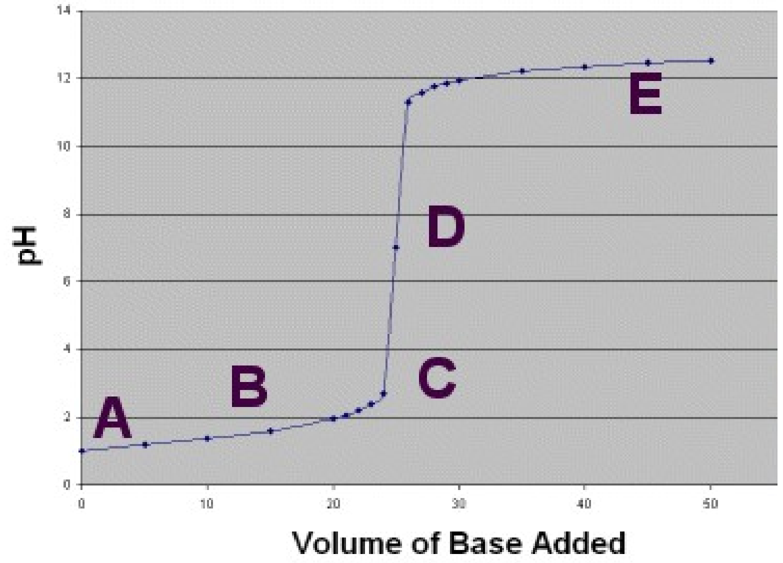
$$K_a = \frac{x * x}{0.1 - x} = \frac{(1.26x10^{-3})^2}{0.1 - 1.26x10^{-3}} = 1.61x10^{-5}$$

    - 1) Write out the equilibrium reaction for the constant given/what you are looking for. If you are given the K_b value, write out the reaction for K_b. In the problem above, they are asking for the K_a, so write out the reaction for K_a (an acid reacting with water).
    - 2) Draw an ICE box and fill out the 3 rows.
    - 3) Write out the equation for K_a or K_b, depending on the problem. Here, write out the equation for K_a because the problem asks you for the K_a value.

        - 4) You will either have to solve for x or solve for the K_a or K_b value depending on what the problem is asking for. In this problem, you need to solve for K_a. But what is x equal to? You are given pH, meaning you can find the hydronium ion concentration at equilibrium. Solve for it, then replace x with the answer and then solve for K_a.
- What is a titration?
    - A **titration** is an analytical technique where an unknown concentration of a substance is determined via a chemical reaction by the addition of a known amount of a known concentration of a substance that reacts with the unknown.
    - A **burette**, a piece of graduated glassware, allows the volume of the known to be measured.
    - The **equivalence point/stoichiometric point** occurs when moles of added known substance have stoichiometrically reacted with the moles of the unknown substance (the reaction is complete.)
    - The ½ **equivalence point** is when [acid] = [conjugate base] or when [base] = [conjugate acid] in the beaker. At this point the pKa = pH (more on this later).
- 3 different titration scenarios
    - Note that in each scenario, the “strong” must always be in the buret!
    - (1) strong acid with strong base. The equivalence point is always at pH = 7.
    - (2) Weak acid with strong base. Equivalence point is always greater than pH = 7.
    - (3) Weak base with strong acid. Equivalence point is always less than pH = 7.
- The henderson-hasselbach equation:
    - Useful equation for titration calculations:

$$pH = pKa + \log\left[\frac{H^-}{HA}\right] \quad \text{or} \quad pOH = pKb + \log\left[\frac{HB^+}{B}\right]$$

    - **IMPORTANT LIMITATION**: $[A^-]$ or $[HB^+]$ and [HA] or [B] must be within a factor of 10 of one another (ratio must be less than 10).
- The titration curve and titration calculations (assuming weak acid titrated with strong base):
    - NOTE: when doing calculations for weak base with strong acid, the opposite applies.



