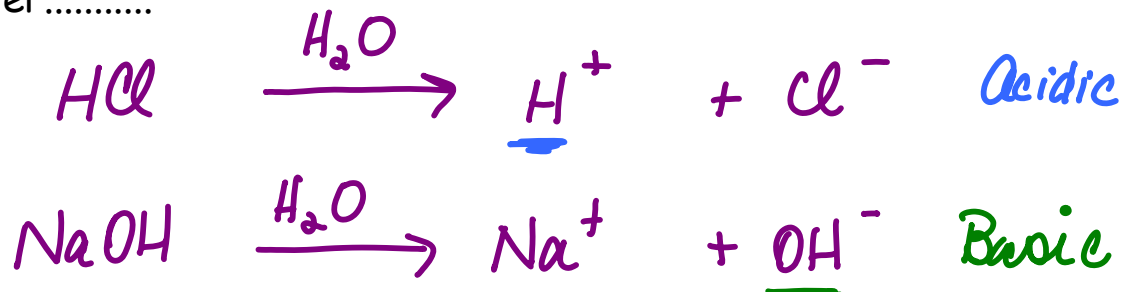


WEAK ACIDS AND BASES

[MH5; Chapter 13]

- Recall that a **strong** acid or base is one which **completely** ionizes in water.....



- In contrast a **weak** acid or base is only **partially** ionized in aqueous solution.....



- The ionization of a weak acid or base in water is an equilibrium situation.
- It is, therefore, governed by an equilibrium constant; K_a for acids and K_b for bases.
- We write these equilibrium constants as:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Notice that....

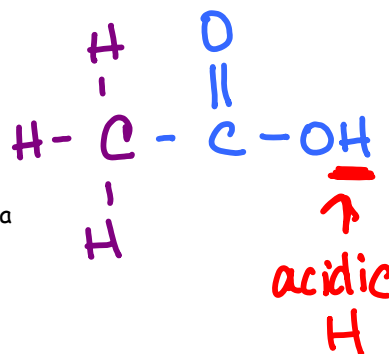
- $[H_2O]$ (constant at $\approx 55.6 M$) does not appear in K_a or K_b .
- The larger the K_a the stronger the acid; the larger the K_b the stronger the base.

EXAMPLE:

CCl_3COOH ; $K_a = 2.0 \times 10^{-1}$ is a stronger acid than
 CH_3COOH ; $K_a = 1.8 \times 10^{-5}$

CH_3NH_2 ; $K_b = 6.4 \times 10^{-4}$ is a stronger base than
 NH_3 ; $K_b = 1.8 \times 10^{-5}$

- H's on C are not (generally) acidic in water -
e.g. CH_3COOH monoprotic (one H^+) and one K_a



- We may define pK_a analogous to pH and pK_w :

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

EXAMPLES:

pK_a for $CCl_3COOH = 0.70$ [$-\log(2.0 \times 10^{-1})$]
 pK_a for $CH_3COOH = 4.74$ [$-\log(1.8 \times 10^{-5})$]

pK_b for $CH_3NH_2 = 3.19$ [$-\log(6.4 \times 10^{-4})$]
 pK_b for $NH_3 = 4.74$ [$-\log(1.8 \times 10^{-5})$]

- Because of the minus sign, the smaller the value of K_a or K_b the larger the value of pK_a , or pK_b

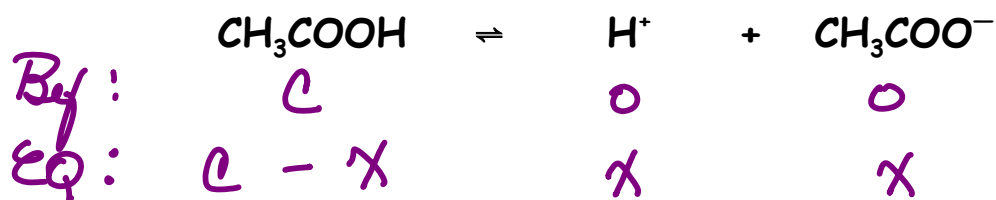
OR

- The weaker the acid or base, the larger the pK_a or pK_b

Calculations Involving Weak Acids

- Suppose that we have a solution of acetic acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$); let its initial concentration be represented by "c" mol L⁻¹.

At equilibrium, "x" mol L⁻¹ have dissociated.....



$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{c-x} = \frac{x^2}{c-x}$$

- This is a quadratic equation in "x". $(ax^2 + bx + c = 0)$
- The quadratic equation may be simplified by assuming that "x" is negligible compared to "c".
- CH_3COOH is a weak acid; so we may assume that the small amount dissociation makes little difference to the amount of undissociated acid left.
- Now let "c" = 0.10 mol L⁻¹..... $\text{So... } c-x \approx c$

$$K_a = \frac{x^2}{0.10 - x} = 1.8 \times 10^{-5}$$

- If x is negligible compared to 0.10 molL^{-1} :

$$\Rightarrow 0.10 - x \approx 0.10$$

$$\text{So... } 1.8 \times 10^{-5} = \frac{x^2}{0.10}$$

$$x^2 = 1.8 \times 10^{-5} \times 0.10$$

$$x = \sqrt{1.8 \times 10^{-5} \times 0.10} = 1.34 \times 10^{-3} = [\text{H}^+]$$

- In this case, x is about 1.3% of 0.10, a negligible error within the accuracy of the original data we were given.
- If we were to solve the equation exactly, $x = 1.333 \times 10^{-3} \text{ M}$, so the approximate answer $1.342 \times 10^{-3} \text{ M}$ only differs from the exact answer by 0.009×10^{-3} , an "error" of less than 1%.

General Guideline:

- This **assumption**; a 'negligible' amount of the acid being ionized - is acceptable if $x \leq 5\%$ of the initial concentration of acid.....
- This will generally be the case if the concentration of the acid, c , divided by the K_a value is > 100 .

EXAMPLE: $[\text{CH}_3\text{COOH}] = 0.10 \text{ M}$; $K_a = 1.8 \times 10^{-5}$

Test the assumption that $c - x \approx c$:

$\frac{c}{K_a}$ must be greater than 100

$$\Rightarrow \frac{0.10}{1.8 \times 10^{-5}} = 5555 \quad \therefore \text{"assumption" is valid}$$

- The quantity $[x / c] \times 100$ is called the degree of dissociation, expressed on a % basis; may also be called **percent dissociation** or **ionization**.

$$\text{Percent dissociation} = \frac{\text{Amount dissociated}}{\text{Original amount}} \times 100\%$$

$$\text{(ionization)} = \frac{x}{c} \times 100$$

$$\text{From example: } \% \text{ ionization} = \frac{1.34 \times 10^{-3}}{0.10} \times 100 = \underline{\underline{1.34\%}}$$

- We can also use x to calculate pH; because in a weak acid equilibrium; $x = [H^+]$

$$[H^+] = 1.34 \times 10^{-3} \text{ M, therefore pH} = 2.87$$

- The degree of dissociation **increases** as the solution is diluted, **although** $[H^+]$ **decreases**.

EXAMPLE: For solutions of HF in water:

$$K_a \text{ for HF} = 6.7 \times 10^{-4}$$

<u>Initial [HF]</u>	<u>Equil. [H⁺]</u>	<u>% Dissoc.</u>	<u>pH</u>
1.0	2.6×10^{-2}	2.6	1.59
0.1	7.9×10^{-3}	7.9	2.10
0.01	2.3×10^{-3}	22	2.64
	decreasing	increasing	increasing

- What if we need to do the exact calculation?

- We have to solve the quadratic:

$$ax^2 + bx + c = 0$$

$$x^2 + K_a x - K_a C = 0$$

(from expansion of $K_a = x^2 / (C - x)$)

$$1.8 \times 10^{-5} = \frac{x^2}{0.100 - x}$$

$$x^2 + 1.8 \times 10^{-5} x - 1.8 \times 10^{-6} = 0$$

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

$$x = 1.333 \times 10^{-3}$$

- What else can we calculate using K_a ??

- The K_a expression says: $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- Depending on the information given, we could also calculate the initial concentration of the weak acid or the actual value of K_a

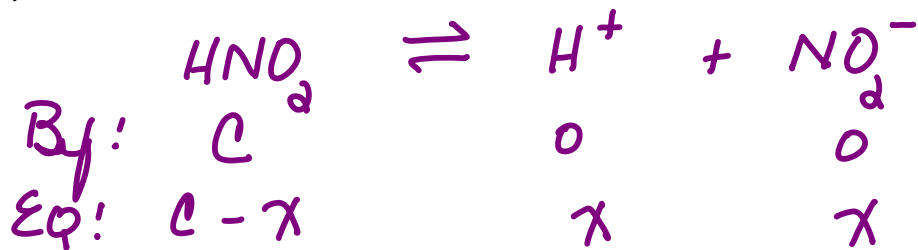
Strategy

- Always write the reaction for the weak acid given in the question.
- Write the equilibrium constant expression for the reaction.
- Identify what you know and what you are asked to find.
- Usually, it's a fairly straightforward matter of substituting for the appropriate variables in the Equilibrium Constant Expression.
- Sometimes there are a few intermediate calculations to perform....

EXAMPLE 1:

Nitrous acid, HNO_2 has a K_a value of 6.0×10^{-4} .

Calculate the initial concentration of HNO_2 if a solution of this acid has a pH of 3.65. "c"



$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = \frac{x^2}{c - x}$$

$$\begin{aligned} \text{pH} = 3.65 &= [\text{H}^+] = 10^{-3.65} \\ &= 2.238 \times 10^{-4} \\ &= \underline{x} \end{aligned}$$

Substitute:

$$6.0 \times 10^{-4} = \frac{(2.238 \times 10^{-4})^2}{c - 2.238 \times 10^{-4}} \quad *$$

Don't neglect x when known

$$c - 2.238 \times 10^{-4} = \frac{(2.238 \times 10^{-4})^2}{6.0 \times 10^{-4}}$$

$$\therefore c = \frac{(2.238 \times 10^{-4})^2}{6.0 \times 10^{-4}} + 2.238 \times 10^{-4} = \underline{\underline{3.1 \times 10^{-4} \text{ M}}}$$

EXAMPLE 2:

→ "c"

acidic H

A 0.025 M solution of formic acid, HCOOH , has a pH of 2.75.

a) Calculate the % ionization of this solution.

b) Calculate the K_a for formic acid.



By: 0.025 0 0

Eq: $0.025 - x$ x x

$\text{pH} = 2.75 \Rightarrow [\text{H}^+] = 10^{-2.75}$
 $= 1.78 \times 10^{-3} \text{ mol/L}^{-1}$

$= x$

a) % Ionization = $\frac{x}{c} \times 100$

$= \frac{1.78 \times 10^{-3}}{0.025} \times 100$

$= 7.12\%$

b) $K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{c - x}$

* Don't neglect x when known

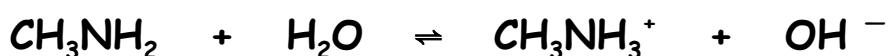
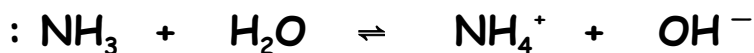
$= \frac{(1.78 \times 10^{-3})^2}{0.025 - 1.78 \times 10^{-3}}$

$= 1.36 \times 10^{-4}$

Calculations Involving Weak Bases

- The most commonly used weak bases are Ammonia (NH_3) and its derivatives.
- In these compounds one (or more) N atom has a pair of electrons not used (yet!) for bonding (a "lone pair").

EXAMPLES:



- We may write K_b expressions for both of these.....

$$K_b(\text{NH}_3) = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

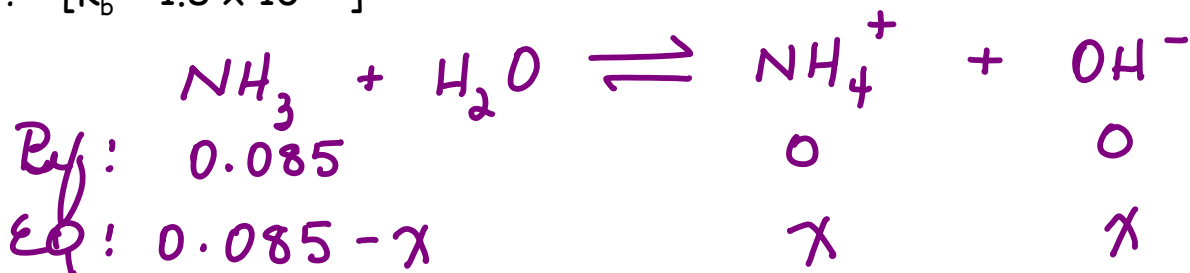
$$K_b(\text{CH}_3\text{NH}_2) = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

- Problems using K_b are treated in the same manner as problems using K_a (weak acid).

