

Chapter 18: Other Aspects of Aqueous Equilibria

Common Ion Effect and Buffer Solutions

In many situations, it is desirable to keep the pH of solutions nearly constant even though considerable amounts of acids and bases are added. (e.g. reactions in the human body).

This is done with the use of buffers. Buffering action is due to the COMMON ION EFFECT - a special case of Le Chatelier's Principle.

Common Ion Effect: refers to the behavior of solutions in which the same ion is produced by two different compounds.

Examples of buffers: (1) weak acid + salt of same weak acid
(2) weak base + salt of same weak base

(1) solution of a weak acid plus a soluble ionic salt of the weak acid

e.g. CH_3COOH and NaCH_3COO

we have 2 sources of the acetate ion, CH_3COO^-

(i) ionization of CH_3COOH : $\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$

and (ii) complete dissociation of salt: $\text{NaCH}_3\text{COO}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$

The extra input of CH_3COO^- from the salt pushes the weak acid equilibrium toward the reactant side, reducing $[\text{H}^+]$ and increasing the pH. The weak acid buffer is less acidic than the weak acid by itself.

(2) solution of a weak base plus a soluble ionic salt of the weak base.

e.g. NH_3 and NH_4Cl

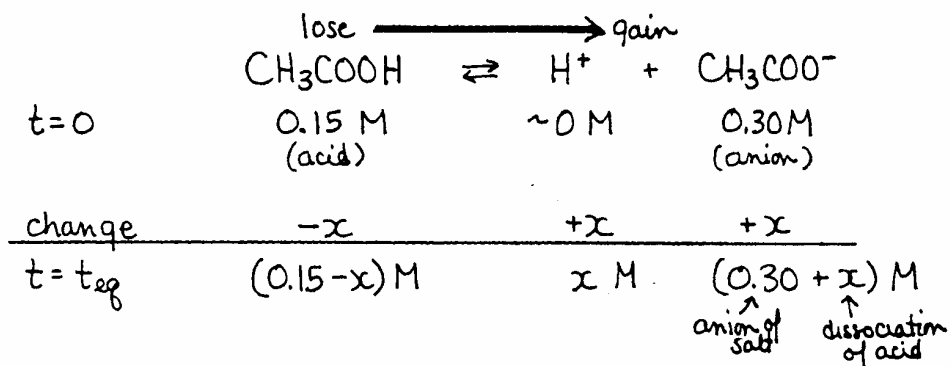
we have 2 sources of the ammonium ion, NH_4^+

(i) ionization of NH_3 : $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

and (ii) complete dissociation of salt: $\text{NH}_4\text{Cl}(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$

The extra NH_4^+ from salt pushes equilibrium to reactants, $[\text{OH}^-] \downarrow$ pH $\downarrow$
The weak base buffer is more acidic than the weak base by itself.

Example: Calculate the concentration of H^+ and pH of a solution that is 0.15 M in acetic acid and 0.30 M in sodium acetate. $K_a = 1.8 \times 10^{-5}$ for acetic acid
 Note: [weak acid] does not have to be same as [salt].



$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} = \frac{(x)(0.30 + x)}{(0.15 - x)}$$

Recall: The rule of thumb worked for the dissociation of a weak acid ($K_a \sim 10^{-5}$ or less). For buffers, x is even smaller and so we can always use the rule of thumb.

$$\therefore K_a = 1.8 \times 10^{-5} \approx \frac{x(0.30)}{(0.15)} ; \quad x = 9.0 \times 10^{-6} \text{ M} = [H^+]$$

$$pH = -\log_{10}(9.0 \times 10^{-6}) = 5.05$$

In general: for buffers made of weak acids and their salts

$$K_a = \frac{[H^+][\text{salt}]}{[\text{acid}]}$$

where [acid] $\geq \sim 0.05 \text{ M}$
 and salt contains 1 mole of anion for every 1 mole of salt.

Therefore,

For acidic buffer: $[H^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$ or anion = $K_a \frac{\text{moles acid}}{\text{moles salt or anion}}$

Example: What is pH of 0.15 M CH_3COOH only, with no salt ($NaCH_3COO$) added?

weak acid that obeys rule of thumb:

$$[H^+] = \sqrt{K_a [\text{acid}]}$$

$$= \sqrt{1.8 \times 10^{-5} \times 0.15}$$

$$= 1.64 \times 10^{-3} \text{ M}$$

$$pH = 2.78$$

$\therefore$ soln of weak acid alone is more acidic than buffer.

OR the pH of a weak acid < pH of weak acid and its salt.

In other words, if a salt containing the anion of the weak acid is added to the weak acid, the weak acid dissociates to a lesser degree, $[H^+] \downarrow$ due to Le Chatelier's principle, and pH $\uparrow$.

Note: Your book presents to you the Henderson - Hasselback equation: it takes the simplified equation one step further

$$[H^+] = K_a \frac{[acid]}{[salt]_{(anion)}}$$

$$\Downarrow$$

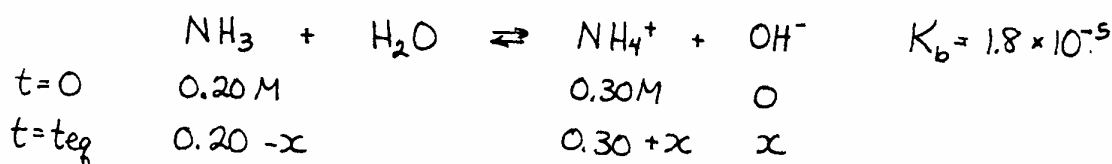
$$pH = pK_a - \log \frac{[acid]}{[salt]_{(anion)}}$$

or

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

Buffer solutions can also be prepared from weak bases and their salts.

Example: Calculate the pH of a solution that is 0.20 M NH_3 and 0.30 M ammonium nitrate, NH_4NO_3 .



$$\therefore K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$= \frac{(0.30 + x)(x)}{(0.20 - x)}$$

$$1.8 \times 10^{-5} = \frac{(0.30)x}{0.20}$$

$$[OH^-] = x = 1.2 \times 10^{-5}$$

$$\therefore pOH = 4.92$$

$$pH = 9.08$$

The $[OH^-]$ for a solution that is 0.20 M in NH_3 alone = $\sqrt{K_b(\text{base})}$
 $\therefore$ pH of this solution = $14 - pOH = 11.28$ $= 1.90 \times 10^{-3} M$

The net result of adding the salt of its cation to a weak base is to lower the $[\text{OH}^-]$ and lower the pH of the solution.

In general for buffers made of weak bases and their salts

$$K_b = \frac{[\text{OH}^-][\text{salt}^{\text{cation}}]}{[\text{base}]}$$

where $[\text{base}]$ is $\sim 0.05 \text{ M}$ or larger
and salt contains 1 mole of cation
for every mole of salt.