    - (A) = No base has been added to the beaker. Use a simple ICE box to determine the $[H_3O^+]$ of the acid, and then from there calculate pH.
    - (Between A and B when 10 mL base has been added) = Base has been added. Find the moles of acid. Moles acid = molarity * volume of acid. Find the moles of base. Moles base = molarity * volume of base. After, place all values into a PUG box (Put in, Use up, Get out). A **PUG box** is essentially the same as an ICE box, but everything is in terms of moles rather than pressures or concentrations. Note that this point, the moles of acid will be greater than the moles of base. Therefore, you will Get out with some moles of acid, 0 moles of original base, and some moles of the conjugate base.

	HA	+ OH^-	→ H_2O	+ A^-
Put in	Mol acid	Mol base	XXXX	0
Use up	- mol base	- mol base	XXXX	+ mol base
Get out	Mol acid – mol base	0	XXXX	Mol base

After completing the PUG table, reconvert the moles of the acid and the conjugate base back into their respective molarities. Because you added base to the beaker, the volume has changed!
New volume = volume of acid + volume of base added. Once you have re-converted back into molarity, use the henderson-hasselbach equation to find the pH of the solution.

- (B) = ½ equivalence point. The amount of moles of HA = moles of A-. At this point, the pH = pKa of the weak acid.
- (D) = Equivalence point (Moles of OH- = moles of HA). Find the moles of acid. Moles acid = molarity * volume of acid. Find the moles of base. Moles base = molarity * volume of base. After, place all values into a PUG box. Because mol base = mol acid, there are no leftover moles of the acid or the base. All that remains is the conjugate base. Convert back the moles of conjugate base back into molarity. Because you added base to the beaker, the volume has changed! New volume = volume of acid + volume of base added.

	HA	+ OH^-	→ H_2O	+ A^-
Put in	Mol acid	Mol base	XXXX	0
Use up	- mol base	- mol base	XXXX	+ mol base
Get out	0	0	XXXX	Mol base

The conjugate base can react with water. Draw an ICE box.

	A^-	+ H_2O	→ HA	+ OH^-
Initial	$\frac{mol\,conjugate\,acid}{new\,volume}$	XXXX	0	0
Change	- x	XXXX	+ x	+ x
Equilibrium	$\frac{mol\,conjugate\,acid}{new\,volume} - x$	XXXX	x	x

In order to solve for x, you will need the K_b value. In these problems, they will give you the K_a of the original acid. Use $K_w = K_a{*}K_b$ to find K_b. Write out the Kb equation and solve for x. Once you solved for x, then find pOH and then convert that to pH.

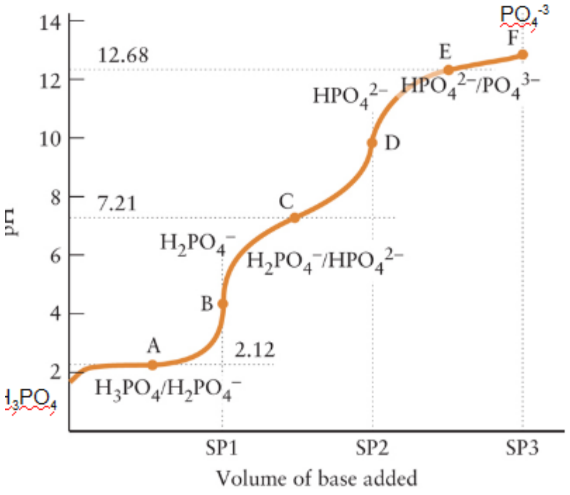
- (E) = Past the equivalence point. Find the moles of acid. Moles acid = molarity * volume of acid. Find the moles of base. Moles base = molarity * volume of base. After, place all values into a PUG box. From the PUG table, you will see that there will be some leftover moles of base and some moles of conjugate acid. You can ignore the moles of conjugate acid because that plays a negligible role in affecting the pH. Convert back the excess moles of OH back into molarity. Because you added base to the beaker, the volume has changed! New volume = volume of acid + volume of base added. Then find pOH and convert to pH.