EXAMPLE 1:

→ "c"

What is the % ionization and pH of a solution of a 0.085 M solution of NH_3 ? [$K_b = 1.8 \times 10^{-5}$]



$$K_b = \frac{x^2}{0.085 - x}$$

check: c/K_b
 $\Rightarrow \frac{0.085}{1.8 \times 10^{-5}} = 4722$
 \therefore OK to neglect x

$$1.8 \times 10^{-5} = \frac{x^2}{0.085}$$

$$\begin{aligned} x &= \sqrt{1.8 \times 10^{-5} \times 0.085} \\ &= 1.24 \times 10^{-3} = \underline{[\text{OH}^-]} \end{aligned}$$

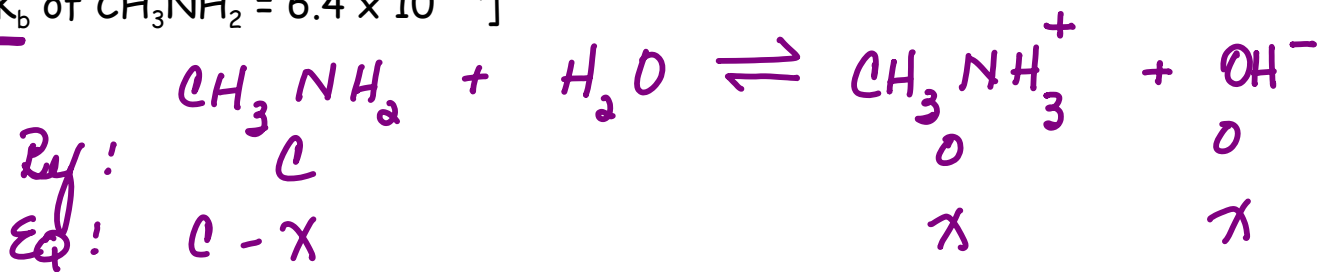
$$\therefore \underline{\text{pOH}} = 2.91 \quad \Rightarrow \quad \text{pH} = 14 - 2.91 = \underline{11.09}$$

$$\begin{aligned} \% \text{ ionization} &= \frac{x}{c} \times 100 \\ &= \frac{1.24 \times 10^{-3}}{0.085} \times 100 \\ &= \underline{1.46\%} \end{aligned}$$

EXAMPLE 2:

A solution of methylamine, CH_3NH_2 , has a pH of 10.45. Calculate the initial concentration of methylamine in this solution.

$[K_b \text{ of } \text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}]$



$\text{pH} = \underline{10.45}$ $\text{pH} > 7$ \therefore Basic Soln

$$\begin{aligned} \therefore \text{pOH} = 3.55 &\Rightarrow [\text{OH}^-] = 10^{-3.55} \\ &= 2.82 \times 10^{-4} \text{ M} \\ &= x \end{aligned}$$

$$K_b = \frac{x^2}{c - x}$$

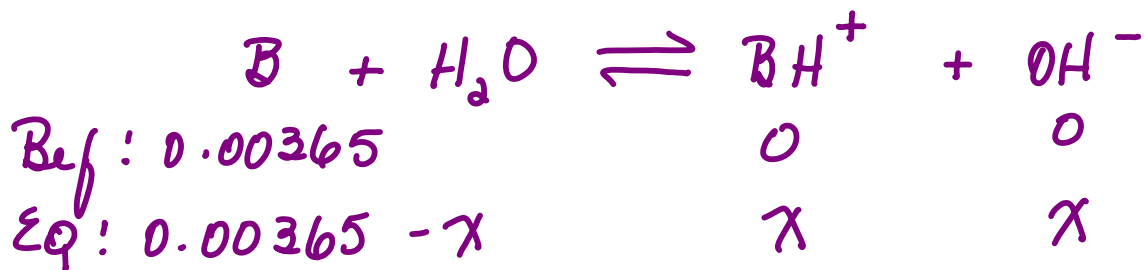
$$6.4 \times 10^{-4} = \frac{(2.82 \times 10^{-4})^2}{c - 2.82 \times 10^{-4}}$$

$$c = \underline{4.06 \times 10^{-4} \text{ mol L}^{-1}}$$

EXAMPLE 3:

→ "C"

Calculate the K_b for the weak base B, if a 0.00365 M solution of that base is 8.50 % ionized.



$$\% \text{ ionization} = \frac{x}{c} \times 100$$

$$\Rightarrow \frac{x}{0.00365} \times 100 = 8.50\%$$

$$\frac{x}{0.00365} = 0.0850$$

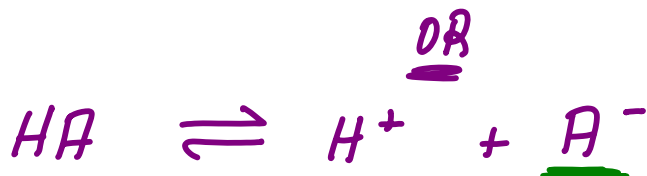
$$\therefore x = 3.102 \times 10^{-4} = [OH^-]$$

$$K_b = \frac{x^2}{c - x} = \frac{(3.102 \times 10^{-4})^2}{0.00365 - 3.102 \times 10^{-4}}$$

$$= \underline{\underline{2.88 \times 10^{-5}}}$$

Reactions of Conjugate Species

- Every weak acid (HA), will produce its **conjugate base** (A^-) when it ionizes in water.



- The conjugate base of any acid is the species that is obtained from the acid by removal of one H^+ (or proton).



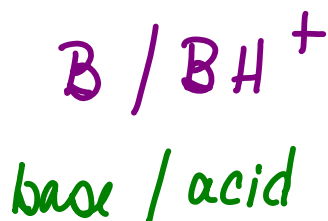
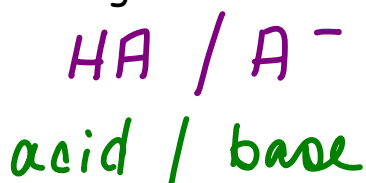
- Every weak base (B), will produce its **conjugate acid** (BH^+) when it ionizes in water.



- Similarly, the conjugate acid of any base is the species that is obtained from the base by addition of a proton (or H^+).

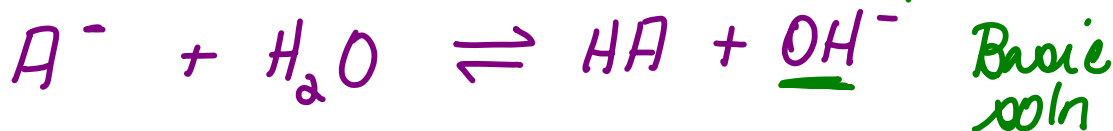


- It is essential to realize that in any conjugate acid/base pair, the acid always has one more H than the base !
- You must be able to recognize conjugate bases and acids, based on the original weak acid or base !

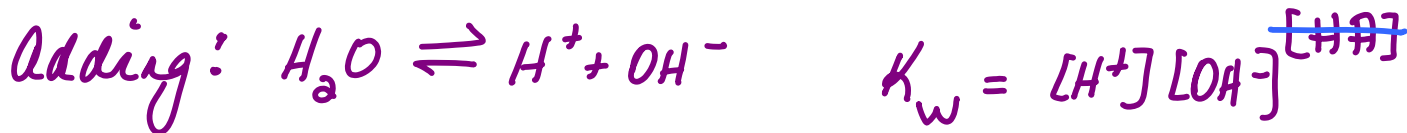
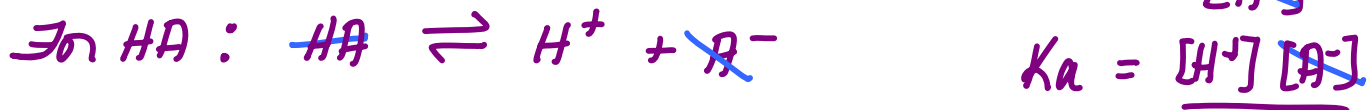
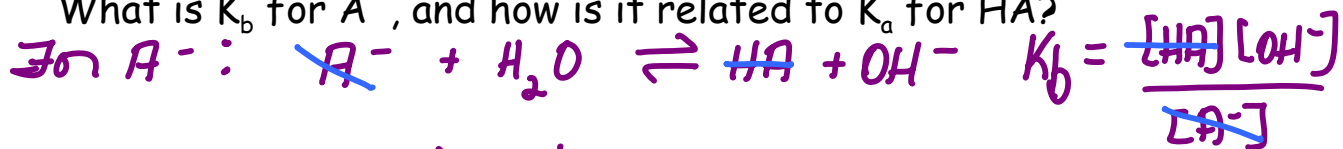


EXAMPLES:

- Consider the weak acid HNO_2 ; its conjugate base is NO_2^- .
- Now look at the weak base NH_3 ; its conjugate acid is NH_4^+ .
- $\text{HNO}_2 / \text{NO}_2^-$ and $\text{NH}_3 / \text{NH}_4^+$ are **conjugate acid-conjugate base pairs** [differing by one H^+]
- How do these conjugate species behave ?
- What happens if you react them with water ?
- Consider the generic weak acid, **HA**; its conjugate base is A^- .
- This species will act as a base: *Base take H^+ from H_2O*



- This reaction is often called **hydrolysis**.
- What is K_b for A^- , and how is it related to K_a for HA?



- Or...to get the same result, we could add the equations, and then (as we have seen earlier in these notes; p. 137) their K 's are multiplied:

$$K_w = K_a \times K_b \quad \text{- for ANY conj acid/base pr.}$$

$$K_b (\text{A}^-) = \frac{K_w}{K_a (\text{HA})}$$

- The relationship $K_a \times K_b = K_w$ is always true for a conjugate acid-base pair.
- The **weaker** the acid, the more **basic** is its conjugate base.

We can also use the log scale.....

$$pK_a + pK_b = pK_w = 14.0$$

EXAMPLE 1:

HF, a weak acid: $K_a = 7.24 \times 10^{-4}$; $pK_a = 3.14$

F^- , (conjugate base of HF)

$$pK_b = 14.00 - 3.14$$

$$= 10.86$$

$$K_b = 1.38 \times 10^{-11}$$

VERY weak base

EXAMPLE 2:

CH_3COOH , a weak acid: $K_a = 1.8 \times 10^{-5}$; $pK_a = 4.74$

CH_3COO^- , (conjugate base of CH_3COOH)

$$pK_b = 14.00 - 4.74$$

$$= 9.26$$

$$K_b = 5.56 \times 10^{-10}$$

$$\underline{OR} \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$$

EXAMPLE 3:

HCN , a very weak acid: $K_a = 4.00 \times 10^{-10}$; $pK_a = 9.40$

CN^- , (conjugate base of HCN)

$$pK_b = 14.00 - 9.40$$

$$= 4.60$$

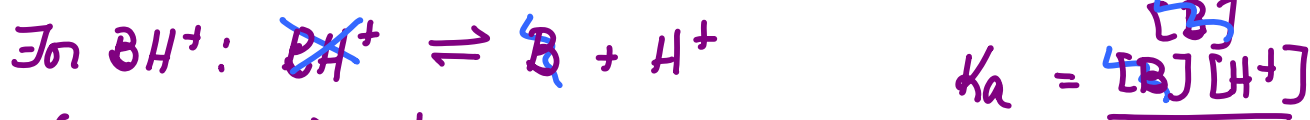
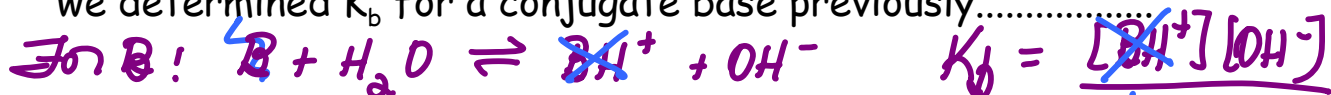
$$K_b = 2.5 \times 10^{-5}$$

- a stronger weak base

- Now look at the generic weak base **B**, whose conjugate acid is **BH⁺**.
- **BH⁺** will act like an acid.....