For basic buffer : $[\text{OH}^-] = K_b \frac{[\text{base}]}{[\text{salt}^{\text{cation}}]} = K_b \frac{\text{moles of base}}{\text{moles of salt}^{\text{cation}}}$

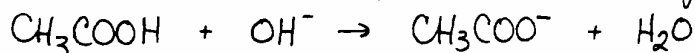
Buffering Action :

Buffer solutions resist changes in pH. If acid or base is added to a buffer solution, it will react with a buffer to reduce the effect of adding the acid or base.

Case 1 : Acidic buffer acid source of its conjugate base
 $\text{CH}_3\text{COOH} / \text{NaCH}_3\text{COO}$

(a) add base (OH^- ions)

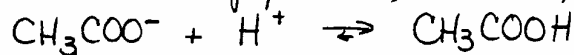
it will react with the acid to form more salt (conjugate base)



solution will get slightly more basic

(b) add acid (H^+ ions)

it will react with conjugate base, i.e. the salt, to form more acid

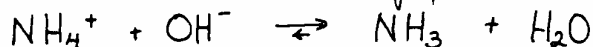


solution will get slightly more acidic

Case 2. Basic buffer base source of its conjugate acid
 $\text{NH}_3 / \text{NH}_4\text{Cl}$

(a) add base (OH^- ions)

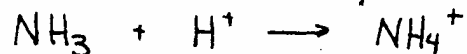
it will react with the salt i.e. its conjugate acid to form more base



solution will get slightly more basic

(b) add acid (H^+ ions)

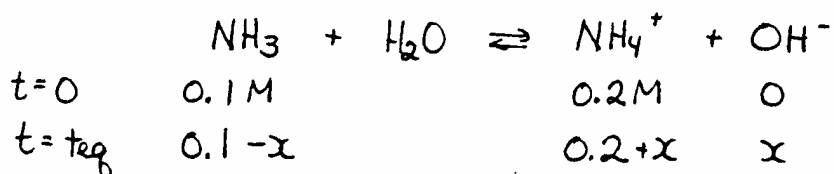
it will react with the base to form more salt (conjugate acid)



solution will get slightly more acidic

Example: Determine the pH change accompanying the addition of 0.020 moles of HCl to 1 L of solution that is 0.10 M in aqueous ammonia and 0.20 M in ammonium chloride. Assume no change in volume

(a) determine pH of buffer initially



$$K_b = 1.8 \times 10^{-5} = \frac{(0.2+x)(x)}{(0.1-x)}$$

$$[OH^-] = x = 9 \times 10^{-6}$$

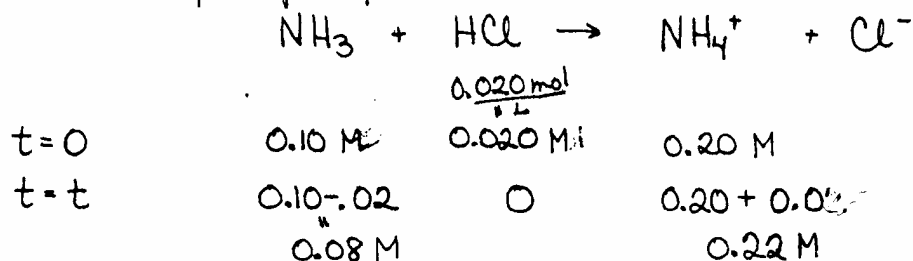
$$pOH = 5.05$$

$$pH = 8.95$$

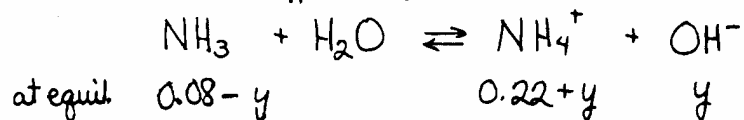
$$\text{or use } [OH^-] = K_b \frac{[base]}{[salt]}$$

(b) determine pH of buffer after 0.020 moles of HCl is added

Limiting reagent problem:



Now we use buffer calculation:



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

$$1.8 \times 10^{-5} = \frac{(0.22 + y)(y)}{(0.08 - y)}$$

$$[\text{OH}^-] = y = 6.55 \times 10^{-6}$$

$$\text{pOH} = 5.18$$

$$\text{pH} = 8.82$$

$$\text{or use } [\text{OH}^-] = K_b \frac{[\text{base}]}{[\text{salt}]} = K_b \frac{\text{moles base}}{\text{moles salt}}$$

$\therefore \text{pH}_{\text{initial}} = 8.95$
 $\text{pH}_{\text{final}} = 8.82$ } adding acid made the buffer slightly more acidic - have lower pH.

Example: Determine the change in pH accompanying the addition of 200 mL of 0.10 M NaOH to 500 mL of solution that is 0.10 M in NH_3 and 0.20 M in ammonium chloride.

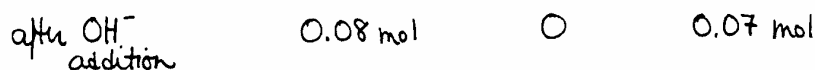
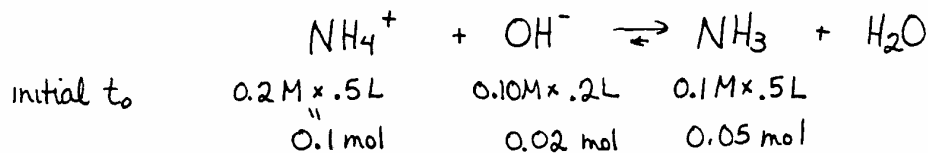
(a) initial pH = 8.95 (see previous example)

(b) pH of solution after NaOH solution has been added.

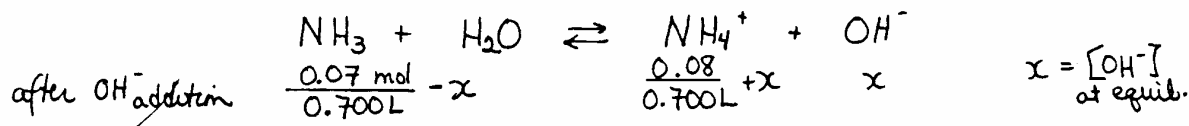
Notice that there is a significant volume change - therefore to work in Molarity, we must do a fair amount of calculations.

An easier, more direct method is to work in moles.