- Indicators
  - An **indicator** is used to tell when the equivalence point has been reached. The goal is to choose an indicator with a pK_{ind} value near the pH of the stoichiometric point. Why is this the case?
    - Indicators are in equilibrium when in water with their deprotonated form: $HInd + H_2O \leftarrow\rightarrow Ind^- + H_3O^+$
    - HInd and Ind^- both have different colors and they are pH dependent:
      - If you add OH^- ions (base), it will react with H_3O^+, and lower $[H_3O^+]$. Due to le chatelier's principle, the reaction will shift right and the overall color will be closer to that of Ind^-.

        - If you add H_3O^+ ions (acid), the reaction will shift left (as you are adding product) and the overall color will be closer to HInd.
        - When [HInd] = $[In^-]$, the color will be in between. You will see a color change occur here.
        - $K_{ind} = \frac{[H^+][Ind^-]}{[HInd]}$. When [HInd] = $[In^-]$, Kind = H^+, so pK_{ind} = pH.
- Polyprotic acid titrations
    - Polyprotic acids have multiple equivalence points and ½ equivalence points.
    - The pH at each ½ equivalence point corresponds to the pKa of the proton that is being ripped off.

Polyprotic Acid Titrations:

H_3PO_4 with Strong Base



A: ½SP1
0.5 equiv OH^- added
pH = pK_{a1} = 2.12
$H_3PO_4 = H_2PO_4^-$

B: SP1
1 equiv OH^- added
Primarily $H_2PO_4^-$

C: ½SP2
1.5 equiv OH^- added
pH = pK_{a2} = 7.21
$H_2PO_4^- = HPO_4^{-2}$

D: SP2
2 equiv OH^- added
Primarily HPO_4^{-2}

E: ½SP3
2.5 equiv OH^- added
pH = pK_{a3} = 12.68
$HPO_4^{-2} = PO_4^{-3}$

F: SP3
3 equiv OH^- added
Primarily PO_4^{-3}

- The $M_1V_1 = M_2V_2$ titration problem
    - From diluting solutions, you should remember the equation $M_1V_1 = M_2V_2$ where M = molarity and V = volume in liters.
    - DAT loves asking equations relating this formula to titrations. The formula is now: $(X)M_{acid}V_{acid} = (Y)M_{base}V_{base}$ You need to be careful in how you approach this:
        - (1) identify the amount of OH ions that are in each molecule of base and the amount of Hs that are in each molecule of acid.
        - (2) Replace "Y" with the number of OH ions you counted and "X" with the number of Hs you counted.
        - (3) Fill in the known variables and solve for the unknown variable.
    - Example: If it takes 50 mL of 0.5 M KOH solution to completely neutralize 125 mL of sulfuric acid (H_2SO_4) solution, what is the concentration of H_2SO_4 solution?
        - (1) For every molecule of base, there is 1 OH. For every molecule of acid, there are 2 Hs.
        - (2) $2*M_{acid}V_{acid} = 1*M_{base}V_{base}$
        - (3) 2*x*.125 = 1 * 0.5 * 0.05 → x = 0.1 M
- Buffers
    - A **buffer** is a solution in which pH resists change when small amounts of acids or bases are added because the system contains a weak acid and its conjugate base.
        - Buffers only exist when $[A^-]$ and [HA] or [B] and $[HB^+]$ are within a factor of 10 of each other. Another way of saying this is that the pH is within 1 unit of the pKa.
        - The region described above is called the **buffering region**. Adding OH^- or H^+ does not significantly change the pH.
    - **Buffer capacity** is the maximum amount of acid or base that can be added to a buffer before the buffer loses its ability to resist large changes in pH.

    - A more concentrated buffer has a higher buffer capacity than a less concentrated buffer.
  - 3 buffer recipes (the pairs must be within a concentration factor of 10):
    - mix weak acid + conjugate base pair
    - strong acid + weak base
    - weak base + strong acid