- We also call this a hydrolysis reaction.
- We can determine K_a for this conjugate acid in the same manner as we determined K_b for a conjugate base previously.....



$$K_b \times K_a = K_w$$

- As was the case with the weak acids, the **weaker** the base, the more **acidic** is its conjugate acid.

EXAMPLE 1:

NH_3 is a weak base; $K_b = 1.8 \times 10^{-5}$; $pK_b = 4.74$

NH_4^+ (conjugate acid of NH_3); $pK_a = 14.00 - 4.74 = 9.26$

$K_a(NH_4^+) = 5.56 \times 10^{-10}$

VERY weak acid.

EXAMPLE 2:

Aniline, $C_6H_5NH_2$, is a very weak base; $K_b = 4.0 \times 10^{-10}$; $pK_b = 9.40$

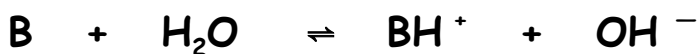
$C_6H_5NH_3^+$ (conjugate acid of $C_6H_5NH_2$); $pK_a =$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$$

- stronger weak acid

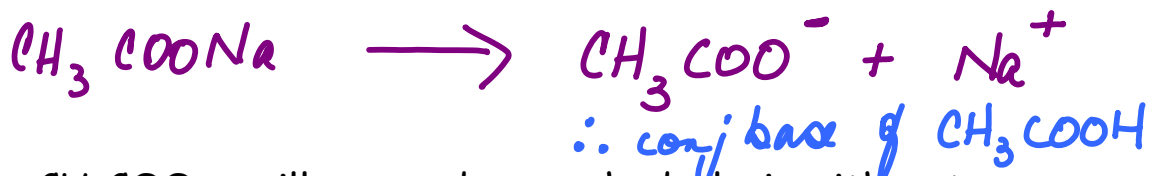
Salts

- You may have noticed that the conjugate base of a weak acid, or the conjugate acid of a weak base is always an ion.
- So where does this ion come from?
- It is always produced when the "parent" weak acid or base ionizes, but these conjugate species can also be found in ionic compounds.
- And ions are formed when an ionic solid is dissolved in water.....
- Remember those solubility rules ????
- This is where they come in handy; so you will know whether or not a solid will dissolve in water to produce ions!!
- First we consider salts that yield the conjugate base of a weak acid.
- Recall that the conjugate base will always behave like a base when in aqueous solution:

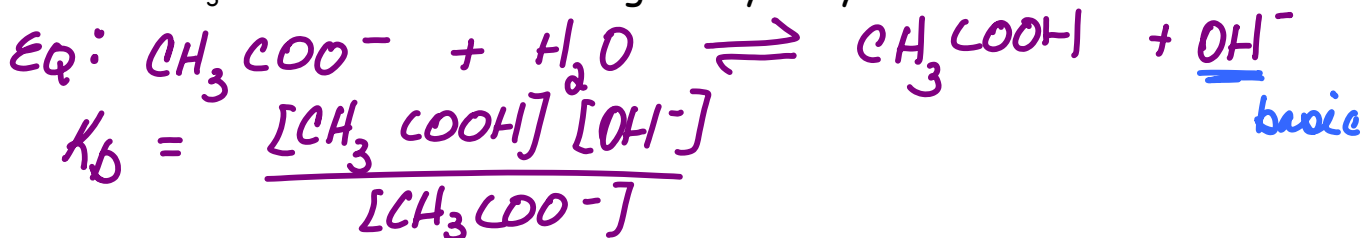


EXAMPLE 1: $(K_a \text{ for } CH_3COOH = 1.8 \times 10^{-5})$

Consider the salt CH_3COONa . In water.....



- The CH_3COO^- will now undergoes hydrolysis with water.....



- The ion that is the **conjugate species** of a weak acid or base is the species that will undergo the **hydrolysis** with water.
- Remember that a conjugate species differs from its "parent" species by only one H^+ !!

EXAMPLE 2:

Calculate the pH and % hydrolysis (% base ionization) in 0.100 M KF.
[K_a for HF = 7.24×10^{-4}]

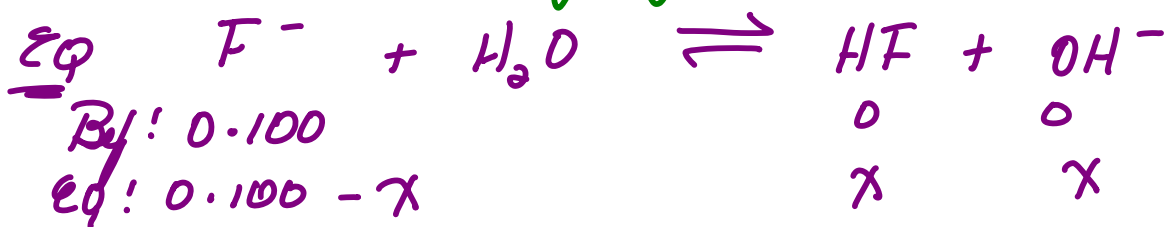


- look at F^- ; one less H than HF

$\therefore F^-$ is a conjugate of HF

- HF is a weak acid (because we know K_a)

$\therefore F^-$ is the conjugate base of HF



$$K_b(F^-) = \frac{K_w}{K_a(HF)} = \frac{1.0 \times 10^{-14}}{7.24 \times 10^{-4}} = 1.38 \times 10^{-11}$$

$$K_b = \frac{[HF][OH^-]}{[F^-]} = \frac{x^2}{0.100 - x} \quad \text{- neglect } x$$

$$\therefore 1.38 \times 10^{-11} = \frac{x^2}{0.100} \Rightarrow x = \sqrt{1.38 \times 10^{-11} \times 0.100} = 1.17 \times 10^{-6} = [OH^-]$$

$$pOH = 5.93 \Rightarrow pH = 14 - 5.93 = \underline{\underline{8.07}}$$

$$\begin{aligned} \% \text{ Ionization} &= \frac{x}{c} \times 100 = \frac{1.17 \times 10^{-6}}{0.100} \times 100 \\ &= \underline{\underline{1.17 \times 10^{-3} \%}} \end{aligned}$$

EXAMPLE 2:

A 0.0285M solution of the sodium salt, NaA of the weak monoprotic acid, HA, has a pH of 9.65. Calculate K_a for the acid, HA.

$$\text{pH} = 9.65 \quad \therefore \text{basic} \Rightarrow \text{pOH} = 4.35$$

$$[\text{OH}^-] = 10^{-4.35} = 4.47 \times 10^{-5} = x$$



If HA is a weak acid, then A^- must be conj base



$$\text{By: } 0.0285$$

$$\text{EQ: } 0.0285 - x$$

$$0$$

$$x$$

$$0$$

$$x$$

$$K_b (\text{for } \text{A}^-) = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{x^2}{0.0285 - x}$$

$$= \frac{(4.47 \times 10^{-5})^2}{0.0285 - 4.47 \times 10^{-5}}$$

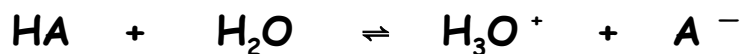
$$= \frac{7.00 \times 10^{-8}}{0.0285 - 4.47 \times 10^{-5}}$$

$$= \underline{7.00 \times 10^{-8}}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{7.00 \times 10^{-8}}$$

$$K_a (\text{for HA}) = \underline{\underline{1.43 \times 10^{-7}}}$$

- Salts that produce the conjugate acids of weak bases will exhibit **acidic** behaviour in solution.....

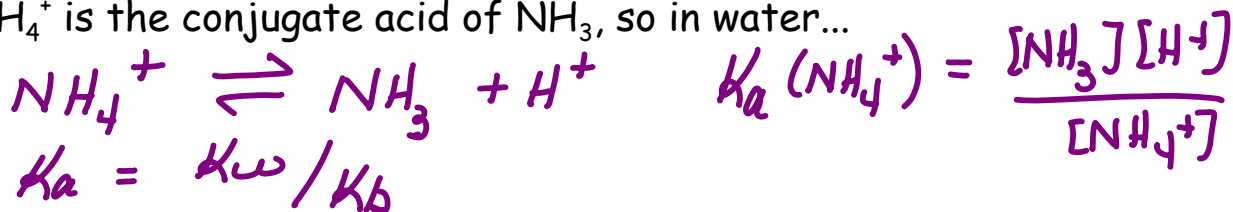


EXAMPLE 1: (K_b for $NH_3 = 1.8 \times 10^{-5}$)

The salt in question is NH_4Cl . In water:



The NH_4^+ is the conjugate acid of NH_3 , so in water...



EXAMPLE 2: Calculate the pH of a solution of 0.175 M NH_4NO_3 .



Ref:	0.175	0	0
Eq:	$0.175 - x$	x	x

$$K_a(\text{for } NH_4^+) = \frac{K_w}{K_b(\text{for } NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

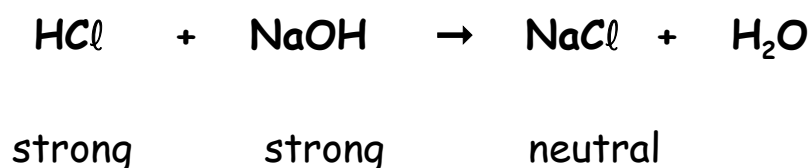
$$K_a = \frac{x^2}{0.175 - x} \Rightarrow 5.56 \times 10^{-10} = \frac{x^2}{0.175 - x}$$

$$x = \sqrt{5.56 \times 10^{-10} \times 0.175} = 9.86 \times 10^{-6} = [H^+]$$

$$\therefore pH = \underline{\underline{5.00}}$$

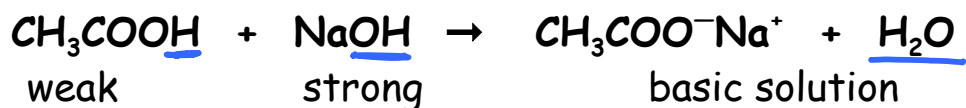
Equivalence Point of a Titration

- This is the point where the stoichiometric quantities of acid and base, defined by the equation, have been mixed.
- It is **really** important to note that the solution is **NOT always** neutral (i.e. pH = 7) at the equivalence point !!
- This is why, earlier, we used the term **equivalence point** rather than neutralization point.
- The pH at the equivalence point is only truly neutral (pH = 7) for a titration of a **strong** acid with a **strong** base.

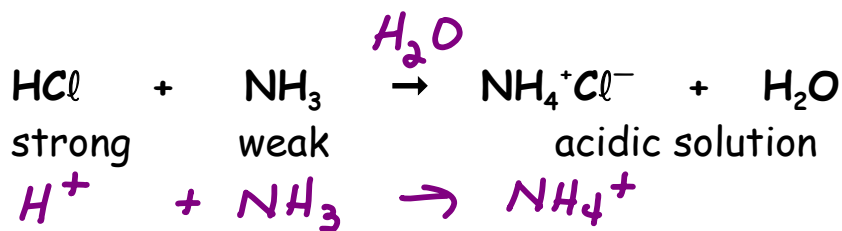


- So **why** is the solution of NaCl neutral?
- Because neither $\text{Na}^+(\text{aq})$ nor Cl^- is the conjugate of a weak species (base or acid).....
- If both ions which form the salt (NaCl in this case) originally came from strong species, they may be termed **spectator ions** and the solution will be neutral.

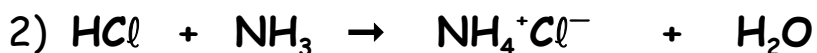
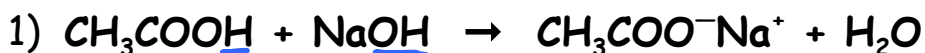
In contrast:



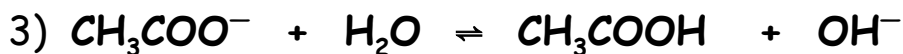
- The salt formed in the reaction is $\text{CH}_3\text{COO}^- \text{Na}^+$.
- The CH_3COO^- is a base ; the conjugate base of the weak acid CH_3COOH .
- That means that this solution will be basic.