An addition of OH^- will react with the conjugate acid of the buffer:



Now let us substitute these values into the equilibrium expression:



then solve for x using $K_b = \frac{(\frac{0.08}{0.70} + x)(x)}{(\frac{0.07}{0.7} - x)}$

18 = 7

Simple way:

$$\therefore [\text{OH}^-] = K_b \frac{\text{moles base}}{\text{moles salt}} = 1.8 \times 10^{-5} \frac{0.07 \text{ mol}}{0.08 \text{ mol}}$$

$$= 1.6 \times 10^{-5} \text{ M}$$

$$[\text{H}^+] = 6.25 \times 10^{-10} \text{ M}$$

$$\text{pH} = 9.20$$

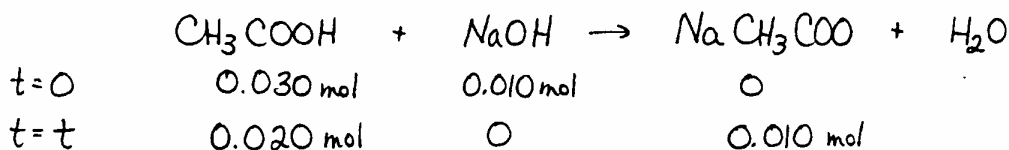
$\therefore$ adding $[\text{OH}^-]$ to a buffer makes the solution slightly more basic.
and pH $\uparrow$ a little. (See next page for a more difficult problem)

Preparation of Buffer Solutions:

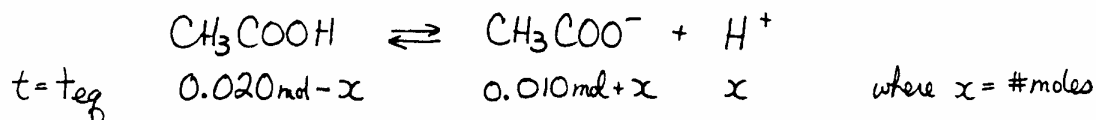
Example: Calculate the concentration of H^+ and the pH of the solution prepared by mixing 200 mL of 0.15 M acetic acid and 100 mL of 0.10 M NaOH solution.

$$\text{moles of acetic acid} = M \times \#L = 0.15 \text{ M} \times 0.200 \text{ L} = 0.030 \text{ mol}$$

$$\text{moles of NaOH} = M \times \#L = 0.10 \text{ M} \times 0.100 \text{ L} = 0.010 \text{ mol}$$



after reaction, we have a buffer solution: weak acid + its salt.
 $\therefore$ write the equilibrium expression:



solving for $[\text{H}^+]$:

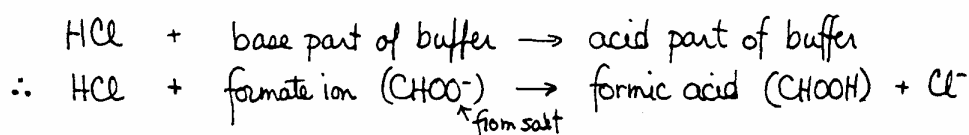
$$[\text{H}^+] = K_a \frac{\text{moles of acid}}{\text{moles of salt}_{(\text{anion})}} = 1.8 \times 10^{-5} \frac{0.020}{0.010} = 3.6 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.44$$

A more difficult problem: adding strong acid or strong base to a buffer.

A buffer is prepared by dissolving 0.500 moles formic acid and 1.00 mole of sodium formate in 1.00 L solution. To 300 mL of this solution, 50.0 mL of 0.200 M HCl is added. What is the final pH? (K_a formic acid = 1.8×10^{-4})

Step 1: Do the acid-base limiting reagent problem



t=0	$\frac{0.200\text{ M} \times 0.0500\text{ L}}{0.0100\text{ mol}}$	$\frac{1.00\text{ M} \times 0.300\text{ L}}{0.300\text{ mol}}$	$\frac{0.500\text{ M} \times 0.300\text{ L}}{0.150\text{ mol}}$
change	- 0.0100 mol	- 0.0100 mol	+ 0.0100 mol
t _{final}	0	0.290 mol	0.160 mol

when reaction is over, we have a DIFFERENT buffer!! but still a buffer.

Step 2: Do the buffer problem

for a weak acid buffer: $[H^+] = K_a \frac{\text{moles acid}}{\text{moles anion}}$

$$= 1.8 \times 10^{-4} \frac{0.160\text{ mol}}{0.290\text{ mol}}$$

$$= 9.9 \times 10^{-5}$$

$$\text{pH} = 4.00$$

OR work through the equilibrium problem:

$$\text{CHOOH} \rightleftharpoons \text{CHOO}^- + \text{H}^+$$

$$t=0 \quad \frac{0.160\text{ mol}}{0.350\text{ L}} \quad \frac{0.290\text{ mol}}{0.350\text{ L}} \quad x$$

$$K_a = \frac{[H^+][CHOO^-]}{[CHOOH]} = \frac{x \left(\frac{0.290}{0.350} \right)}{\left(\frac{0.160}{0.350} \right)} = 1.8 \times 10^{-4}$$

$$\therefore x = [H^+] = 9.9 \times 10^{-5} \Rightarrow \text{pH} = 4.00$$

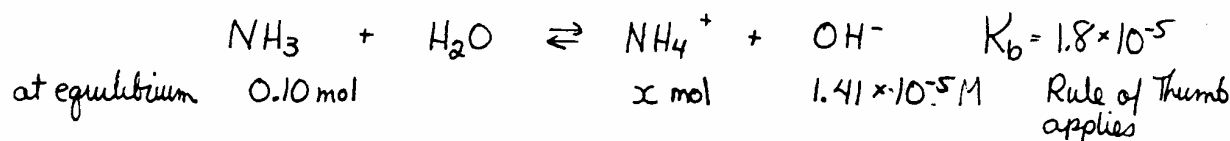
Sometimes, one wishes to prepare a buffer of known pH.

Example: Calculate the number of moles of solid NH_4Cl that must be used to prepare 1.00 liter of a buffer solution that is 0.10 M in aqueous ammonia and has a pH of 9.15. Find $[\text{NH}_3]/[\text{NH}_4^+]$

$$\text{pH} = 9.15. \quad \text{Therefore } \text{pOH} = 4.85$$

$$[\text{OH}^-] = 1.41 \times 10^{-5} \text{ M}$$

we know the equilibrium for ionization of ammonia



where x = number of moles NH_4^+

$$\begin{aligned} [\text{OH}^-] &= K_b \left(\frac{\text{moles of base}}{\text{moles of salt (cation)}} \right) & \frac{[\text{NH}_3]}{[\text{NH}_4^+]} &= \frac{[\text{OH}^-]}{K_b} \\ \text{moles of salt} &= K_b \frac{\text{moles of base}}{[\text{OH}^-]} & &= \frac{1.4 \times 10^{-5}}{1.8 \times 10^{-5}} \\ & & &= 0.778 \\ &= 1.8 \times 10^{-5} \frac{0.10}{1.41 \times 10^{-5}} \\ &= 0.128 \text{ moles.} \end{aligned}$$

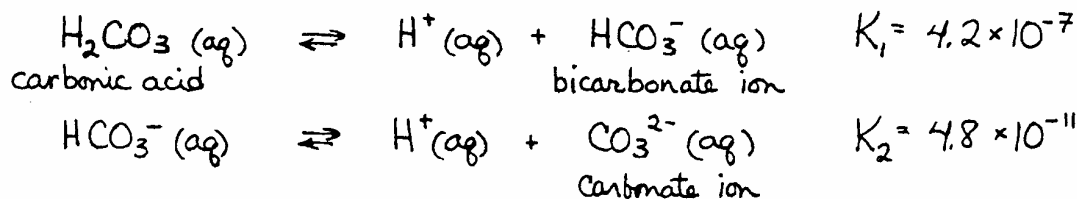
Polyprotic Acids (not for testing)

Until now, we have only discussed the behavior of weak monoprotic acids: acids with 1 acidic hydrogen per formula unit.