- The salt formed in this reaction is NH_4^+Cl^- .
- The NH_4^+ is an acid; the conjugate acid of the weak base NH_3 .
- So this solution will be acidic.
- There is one other possible combination; that of a weak acid + a weak base: acidic or basic at equivalence depending upon the relative strengths of the acid and base involved..... Ignore!
- What is **really** happening at the equivalence point in titrations of a weak species with a strong species ?



- Because one of the species involved in the titration - CH_3COOH in (1) and NH_3 in (2) - is a **weak** species, the reactions are not quite complete (because the weak species never completely ionize.)
- They are, however, close enough to complete that we can assume that the salt is by far the major species at equilibrium.
- So... as a first approximation, we start our calculation by assuming complete reaction to the salt. [As shown by equations 1) & 2).]
- To correct this not-quite-true first approximation, we correct it by allowing a back reaction; this is hydrolysis of water by the salt.



- These hydrolysis reactions are actually the **ionic** equations corresponding to the reverse of (1) and (2) !!

- How do we put all this information together to solve an equivalence point problem ?
- The steps are:

1) Write an equation for the acid base **reaction**. (Similar to equations 1) or 2) on the previous page.)

2) Determine the number of moles of the acid and base.....recall that at the equivalence point, these will be equal.

3) Determine the number of moles of salt formed (equal to the number of moles of acid or base).

4) Determine the total volume of the solution, and the Molarity of the salt solution.

5) Now write an equation for the hydrolysis reaction by the salt. (Similar to equations 3) and 4) on the previous page.)

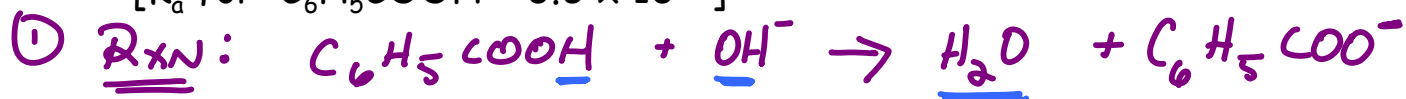
6) Using K_w , calculate K_a or K_b for the salt.

7) Now calculate the concentration of either the H_3O^+ or the OH^- formed as a result of hydrolysis.

8) Finally, calculate the pH.

EXAMPLE 1:

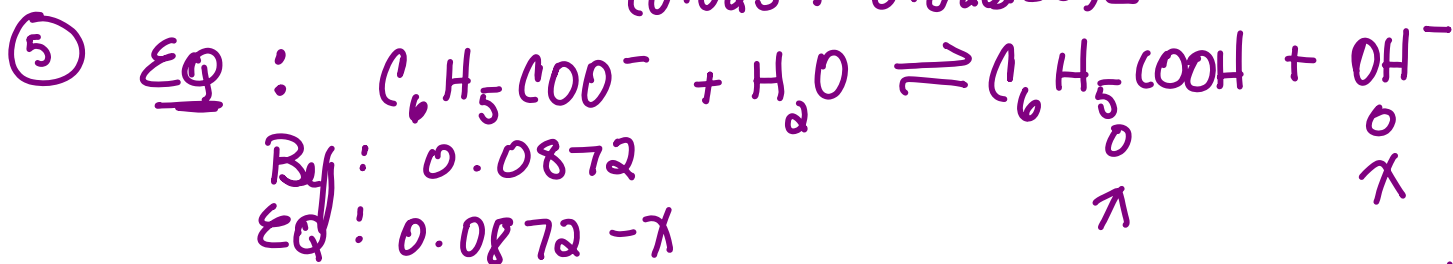
Calculate the pH at the equivalence point of the titration of 25.00 mL of 0.165 M benzoic acid, C_6H_5COOH , with 0.185 M KOH. $KOH \rightarrow K^+ + OH^-$
[K_a for $C_6H_5COOH = 6.6 \times 10^{-5}$]



② mol $C_6H_5COOH = 0.165 M \times 0.025 L = 0.004125 \text{ mol}$
 $= \text{mol } H^+ \text{ reacted} = \text{mol } OH^- \text{ used}$
 $= \text{mol } C_6H_5COO^- \text{ formed}$ ③

④ Vol KOH = $\frac{0.004125 \text{ mol}}{0.185 M} = 0.02230 L$

$$[C_6H_5COO^-] = \frac{0.004125 \text{ mol}}{(0.025 + 0.02230) L} = 0.0872 M$$



⑥ $K_b(\text{for } C_6H_5COO^-) = \frac{K_w}{K_a(\text{for } C_6H_5COOH)} = \frac{1.0 \times 10^{-14}}{6.6 \times 10^{-5}}$
 $= 1.51 \times 10^{-10}$

⑦ $K_b = \frac{\lambda^2}{0.0872 - \lambda} \Rightarrow 1.51 \times 10^{-10} = \frac{\lambda^2}{0.0872}$

$$\lambda = \sqrt{1.51 \times 10^{-10} \times 0.0872} = 3.63 \times 10^{-6}$$

$= [OH^-]$

⑧ pOH = 5.44 pH = 8.56

EXAMPLE 2:

Calculate the pH at the equivalence point of the titration of 0.175 M methylamine, CH_3NH_2 , with 0.250 M HNO_3 . \rightarrow *wt acid*

$[K_b \text{ for } \underline{\text{CH}_3\text{NH}_2} = 6.4 \times 10^{-4}]$ *wk base*

* Pick a volume for ONE species; calculate the volume of the other.

* Assume 50.0 mL of CH_3NH_2
 $\therefore \text{mol } \text{CH}_3\text{NH}_2 = 0.175 \text{ M} \times 0.050 \text{ L} = 0.00875 \text{ mol}$

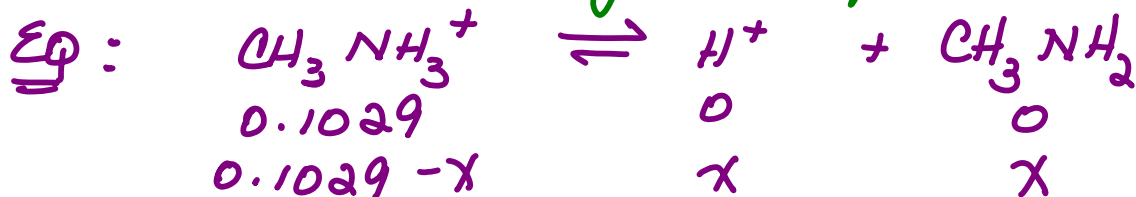
At Eq Pt: $\text{mol } \text{CH}_3\text{NH}_2 = \text{mol } \text{H}^+ = 0.00875 \text{ mol}$

$$\text{Vol } \text{HNO}_3 = \frac{0.00875 \text{ mol}}{0.250 \text{ M}} = 0.035 \text{ L}$$



$$[\text{CH}_3\text{NH}_3^+] = \frac{0.00875 \text{ mol}}{(0.05 + 0.035) \text{ L}} = 0.1029 \text{ M}$$

CH_3NH_3^+ is the conj acid of CH_3NH_2



$$K_a(\text{CH}_3\text{NH}_3^+) = \frac{K_w}{K_b(\text{CH}_3\text{NH}_2)} = \frac{1.0 \times 10^{-14}}{6.4 \times 10^{-4}} = 1.56 \times 10^{-11}$$

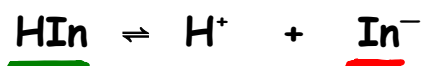
$$1.56 \times 10^{-11} = \frac{x^2}{0.1029 - x}$$

$$x = \sqrt{1.56 \times 10^{-11} \times 0.1029} = 1.266 \times 10^{-6} = [\text{H}^+]$$

$$\therefore \text{pH} = \underline{\underline{5.90}}$$

Acid Base Indicators [MH5; 14.2]

- Indicators are used to detect the equivalence point of a titration.
- An indicator is a weak organic acid that has the particular property of being a noticeably different colour from its conjugate base.
- The indicator used must change colour at a pH that closely matches the pH expected at the equivalence point of the titration
- Over the small pH range where the acid changes over to the conjugate base, we see a change of colour.....



$$K_{\text{In}} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

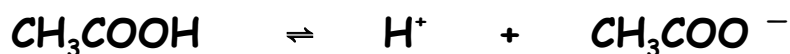
- At the **end-point**, the indicator is changing colour; this is when $[\text{In}^-] = [\text{HIn}]$
- At this point, K_a (aka K_{HIn}) = $[\text{H}^+]$ and $\text{p}K_a$ (aka $\text{p}K_{\text{HIn}}$) = pH
- Note: This is the $\text{p}K_a$ value of the **indicator**, not that of the acid being titrated!
 $\text{p}K_a(\text{indicator}) = \text{pH at colour change.}$
- At 1 pH unit below this $\text{p}K_a$ value (acidic) the indicator is 90% in the HIn form.
- At 1 pH unit above this $\text{p}K_a$ value (basic) the indicator is 90% in the In^- form.
- The approximate range for colour change: 2 pH units.

Selection of Indicator

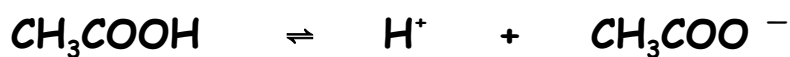
- The indicator must change colour near the equivalence point.
- For a strong acid/strong base titration: the $\text{p}K_a$ of the indicator should be 5 - 9, although in practice the pH changes so rapidly at the end-point that **any** indicator is suitable.
- For a weak acid/strong base titration: the $\text{p}K_a$ of the indicator must be in the basic region, for example: phenolphthalein, $\text{p}K_a \approx 9$
- For a strong acid/weak base titration: the $\text{p}K_a$ of the indicator must be in the acidic region, for example: methyl orange, $\text{p}K_a \approx 3.4$

The Common Ion Effect

- Recall that the **common ion effect** refers to a system at equilibrium which has present an ion that is present as a result of that equilibrium, but is also present from some other source.
- Consider a solution of Acetic Acid, CH_3COOH ($K_a = 1.8 \times 10^{-5}$)



- When we place the acid in water, equilibrium is established very rapidly ($\approx 10^{-(8-10)}$ seconds).....
- What happens (non-quantitatively) to the percent dissociation of the acetic acid (CH_3COOH) if.....
- A strong acid is added to the same solution (so H^+ is the added "common ion")?
- Or, equivalently, the CH_3COOH ionizes into a solution of a strong acid, instead of into water? (For acid-base reactions in water, the order of addition is unimportant.)



2 sources of H^+ :

- 1) from ionization of CH_3COOH
- 2) from the strong acid (eg; HCl)

Le Chatelier: - equilibrium shifts away from the H^+

\therefore less CH_3COOH ionizes

- How do we treat such problems quantitatively?

EXAMPLE 1:

→ wk acid

→ st. acid

A solution is 0.20 M in CH_3COOH ($K_a = 1.8 \times 10^{-5}$) and 0.050 M in HCl .

What the % ionization of the CH_3COOH ? What is the pH of this solution?

$$[\text{H}^+]_{\text{HCl}} = \underline{0.050 \text{ M}}$$

- get H^+ from ionization of CH_3COOH

∴ 2 sources of H^+



Ref: 0.20 0.050 0

Eq: 0.20 - x $x + 0.050$ x

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x + 0.050)(x)}{(0.20 - x)}$$

- we know that " x " (amt ionized) is small
- in presence of a common ion, x is even smaller

$$\Rightarrow 1.8 \times 10^{-5} = \frac{(0.050)(x)}{(0.20)}$$

$$x = 7.2 \times 10^{-5} = [\text{CH}_3\text{COO}^-]$$

$$\% \text{ ionization} = \frac{x}{c} \times 100 = \frac{7.2 \times 10^{-5}}{0.20} \times 100$$

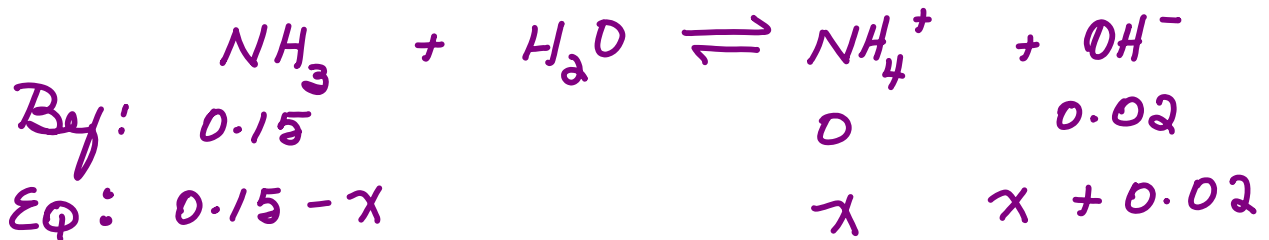
pH? $[\text{H}^+] = 0.05 + x$
 $\approx 0.05 \text{ M}$ 0.036 %

pH = 1.30

- A similar situation arises if a weak base dissociates into a solution of a strong base (or, equivalently, a strong base is added to a solution of a weak base).

EXAMPLE 2: \rightarrow str base ; $[OH^-] = 0.020 M$
 \rightarrow wk base

In a solution $[NaOH] = 0.020 M$ and $[NH_3] = 0.15 M$. ($K_b = 1.8 \times 10^{-5}$)
 What is the % ionization of the NH_3 ? What is the pH of this solution?



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} = \frac{(x)(x + 0.02)}{(0.15 - x)}$$

$$\therefore x = 1.35 \times 10^{-4} = [NH_4^+]$$

$$\% \text{ ionization} = \frac{x}{c} \times 100 = \frac{1.35 \times 10^{-4}}{0.15} \times 100 = \underline{\underline{0.09 \%}}$$

pH? Basic soln so use pOH!

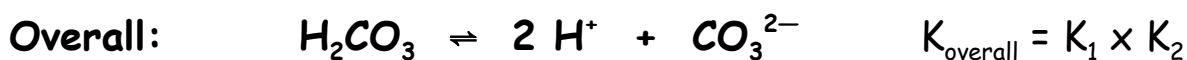
$$[OH^-] = 0.02 + 1.35 \times 10^{-4} = 2.014 \times 10^{-2} M$$

$$pOH = 1.7 \quad \therefore pH = \underline{\underline{12.30}}$$

Polyprotic Acids [MH5;13.4, page 364]

- Polyprotic acids are those which have more than one "acidic" hydrogen.
- This means that they dissociate (or ionize) in stages, with K_a values for each step.

EXAMPLE: Carbonic acid is H_2CO_3



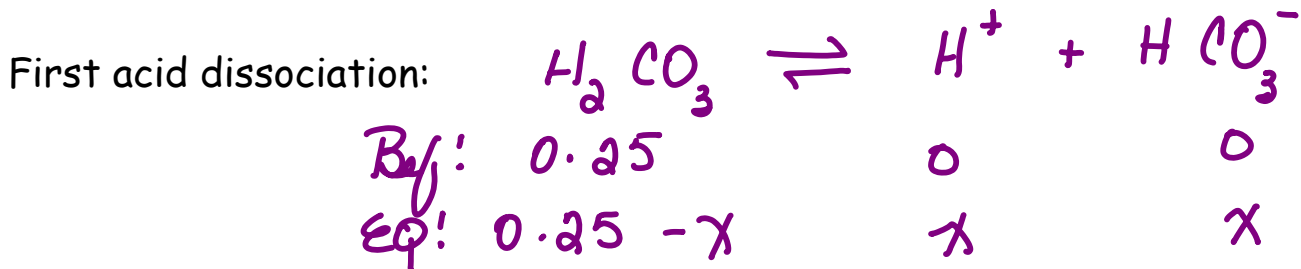
- These equilibria are typical of polyprotic acids; $K_1 \gg K_2$.
- As a result: \approx all the $[H^+]$ is due to the first acid ionization.....
- These dissociations also illustrate **simultaneous equilibria** in the acid dissociation of a polyprotic acid; both are happening at the same time.
- So both bicarbonate anion, HCO_3^- , **and** carbonate anion, CO_3^{2-} , are present in the equilibrium mixture in solution.

EXAMPLE:

Consider the acid dissociation of 0.25 M H_2CO_3 .

What are the concentrations of all species in the equilibrium mixture, the % dissociation in each stage, and the pH?

[$K_1 = 4.2 \times 10^{-7}$, $K_2 = 4.8 \times 10^{-11}$]



$$K_1 = 4.2 \times 10^{-7} = \frac{x^2}{0.25 - x}$$

$$x = \sqrt{4.2 \times 10^{-7} \times 0.25}$$

$$= 3.24 \times 10^{-4}$$

$$= [\text{H}^+] = [\text{HCO}_3^-]$$

$$\% \text{ dissociation} = \frac{x}{c} \times 100 = \frac{3.24 \times 10^{-4}}{0.25} \times 100$$

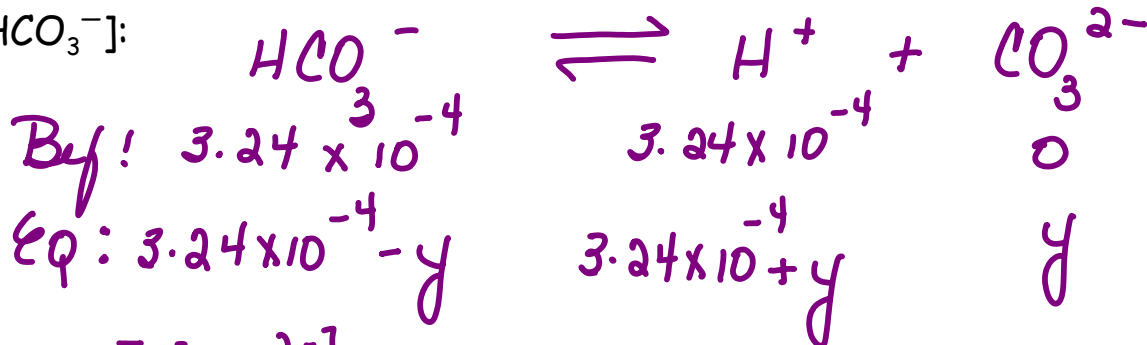
$$= \underline{\underline{0.13\%}}$$

$$\text{pH} = -\log (3.24 \times 10^{-4})$$

$$= \underline{\underline{3.49}}$$

Second acid dissociation:

Because $K_2 \ll K_1$, the second acid dissociation does not affect either $[H^+]$ or $[HCO_3^-]$:



$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

$$4.8 \times 10^{-11} = \frac{(\cancel{3.24 \times 10^{-4}} - y)(y)}{(\cancel{3.24 \times 10^{-4}} - y)}$$

$$\therefore y = 4.8 \times 10^{-11} = [CO_3^{2-}]$$

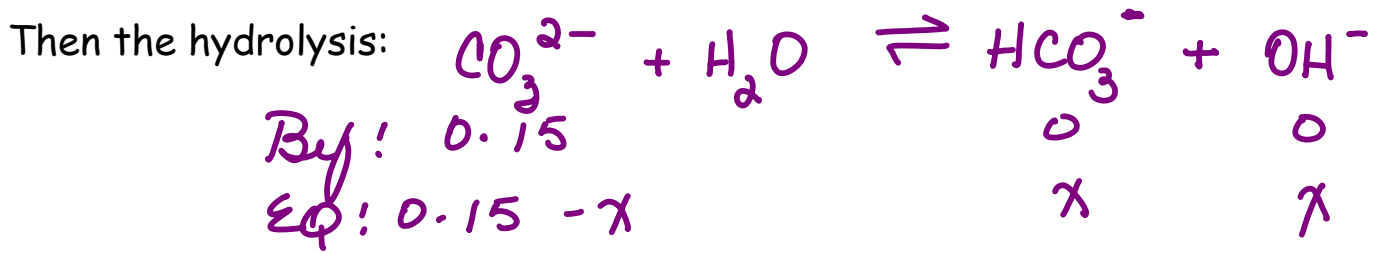
$$\begin{aligned}
 \text{pH? } [H^+] &= 3.24 \times 10^{-4} + 4.8 \times 10^{-11} \\
 &= 3.24 \times 10^{-4}
 \end{aligned}$$

$$\text{pH} = \underline{\underline{3.49}}$$

General Result: for a diprotic acid H_2A in water; $[A^{2-}] = K_2$

- Since K_2 is very small (4.8×10^{-11}), CO_3^{2-} is quite a strong base
- $K_b = 2.08 \times 10^{-4}$ (from $K_a \times K_b = K_w$).

EXAMPLE: What is the pH of 0.150 M Na_2CO_3 solution?



$$K_b (\text{for } \text{CO}_3^{2-}) = 2.08 \times 10^{-4} = \frac{x^2}{0.15 - x}$$

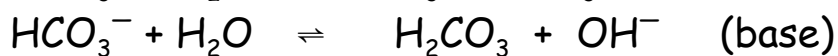
$$x = \sqrt{2.08 \times 10^{-4} \times 0.15}$$
$$= 5.58 \times 10^{-3} = [\text{OH}^-]$$

$$\text{pOH} = 2.25$$

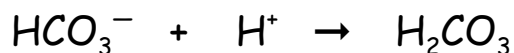
$$\text{pH} = 14 - 2.25$$
$$= \underline{11.75}$$

- Further reaction of HCO_3^- with H_2O is negligible;
 $K_b(\text{HCO}_3^-) = 2.38 \times 10^{-8} \ll K_b(\text{CO}_3^{2-}) = 2.08 \times 10^{-4}$

Note that HCO_3^- may act as either an acid or a base:



OR: If acid or base is added to HCO_3^-



BUFFER SOLUTIONS

- So far, we have looked at the behaviour of weak acids and bases in solution, as well as the behaviour of their conjugate species.
- But initially, we have had **only** the weak acid or base or **only** the conjugate species present (in water, of course!)
- What happens if we put a weak acid and its conjugate base in the **same** solution (or, a weak base and its conjugate acid) ?
- This type of solution is the one which call a **Buffer Solution**; probably named as such because these solutions tend to resist changes in pH even when small amounts of strong acid or base are added to them.
- **A Buffer Solution contains a weak acid and its conjugate base (or a weak base and its conjugate acid) in roughly equal amounts.**
- within a factor of 10
- A buffer solution can always be treated as a weak acid or base equilibrium, with the conjugate species behaving as a "common ion" (see p. 189 - 191).
- As there are several ways to combine solutions to produce a buffer solution, the trickiest part of dealing with buffer solutions is recognizing that a solution is, in fact, a buffer solution.
- Once recognized, the equilibrium can be set up and the calculation completed.....
- Let's start with looking at buffers which contain a weak acid and its conjugate base.
- The first examples are straightforward; a weak acid and its conjugate base (in the form of a salt) are mixed together in one solution.

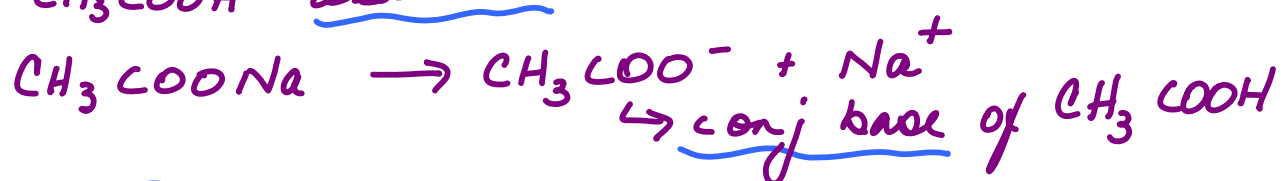
Calculation Involving Buffer Solutions [MH5; 14.1]

EXAMPLE 1:

A solution contains 0.20 mol acetic acid, CH_3COOH , and 0.10 mol of sodium acetate, CH_3COONa , made up to 1.0 L volume. Calculate the pH of the solution.