Many weak acids have 2 or more acidic hydrogens.

examples: H_2CO_3 carbonic acid
 H_3PO_4 phosphoric acid
 $(\text{COOH})_2$ oxalic acid

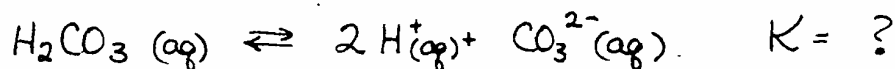
Consider carbonic acid, H_2CO_3 :



Note that $K_2 \ll K_1$, $\therefore$ the second ionization occurs to a much lesser extent

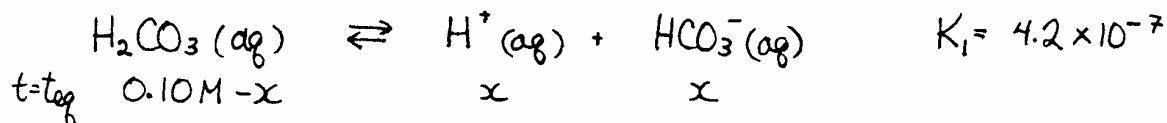
$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

Consider the overall ionization of carbonic acid (add the two equations together and cancel out terms appearing on both sides).



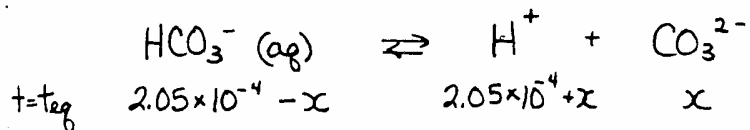
$$K = \frac{[\text{H}^+]^2 [\text{CO}_3^{2-}]}{[\text{H}_2\text{CO}_3]} = K_1 K_2$$

Example: Calculate the concentrations of various species in 0.10 M H_2CO_3 : $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and $[\text{H}_2\text{CO}_3]$.



$$\begin{aligned} [\text{HCO}_3^-] &= [\text{H}^+] = \sqrt{K_a [\text{acid}]} \quad \text{since Rule of Thumb applies} \\ &= \sqrt{4.2 \times 10^{-7} (0.10)} \\ &= 2.05 \times 10^{-4} \text{ M} \end{aligned}$$

$$\therefore [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14}}{2.05 \times 10^{-4}} = 4.88 \times 10^{-11} \text{ M}$$



$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$4.8 \times 10^{-11} = \frac{(2.05 \times 10^{-4} + x)(x)}{(2.05 \times 10^{-4} - x)}$$

since Rule of Thumb applies

$$4.8 \times 10^{-11} = x = [\text{CO}_3^{2-}]$$

$$\therefore [\text{H}_2\text{CO}_3] = 0.10 \text{ M}$$

$$[\text{HCO}_3^-] = 2.05 \times 10^{-4} \text{ M}$$

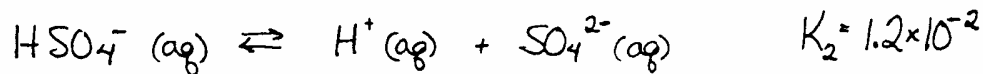
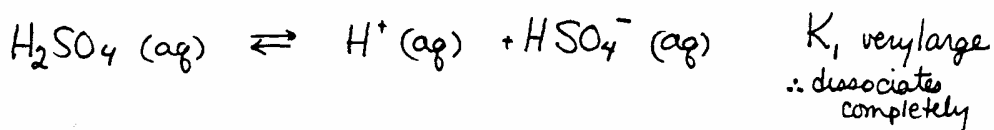
$$[\text{CO}_3^{2-}] = 4.8 \times 10^{-11} \text{ M}$$

$$[\text{H}^+] = 2.05 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 4.88 \times 10^{-11} \text{ M}$$

Before we leave polyprotic acids, H_2SO_4 is a polyprotic acid as well.

We have mentioned that H_2SO_4 is a strong acid, BUT it is only the first hydrogen that dissociates completely.



Salt pH

Review:

- (1) salts of strong acids + strong bases $\Rightarrow$ neutral solution
since neither the anion of strong acid nor cation of strong base hydrolyzes.
- (2) salts of strong bases + weak acids $\Rightarrow$ basic solution
since anions of weak acids hydrolyze to form OH^-
- (3) salts of strong acids + weak bases $\Rightarrow$ acidic solution
since cations of weak bases hydrolyze to form H_3O^+
- (4) salts of weak acids and weak bases $\Rightarrow$ acidic, basic or neutral solutions
depending on which ion hydrolyzes to greater extent

$K_a^{\text{parent (acid)}} > K_b^{\text{parent (base)}}$	acidic	$K_a = K_b$	neutral
$K_a < K_b$	basic		

ACID - BASE TITRATIONS

titration: a procedure in which a solution of accurately known concentration is added to a solution of unknown concentration until the chemical reaction between the two solutes is complete - this is the equivalence point.

How can we tell when the equivalence point in an acid-base reaction is reached?

- (1) follow the titration with a pH electrode - measures pH ($-\log[\text{H}^+]$) directly
- (2) use an indicator which changes color at the desired point.
 - The point at which the color change occurs is the endpoint.
 - Hopefully, if the indicator is chosen correctly, the endpoint will be close to the equivalence point.

Titration of Strong Acids with Strong Bases (or vice versa)

Consider the titration of 15.0 mL of 0.200 M KOH with 0.100 M HClO_4 .

formula unit equation: $\text{KOH}(\text{aq}) + \text{HClO}_4(\text{aq}) \rightarrow \text{KClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$

total ionic equation: $\text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{ClO}_4^-(\text{aq}) \rightarrow$
 $\text{K}^+(\text{aq}) + \text{ClO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$

net ionic equation: $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

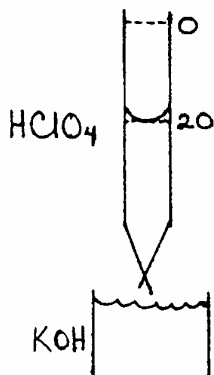
(1) Initial pH = pH of strong base solution

$$pOH = -\log_{10}(0.200 M) = 0.70 \quad \therefore pH = 14 - pOH = 13.30$$

$\therefore$ the kind of calculations that follow are applicable to any titration using strong acids and strong bases.