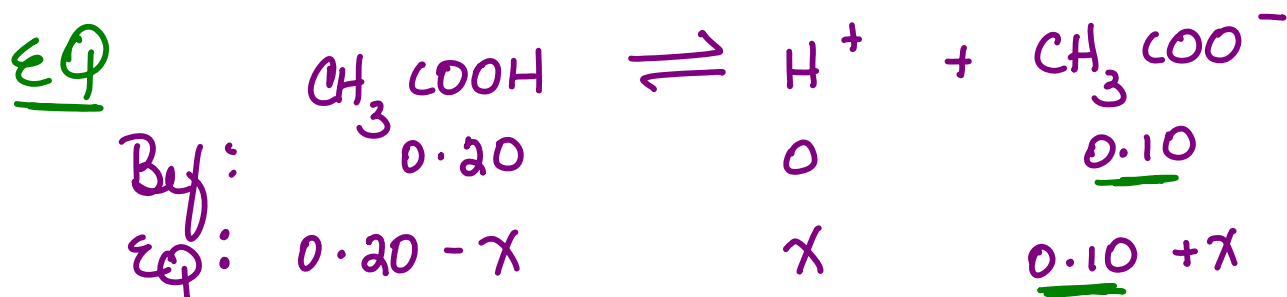
$$[K_a \text{ for } \text{CH}_3\text{COOH} = 1.8 \times 10^{-5}]$$

CH_3COOH - weak acid



\therefore Buffer

$$[\text{CH}_3\text{COOH}] = 0.20 \text{ M} \quad [\text{CH}_3\text{COO}^-] = \underline{0.10 \text{ M}}$$



$$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.10 + \cancel{x})}{(0.20 - \cancel{x})}$$

neglect x 's

$$1.8 \times 10^{-5} = \frac{(x)(0.10)}{(0.20)} \quad x = 3.6 \times 10^{-5}$$
$$= [\text{H}^+]$$

$$\text{pH} = \underline{\underline{4.44}}$$

EXAMPLE 2:

What is the pH of the previous solution if it was diluted to a volume of 10.0 L?

After dilution:

$$[\text{CH}_3\text{COOH}] = \frac{0.2 \text{ mol}}{10.0 \text{ L}} = 0.02 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{0.1 \text{ mol}}{10.0 \text{ L}} = 0.01 \text{ M}$$

$$\Rightarrow K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\Rightarrow 1.8 \times 10^{-5} = \frac{(\chi)(0.01)}{(0.02)}$$

$$\chi = 3.6 \times 10^{-5}$$

$$= [\text{H}^+]$$

$$\therefore \text{pH} = \underline{4.44}$$

* Ratio of $\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ did not change

- What does this result tell us about buffer solutions?

- dilution of a buffer solution has no effect on pH

EXAMPLE 3:

What mass, in grams, of NaNO_2 must be added to 700 mL of 0.165 M HNO_2 to produce a solution with a pH of 3.50?

$[K_a(\text{HNO}_2) = 6.0 \times 10^{-4}]$

HNO_2 : weak acid



\therefore Buffer!

$$\text{pH} = 3.50 \quad \therefore [\text{H}^+] = 10^{-3.50} = 3.16 \times 10^{-4} \text{ mol L}^{-1}$$



$$K_a = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

$$6.0 \times 10^{-4} = \frac{(3.16 \times 10^{-4}) [\text{NO}_2^-]}{(0.165)}$$

$$[\text{NO}_2^-] = 0.313 \text{ mol L}^{-1}$$

$$\begin{aligned} \text{mol NO}_2^- &= 0.313 \text{ mol L}^{-1} \times 0.700 \text{ L} \\ &= 0.219 \text{ mol} = \text{mol NaNO}_2 \end{aligned}$$

$$\begin{aligned} \text{mass NaNO}_2 &= 0.219 \text{ mol} \times 69 \text{ g mol}^{-1} \\ &= \underline{\underline{15.1 \text{ g}}} \end{aligned}$$

- But buffer solutions are not only made from weak acids.....
- Let's look at a buffer solution made from a weak base and its conjugate acid:

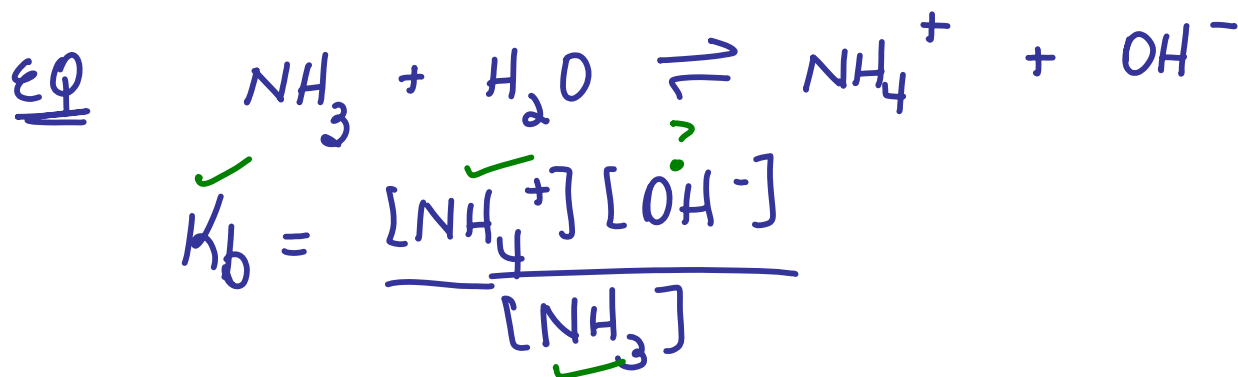
EXAMPLE 1:

A solution was prepared by adding 21.5 g of NH_4Cl to 1.50 L of 0.25 M $\text{NH}_3(\text{aq})$. Calculate the pH of this solution. [K_b for $\text{NH}_3 = 1.8 \times 10^{-5}$]

THINK: NH_3 : weak base
 $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$
 \hookrightarrow conj acid of NH_3
 \therefore Buffer

$$\text{mol } \text{NH}_4\text{Cl} = \frac{21.5 \text{ g}}{53.5 \text{ g mol}^{-1}} = 0.4019 \text{ mol} = \text{mol } \text{NH}_4^+$$

$$[\text{NH}_4^+] = \frac{0.4019 \text{ mol}}{1.50 \text{ L}} = 0.2679 \text{ mol L}^{-1}$$



$$1.8 \times 10^{-5} = \frac{(0.2679)[\text{OH}^-]}{(0.25)}$$

$$[\text{OH}^-] = 1.68 \times 10^{-5}$$

$$\text{pOH} = 4.77$$

$$\text{pH} = \underline{\underline{9.22}}$$

$$\text{mass} = 12.9 \text{ g}$$

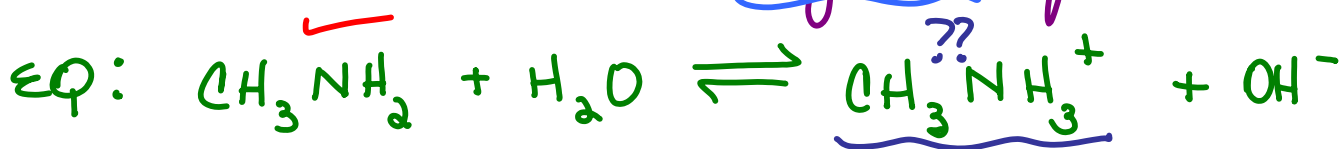
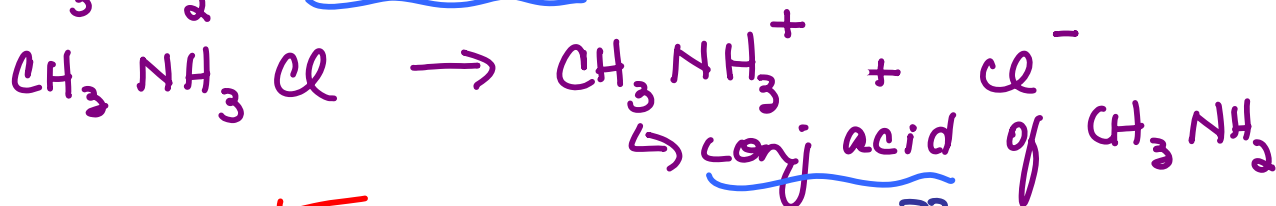
EXAMPLE 2:

What mass of $\text{CH}_3\text{NH}_3\text{Cl}$ must be added to 650 mL of a 0.145 M solution of CH_3NH_2 to produce a solution with $\text{pH} = 10.50$?

$[K_b \text{ of } \text{CH}_3\text{NH}_2 = 6.4 \times 10^{-4}]$

CH_3NH_2 : wk base.

\therefore Buffer



$\text{pH} = 10.50 \quad \therefore$ Basic $\Rightarrow \text{pOH} = 3.50$

$\therefore [\text{OH}^-] = 10^{-3.50} = 3.16 \times 10^{-4} \text{ M}$

$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = 6.4 \times 10^{-4}$

Substitue: $6.4 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+](3.16 \times 10^{-4})}{(0.145)}$

$\therefore [\text{CH}_3\text{NH}_3^+] = 0.294 \text{ mol L}^{-1}$

$\text{mol } \text{CH}_3\text{NH}_3^+ = 0.294 \text{ mol L}^{-1} \times 0.650 \text{ L}$
 $= 0.191 \text{ mol} = \text{mol } \text{CH}_3\text{NH}_3\text{Cl}$

$\text{mass} = 0.191 \text{ mol} \times 67.5 \text{ g mol}^{-1}$
 $= \underline{\underline{12.9 \text{ g}}}$

- Another way of preparing a buffer is to mix an excess of weak acid with a strong base...the reaction produces the conjugate species.

EXAMPLE 1:

→ weak acid

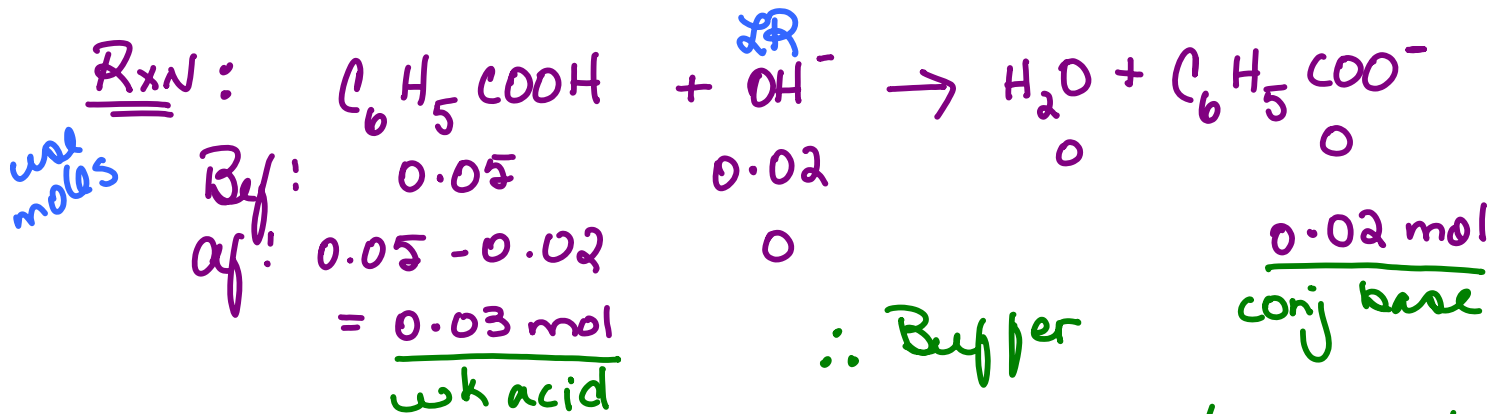
100 mL of 0.50 M Benzoic Acid, C_6H_5COOH , is mixed with 100 mL of 0.20 M NaOH. What is the pH of the resulting solution?

$[K_a \text{ of } C_6H_5COOH = 6.6 \times 10^{-5}]$

Acid and Base ALWAYS react first!!

mol $C_6H_5COOH = 0.50M \times 0.100L = 0.050 \text{ mol}$

mol $NaOH = 0.20M \times 0.100L = 0.020 \text{ mol} = \text{mol } OH^-$



after rxn; both wk acid and conj base exist
 ⇒ set up an equilibrium

Eq: $C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$

use Molarity
 $K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]}$

$6.6 \times 10^{-5} = \frac{[H^+] \left(\frac{0.02 \text{ mol}}{0.2L} \right)}{\left(\frac{0.03 \text{ mol}}{0.2L} \right)}$

$[H^+] = 9.90 \times 10^{-5}$

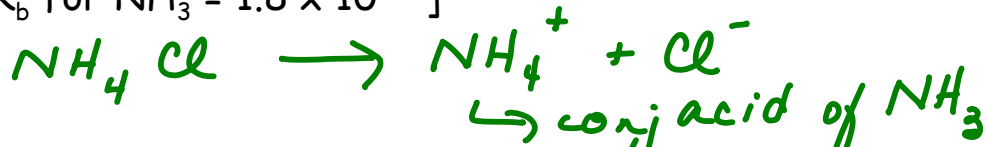
pH = 4.00

- Remember that conjugate acids behave like acids too....

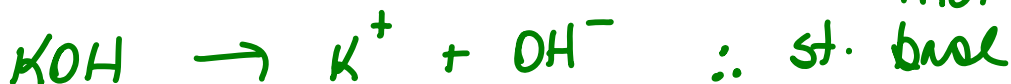
EXAMPLE 2:

Calculate the pH of a solution prepared by mixing 150 mL of 0.140 M ammonium chloride, NH_4Cl , with 100 mL of 0.112 M KOH.

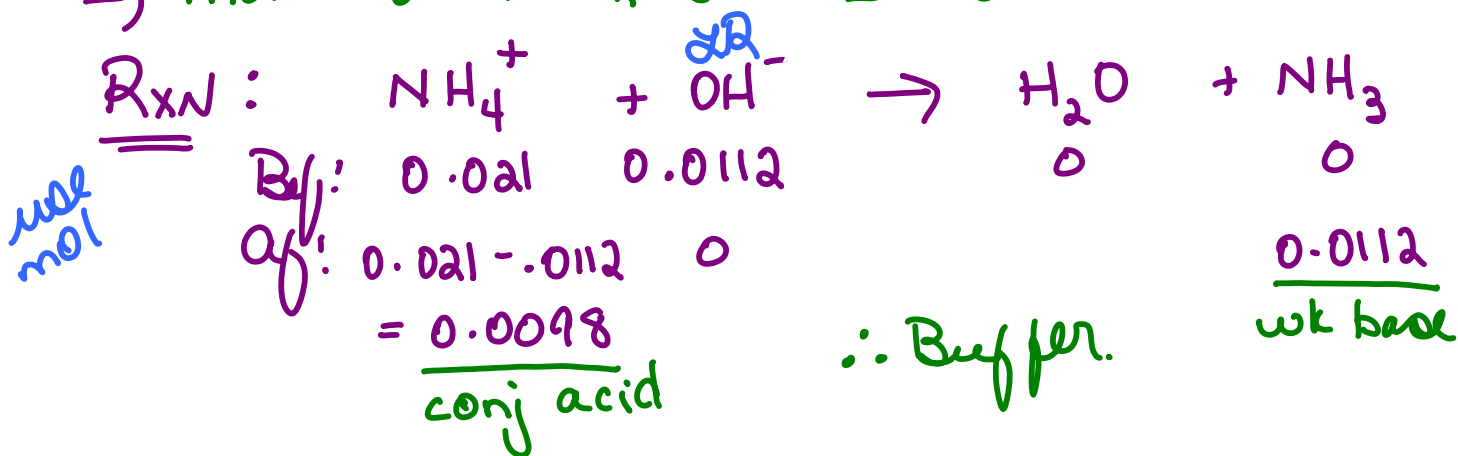
$[K_b \text{ for } \text{NH}_3 = 1.8 \times 10^{-5}]$



$$\Rightarrow \text{mol} = 0.140 \text{ M} \times 0.150 \text{ L} = 0.021 \text{ mol} = \text{mol } \text{NH}_4^+$$



$$\Rightarrow \text{mol} = 0.112 \text{ M} \times 0.100 \text{ L} = 0.0112 \text{ mol} = \text{mol } \text{OH}^-$$



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{\left(\frac{0.0098 \text{ mol}}{0.250 \text{ L}}\right) [\text{OH}^-]}{\left(\frac{0.0112 \text{ mol}}{0.250 \text{ L}}\right)}$$

$$[\text{OH}^-] = 2.057 \times 10^{-5} \text{ M} \quad \therefore \text{pOH} = 4.69$$

$$\text{pH} = \underline{9.31}$$

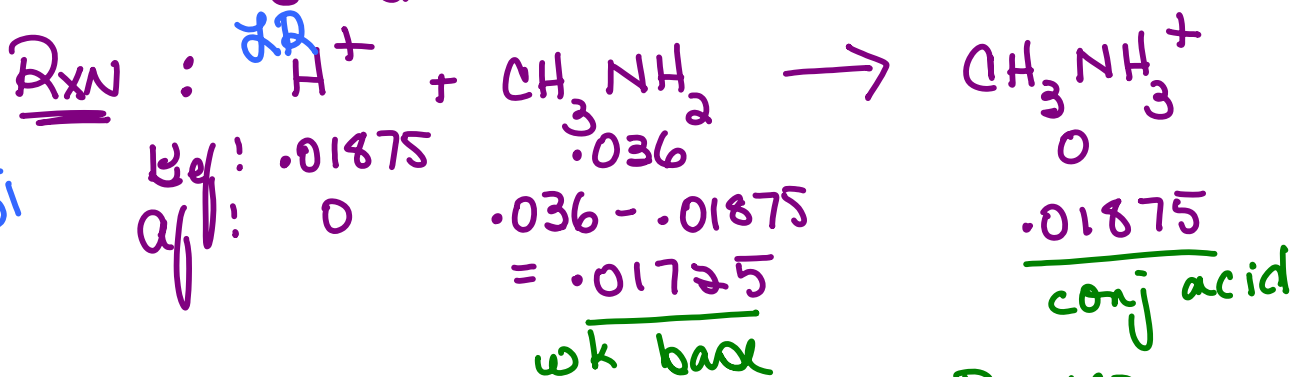
- What if we could react an excess amount of weak base (which could also be a conjugate base) with a strong acid....the reaction produces the conjugate acid.

EXAMPLE 1: $K_b(\text{CH}_3\text{NH}_2) = 6.4 \times 10^{-4}$ \rightarrow wk base

200 mL of a 0.180 M solution of methylamine, CH_3NH_2 , are mixed with 150 mL of a 0.125 M solution of HClO_4 . What is the pH of this solution? \hookrightarrow str. acid

$$\text{mol HClO}_4 = 0.125 \text{ M} \times 0.150 \text{ L} = 0.01875 \text{ mol} = \text{mol H}^+$$

$$\text{mol CH}_3\text{NH}_2 = 0.180 \text{ M} \times 0.200 \text{ L} = 0.036 \text{ mol}$$



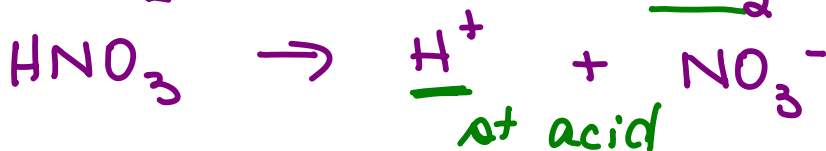
\therefore Buffer.



$$K_b = 6.4 \times 10^{-4} = \frac{(0.01875)[\text{OH}^-]}{(0.01725)}$$

$$[\text{OH}^-] = 5.89 \times 10^{-4} \Rightarrow \text{pOH} = 3.23 \Rightarrow \text{pH} = \underline{\underline{10.77}}$$

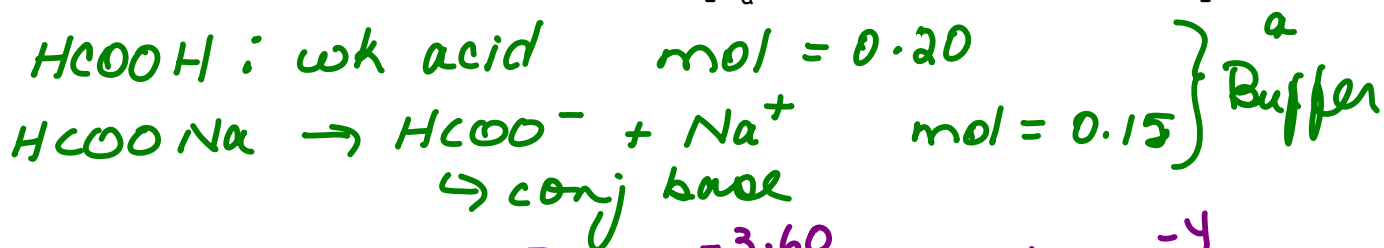
EXAMPLE 2: What is the reaction that would occur between excess potassium nitrite, KNO_2 , and HNO_3 ? *Need K_a for HNO_2*



- On p. 196 we mentioned that buffer solutions tend to resist large changes in pH, even when small amounts of strong acid or base are added to them.
- How do they do this, and does one calculate any change in pH of a buffer solution?

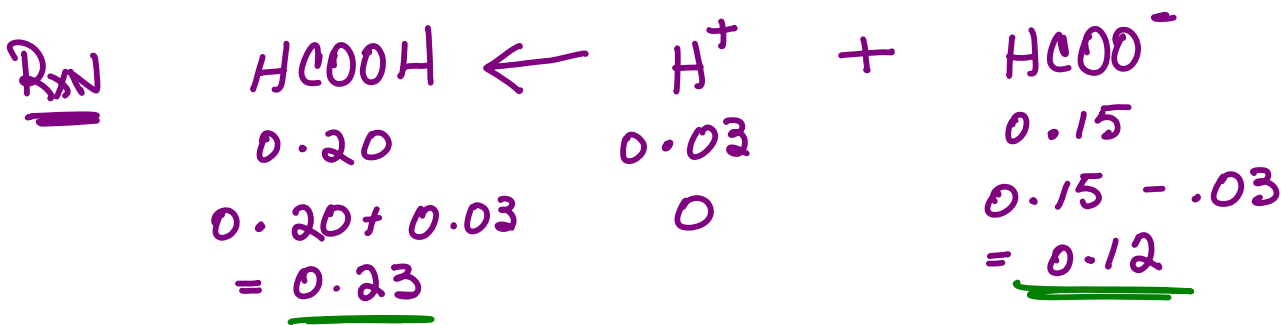
EXAMPLE 1:

0.20 mol of formic acid, HCOOH, and 0.15 mol of sodium formate, HCOONa, are made up to 1.0 L volume, to give a solution having pH = 3.60. What happens to the pH if we add 0.03 mol of HCl to this solution? $[K_a \text{ of HCOOH} = 1.9 \times 10^{-4}]$



$\text{pH} = 3.60 \Rightarrow [\text{H}^+] = 10^{-3.60} = 2.51 \times 10^{-4} \text{ M}$

Add 0.03 mol of HCl = 0.03 mol H^+



EQ

$$\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$$

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \Rightarrow 1.9 \times 10^{-4} = \frac{[\text{H}^+] (0.12 \text{ mol})}{(0.23 \text{ mol})}$$

$[\text{H}^+] = 3.64 \times 10^{-4} \quad \therefore \text{pH} = 3.43$

$\Delta \text{pH} = 3.60 - 3.43$
 $= 0.17$

Obviously, we could also add strong base to this buffer solution.

$$pH = 3.80$$

EXAMPLE 2:

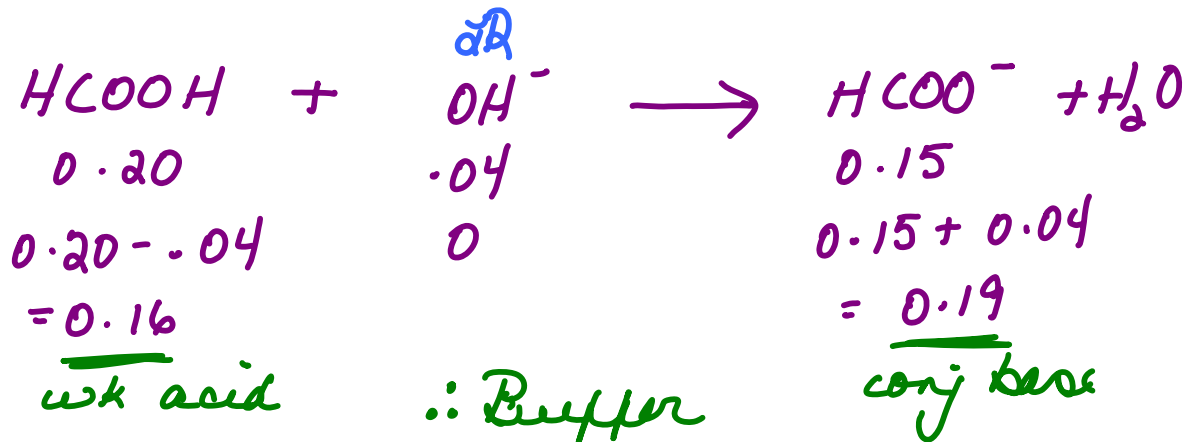
0.20 mol of formic acid, HCOOH, and 0.15 mol of sodium formate, HCOONa are made up to 1.0 L volume, to give a solution having pH = 3.60. Then 1.60 g of NaOH are added to the solution. What is the change in the pH? [K_a of HCOOH = 1.9 × 10⁻⁴]

$$\text{mol HCOOH} = 0.20$$

$$\text{mol HCOO}^- = 0.15$$

$$\text{mol NaOH} = \frac{1.60 \text{ g}}{40 \text{ g mol}^{-1}} = 0.04 \text{ mol} = \text{mol OH}^-$$

Rxn: what reacts with OH⁻?