Sample calculations (Limiting Reagent Problems)

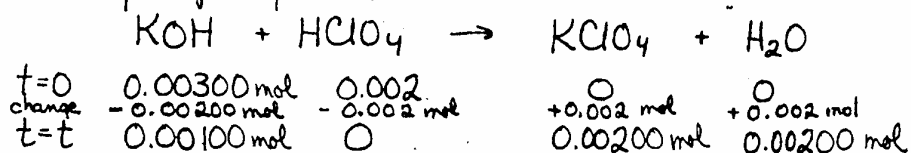
(a) after 20.0 mL of 0.100 M $HClO_4$ has been added:



$$\begin{aligned} \text{moles of } HClO_4 \text{ added} &= M \times \#L = 0.100 M \times 0.0200 L \\ &= 0.00200 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{moles of } KOH \text{ at start} &= M \times \#L = 0.200 M \times 0.0150 L \\ &= 0.00300 \text{ mol} \end{aligned}$$

limiting reagent problem:



$\therefore$ we have excess base after the reaction has occurred.

$$[KOH] = [OH^-] = \frac{\# \text{ moles}}{\# L \text{ total}} = \frac{0.00100 \text{ mol}}{(0.0150 L + 0.0200 L)} = 0.0286 M$$

$\uparrow$ $\uparrow$
 KOH $HClO_4$
 added

$$\therefore pOH = 1.54$$

$$pH = 14 - pOH = 12.46$$

(3) after 30.0 mL of 0.100 M $HClO_4$ has been added

$$\text{moles of } HClO_4 \text{ added} = M \times \#L = 0.00300 \text{ mol}$$

$$\text{moles of } KOH \text{ present initially} = M \times \#L = 0.00300 \text{ mol}$$

$\therefore$ we have stoichiometric amounts of both acid and base present and the final solution contains no ^{excess} base or acid, only salt and H_2O .

$\therefore [H^+] = [OH^-]$ is derived from the ionization of water.

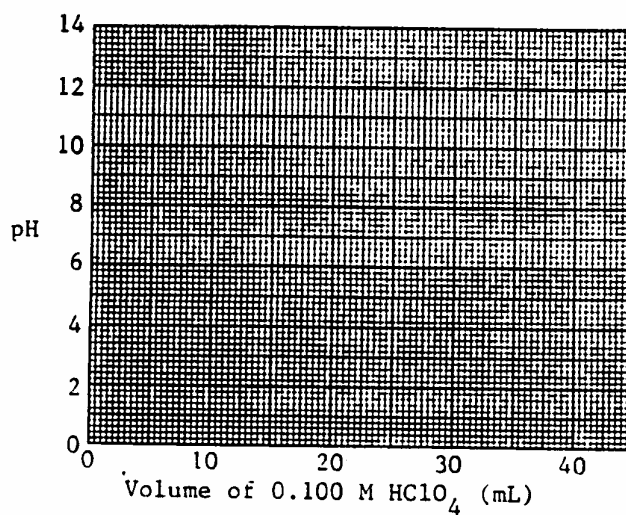
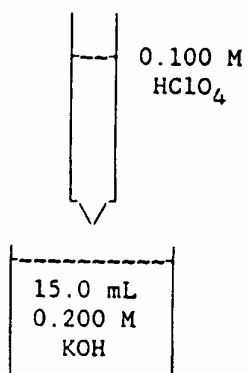
$$= 1.00 \times 10^{-7} M \text{ at } 25^\circ C \quad \text{since salt is derived from a}$$

$$\therefore pH = 7$$

strong acid and a strong base

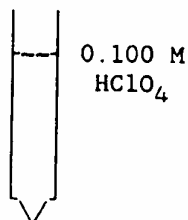
Titration of 15.0 mL of 0.200 M KOH with 0.100 M HClO_4

mL of 0.100 M HClO_4 added	moles of HClO_4 added	moles of excess acid or base	total volume	$[\text{H}^+]$ or $[\text{OH}^-]$	pH
0.0					
10.0					
20.0					
29.0					
29.9					
30.0					
30.1					
40.0					

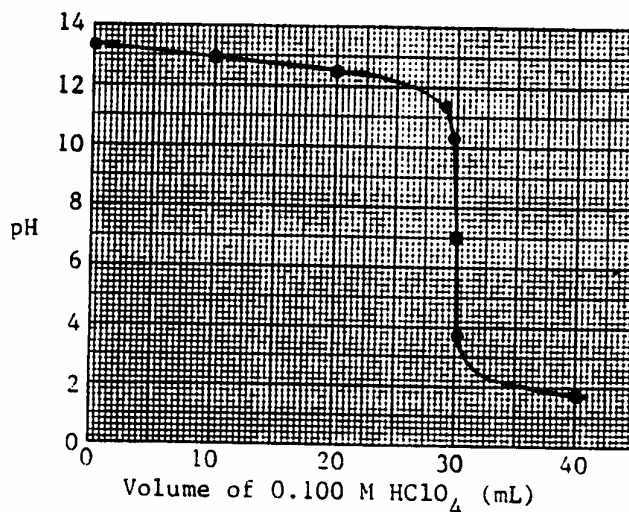


Titration of 15.0 mL of 0.200 M KOH with 0.100 M HClO₄
 $(0.200 \text{ M} \times 0.0150 \text{ L}) = 0.00300 \text{ moles KOH}$

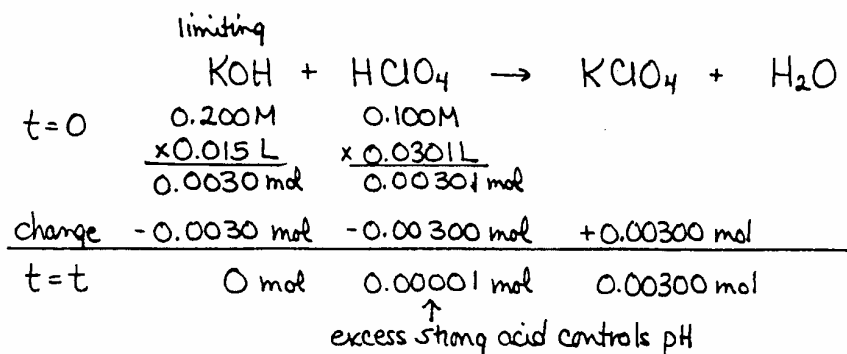
mL of 0.100 M HClO ₄ added	moles of HClO ₄ added	moles of excess acid or base	total volume	[H ⁺] or [OH ⁻]	pH
0.0	0 mol	moles KOH - moles HClO ₄ = 0.00300 mol KOH	0.0150 L	0.200 M OH ⁻	13.30
10.0	$0.100 \text{ M} \times 0.0100 \text{ L}$ = 0.00100 mol	0.00300 mol KOH - 0.00100 mol HClO ₄ = 0.00200 mol KOH	10 mL + 15 mL HClO ₄ KOH = 0.0250 L	0.0800 M OH ⁻	12.90
20.0	$0.100 \text{ M} \times 0.0200 \text{ L}$ = 0.00200 mol	0.00300 mol KOH - 0.00200 mol HClO ₄ = 0.00100 mol KOH	20 mL + 15 mL HClO ₄ KOH = 0.0350 L	0.0286 M OH ⁻	12.46
29.0	$0.100 \text{ M} \times 0.0290 \text{ L}$ = 0.00290 mol	0.00300 mol KOH - 0.00290 mol HClO ₄ = 0.00010 mol KOH	29.0 mL + 15 mL HClO ₄ KOH = 0.0440 L	0.0023 M OH ⁻	11.36
29.9	$0.100 \text{ M} \times 0.0299 \text{ L}$ = 0.00299 mol	0.00300 mol KOH - 0.00299 mol HClO ₄ = 0.00001 mol KOH	29.9 mL + 15 mL HClO ₄ KOH = 0.0449 L	$2 \times 10^{-4} \text{ M}$ OH ⁻	10.3
30.0	$0.100 \text{ M} \times 0.0300 \text{ L}$ = 0.00300 mol	$\therefore [\text{H}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$ at 25°C	-	$1.00 \times 10^{-7} \text{ M}$ H ⁺ and OH ⁻	7.00
30.1	$0.100 \text{ M} \times 0.0301 \text{ L}$ = 0.00301 mol	0.00301 mol HClO ₄ - 0.00300 mol KOH = 0.00001 mol HClO ₄	30.1 mL + 15 mL HClO ₄ KOH = 0.0451 L	$2 \times 10^{-4} \text{ M}$ H ⁺	3.7
40.0	$0.100 \text{ M} \times 0.0400 \text{ L}$ = 0.00400 mol	0.00400 mol HClO ₄ - 0.00300 mol KOH = 0.00100 mol HClO ₄	40 mL + 15 mL HClO ₄ KOH = 0.0550 L	0.0182 M H ⁺	1.74



$$\text{moles KOH} = 0.200 \text{ M} \times 0.0150 \text{ L} = 0.00300 \text{ mol}$$



(4) After 30.1 mL of 0.100 M HClO_4 has been added



$$[\text{H}^+] = \frac{\text{mol H}^+}{\text{total Volume (L)}} = \frac{1 \times 10^{-5} \text{ mol}}{\begin{array}{c} (0.015\text{L} + 0.0301\text{L}) \\ \uparrow \quad \uparrow \\ \text{KOH} \quad \text{HClO}_4 \end{array}} = 2.2 \times 10^{-4} \text{ M}$$

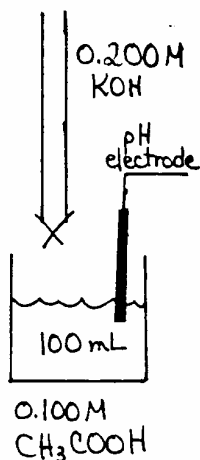
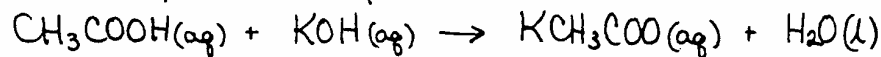
$$\text{pH} = -\log [\text{H}^+] = 3.65$$

Question: Which indicator(s) would be appropriate for this titration?

Answer: Litmus and phenolphthalein since the endpoint of the titration as denoted by the color change of the indicator occurs at the same pH as the equivalence point. (litmus: 4.7-8.2 ; phenolphthalein: 8.3-10.0)

Titration of a Weak Acid with a Strong Base

Consider the titration of 100.00 mL of 0.100 M CH_3COOH with 0.200 M KOH

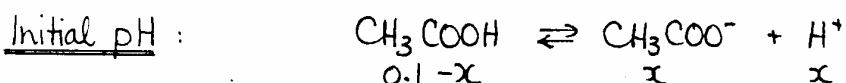


Parts of Titration Curve:

- (1) Before titration begins - pH set by concentration of weak acid
- (2) Before the equivalence point - KOH is limiting reagent (all used up).
solution: weak acid and its salt
pH is set by the weak acid buffer
- (3) At the equivalence point - solution is salt + water
pH is set by the concentration of salt of strong base/weak acid
 $\text{pH} > 7$

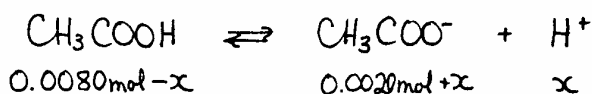
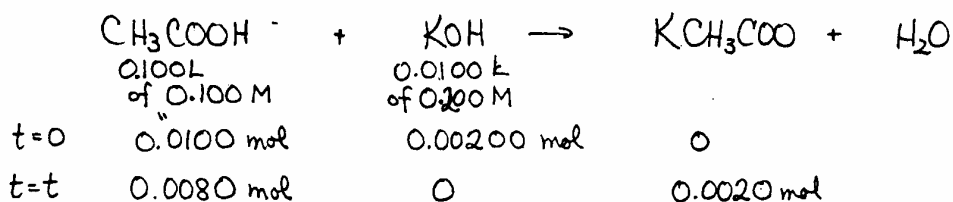
- ④ After the equivalence point :
 solution $\neq$ excess base
 pH is set by concentration of excess base.

$\therefore$ the titration of a weak base with a strong acid uses theory we already know!!



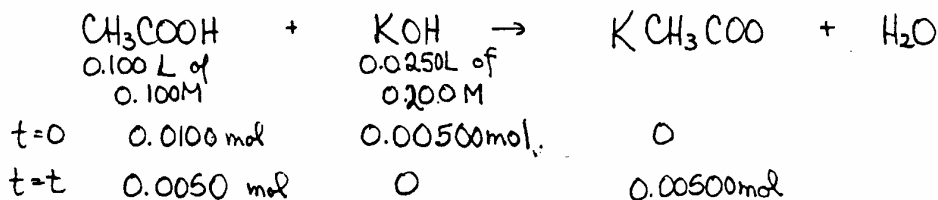
$$\begin{aligned} [\text{H}^+] &= \sqrt{K_a [\text{acid}]} & \text{pH} &= 2.87 \\ &= \sqrt{1.8 \times 10^{-5} (0.1)} \\ &= 1.3 \times 10^{-3} \text{ M} \end{aligned}$$

After 10.0 mL of 0.200 M KOH is added



$$\begin{aligned} [\text{H}^+] &= K_a \frac{\text{mol acid}}{\text{mol salt}} & \text{pH} &= 4.14 \\ &= 1.8 \times 10^{-5} \frac{0.0080}{0.0020} \\ &= 7.2 \times 10^{-5} \text{ M} \end{aligned}$$

After 25.0 mL of 0.200 M KOH is added (HALFWAY TO EQUIVALENCE)



∴ halfway to equivalence, number of moles acid = number of moles of its conjugate base.