$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$1.9 \times 10^{-4} = \frac{[H^+] \left(\frac{0.19 \text{ mol}}{1.0 \text{ L}} \right)}{\left(\frac{0.16 \text{ mol}}{1.0 \text{ L}} \right)}$$

$$\therefore [H^+] = 1.6 \times 10^{-4} \Rightarrow pH = 3.80$$

pH is 0.20 units higher

EXAMPLE 3:

What change in pH would occur if we added the same amounts of HCl (as in Ex. 1) and NaOH (as in Ex. 2) to 1.0 L of just water (instead of buffer)?

$$\text{mol HCl} = 0.03 \text{ mol} = \text{mol H}^+$$

$$[\text{H}^+] = \frac{0.03 \text{ mol}}{1.0 \text{ L}} = 0.03 \text{ M}$$

$$\text{pH} = 1.52$$

$$\text{mol NaOH} = 0.04 \text{ mol} = \text{mol OH}^-$$

$$[\text{OH}^-] = \frac{0.04 \text{ mol}}{1.0 \text{ L}} = 0.04 \text{ M}$$

$$\text{pOH} = 1.40 \Rightarrow \text{pH} = 12.60$$

EXAMPLE 2:

A solution contains 0.60 mol of NH_4Cl and 0.30 mol of $\text{NH}_3(\text{aq})$ in 1.5 L. The pH of the solution is 8.95. What will be the change in pH if we add 0.07 mol of HCl to this solution? $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$

NH_3 (wk base): mol = 0.30 mol \therefore Buffer



use mol

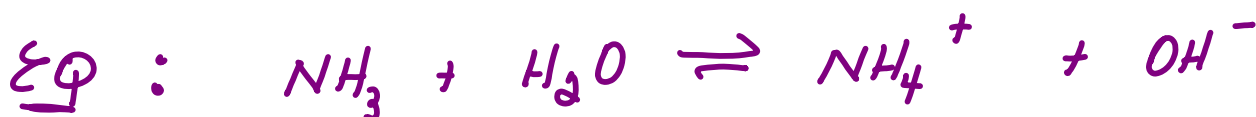
Ref: 0.30 0.07 0.60

Af: 0.23 0 0.67

wk base

conj acid

\therefore Buffer



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{\left(\frac{0.67 \text{ mol}}{1.50 \text{ L}}\right) [\text{OH}^-]}{\left(\frac{0.23 \text{ mol}}{1.50 \text{ L}}\right)}$$

$$\therefore [\text{OH}^-] = 6.1 \times 10^{-6}$$

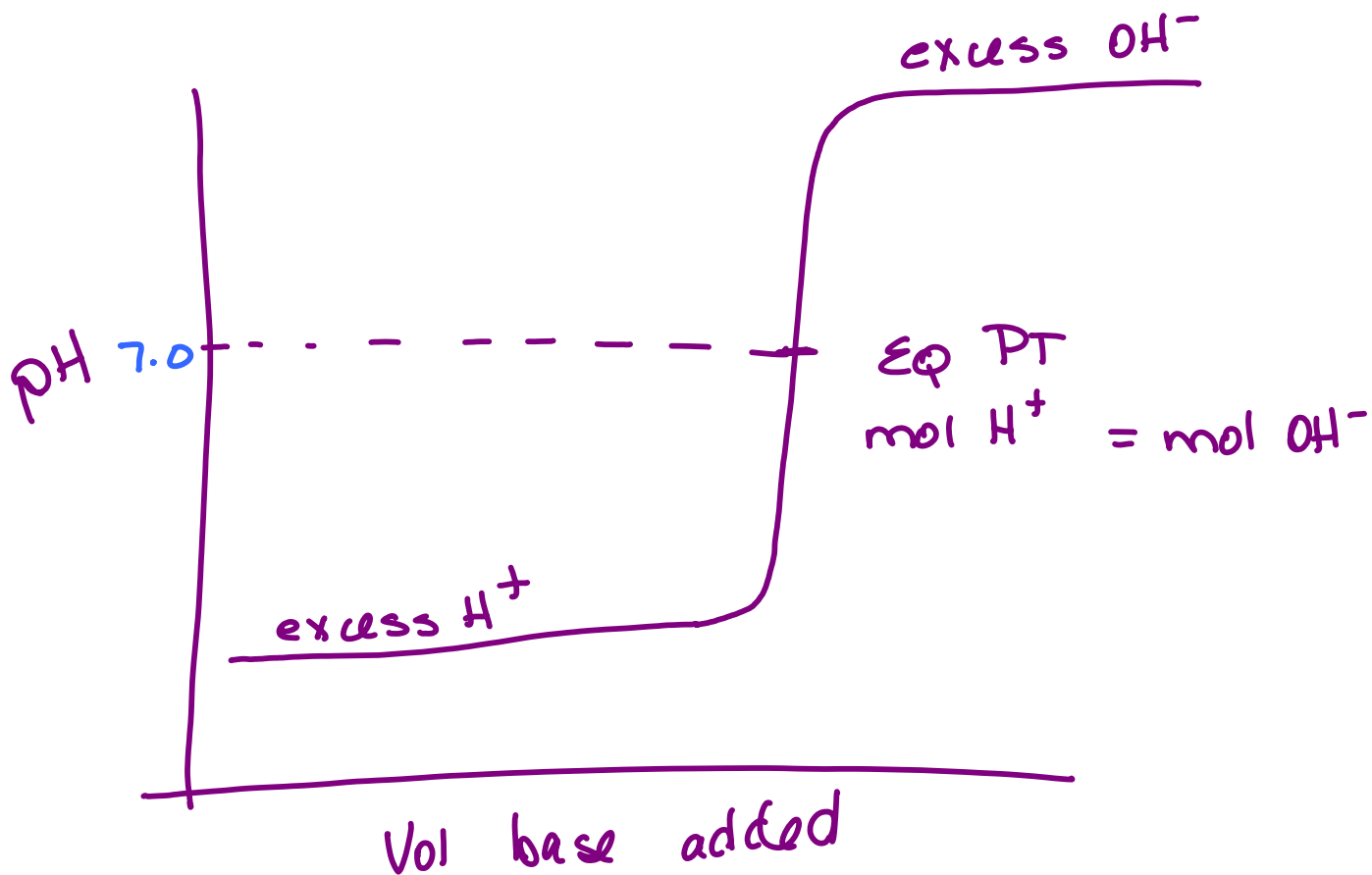
$$\text{pOH} = 5.21 \quad \Rightarrow \quad \text{pH} = \underline{8.79}$$

pH dropped by 0.16 pH units

Acid Base Titration Curves [MH5; 14.3]

1) Strong Acid - Strong Base:

There is no buffering action and the pH changes **abruptly** at the equivalence point.

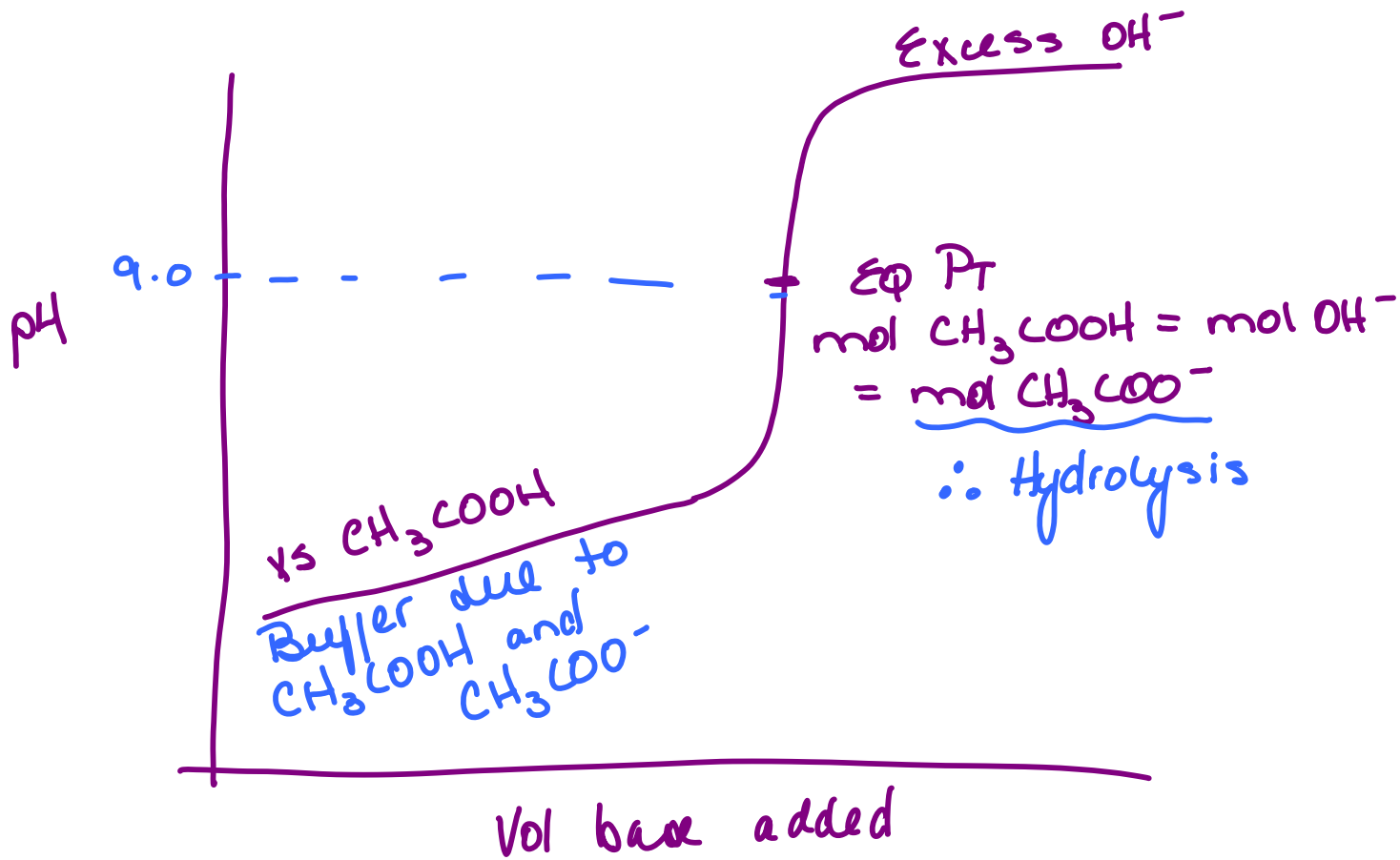


2) Weak acid - Strong Base:

Adding strong base to a weak acid, the solution is buffered before the equivalence point, where we have the acid + conjugate base present.

The pH changes slowly and the solution is basic at the equivalence point.

The "vertical step around equivalence is < in (1), so choice of indicator more important.



3) Strong Acid - Weak Base:

Adding weak base to a strong acid, the solution is not buffered until after the equivalence point.

Before the equivalence point, the pH of the solution is controlled by the strong acid.

After the equivalence point, there exists the mixture of weak base and its conjugate acid.

The pH changes very slowly before the equivalence point; at which the solution is acidic.

The "vertical step around equivalence is < in (1), so choice of indicator more important.