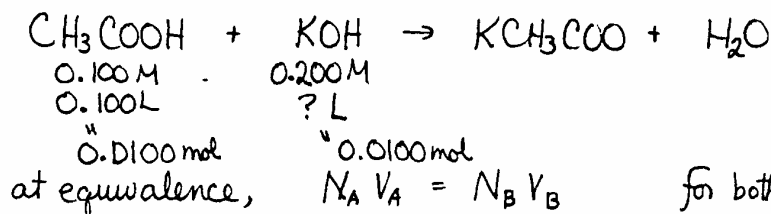
$$\begin{aligned}
 [H^+] &= K_a \frac{\text{moles acid}}{\text{moles salt}} \\
 &= 1.8 \times 10^{-5} \times \frac{0.0050}{0.0050} \\
 &= 1.8 \times 10^{-5}
 \end{aligned}$$

$$\boxed{\text{pH} = 4.74}$$

∴ halfway to equivalence, $\text{pH} = \text{p}K_a$

At the Equivalence Point

at this point, we have no excess acid or excess base, only salt and water
 ∴ pH is determined by [salt of weak acid and strong base]



for both acid + base,
 $N = M \times V$

For 1:1 reaction,

$$\#L_B = \frac{\text{moles}}{M} = \frac{0.0100 \text{ mol}}{0.200 \text{ M}} = 0.0500 \text{ L}$$

$$\begin{aligned}
 0.100 \text{ N} \times 0.100 \text{ L} &= 0.200 \text{ N} \times V_B \\
 V_B &= 0.0500 \text{ L}
 \end{aligned}$$

$$\therefore \text{total volume at equivalence} = 0.100 \text{ L} + 0.0500 \text{ L} = 0.150 \text{ L}$$

$$\therefore [\text{KCH}_3\text{COO}]_{\text{equil}} = \frac{0.0100 \text{ mol}}{0.150 \text{ L}} = 6.67 \times 10^{-2} \text{ M}$$

$$\begin{aligned}
 [\text{OH}^-] &= \sqrt{\frac{K_w}{K_a} [\text{salt}]} \\
 &= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} \cdot 0.0667}
 \end{aligned}$$

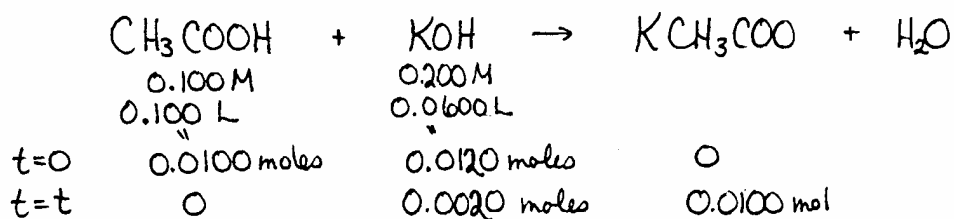
$$\boxed{\text{pH} = 8.78}$$

$$= 6.1 \times 10^{-6}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = 1.6 \times 10^{-9}$$

After the Equivalence Point: After 60.0 mL of 0.200 M KOH is added

the pH is determined by the concentration of excess KOH.



$$\therefore [\text{OH}^-] = \frac{0.0020 \text{ mol}}{0.100 + 0.060 \text{ L}} = 1.25 \times 10^{-2} \text{ M}$$

0.160 L

$$\text{pOH} = 1.90$$

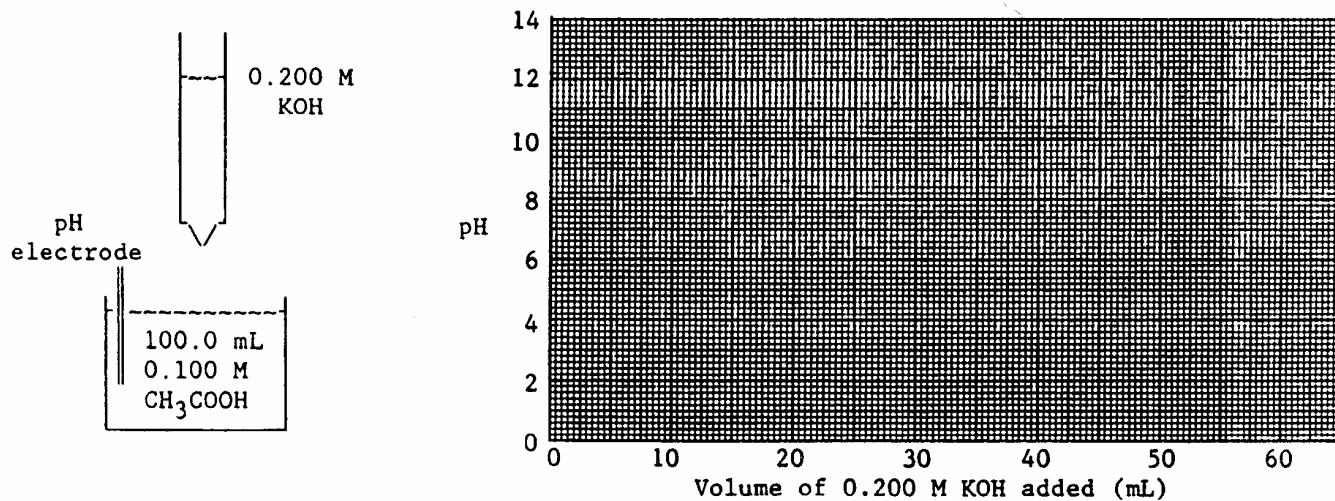
$$\text{pH} = 12.10$$

Data

mL of 0.100 M NaOH added	pH	System	Equation
0	2.87	weak acid	$K_a = \frac{x^2}{[\text{acid}]}$ $[\text{H}^+] = \sqrt{K_a [\text{acid}]}$
10 mL	4.14	weak acid + salt	$K_a = \frac{[\text{H}^+][\text{salt}]}{[\text{acid}]}$
25 mL	4.74	buffer	$[\text{H}^+] = K_a \frac{[\text{acid}]}{[\text{salt}]}$
50 mL	8.78	salt of weak acid + strong base	$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} [\text{salt}]}$ $K_b = \frac{K_w}{K_a} = \frac{x^2}{[\text{salt}]}$
60 mL	12.10	excess base	

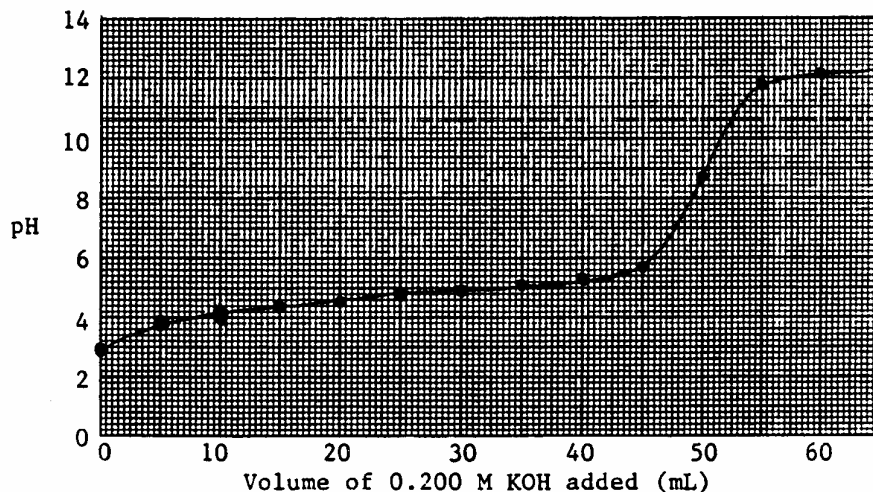
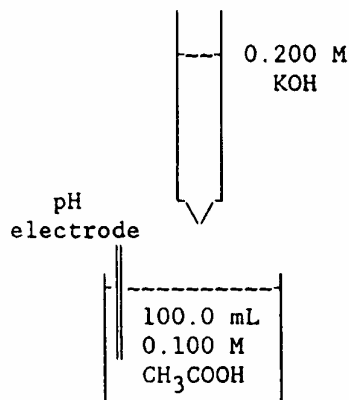
Titration of 100.0 mL of 0.100 M CH_3COOH with 0.200 M KOH: $\text{CH}_3\text{COOH} + \text{KOH} \rightarrow \text{KCH}_3\text{COO} + \text{H}_2\text{O}$

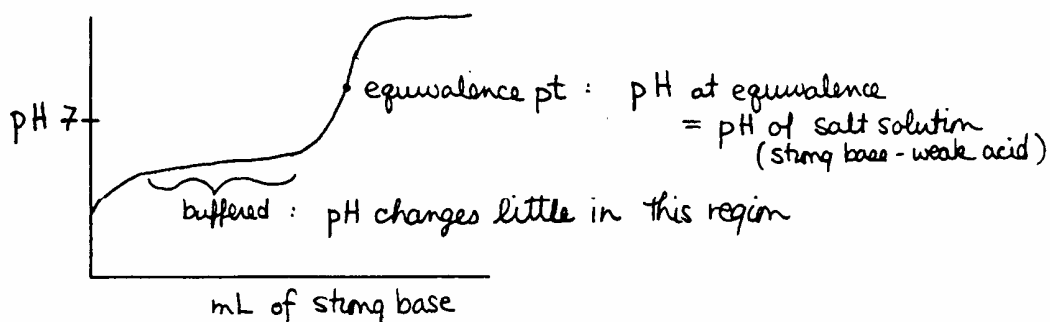
mL of 0.200 M KOH added	moles of KOH added	moles of CH_3COOH moles of KCH_3COO	System and Formula	$[\text{H}^+]$ or $[\text{OH}^-]$	pH
0.0	0.0	CH_3COOH : KCH_3COO :			
10.0		CH_3COOH : KCH_3COO :			
25.0		CH_3COOH : KCH_3COO :			
50.0		CH_3COOH : KCH_3COO :			
60.0		CH_3COOH : KCH_3COO :			



Titration of 100.0 mL of 0.100 M CH_3COOH with 0.200 M KOH: $\text{CH}_3\text{COOH} + \text{KOH} \rightarrow \text{KCH}_3\text{COO} + \text{H}_2\text{O}$

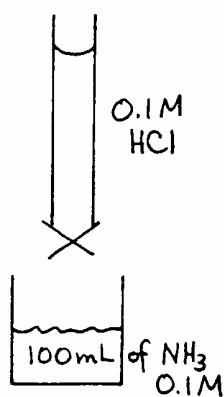
mL of 0.200 M KOH added	moles of KOH added	moles of CH_3COOH moles of KCH_3COO	System and Formula	$[\text{H}^+]$ or $[\text{OH}^-]$	pH
0.0	0.0	CH_3COOH : $0.100 \text{ M} \times 0.100 \text{ L} = 0.0100 \text{ mol}$ KCH_3COO : 0.0 mol	weak acid $[\text{H}^+] = \sqrt{K_a [\text{acid}]}$ $K_a = 1.8 \times 10^{-5}$	$[\text{H}^+] = 1.3 \times 10^{-3} \text{ M}$	2.87
10.0	# mol = $M \times \#L$ $= 0.200 \text{ M} \times 0.0100 \text{ L}$ $= 0.00200 \text{ mol}$	CH_3COOH : $0.0100 - 0.0020$ $= 0.0080 \text{ mol}$ KCH_3COO : 0.0020 mol	weak acid buffer $[\text{H}^+] = K_a \frac{\text{mol acid}}{\text{mol salt}}$	$[\text{H}^+] = 7.2 \times 10^{-5} \text{ M}$	4.14
25.0 HALFWAY TO EQUIVALENCE POINT	# mol $= 0.200 \text{ M} \times 0.0250 \text{ L}$ $= 0.00500 \text{ mol}$	CH_3COOH : $0.0100 - 0.0050$ $= 0.0050 \text{ mol}$ KCH_3COO : 0.0050 mol	weak acid buffer $[\text{H}^+] = K_a \frac{\text{mol acid}}{\text{mol salt}}$ but mol acid = mol salt $\therefore [\text{H}^+] = K_a$	$[\text{H}^+] = 1.8 \times 10^{-5} \text{ M}$	4.74
50.0 EQUIVALENCE POINT	# mol $= 0.200 \text{ M} \times 0.0500 \text{ L}$ $= 0.0100 \text{ mol}$	CH_3COOH : $0.0100 - 0.0100$ $= 0.0000 \text{ mol}$ KCH_3COO : 0.0100 mol	salt of weak acid and strong base $[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} [\text{salt}]}$ where $[\text{salt}] = \frac{0.0100 \text{ mol}}{0.150 \text{ L}}$	$[\text{OH}^-] = 6.1 \times 10^{-6} \text{ M}$ $[\text{H}^+] = 1.6 \times 10^{-9} \text{ M}$	8.78
60.0	# mol $= 0.200 \text{ M} \times 0.0600 \text{ L}$ $= 0.0120 \text{ mol}$	CH_3COOH : 0.0000 mol KCH_3COO : 0.0100 mol	excess strong base $[\text{OH}^-] = \frac{\text{mol excess base}}{\text{total V (L)}}$ $= \frac{0.0020 \text{ mol}}{0.100 \text{ L} + 0.060 \text{ L}}$ $= 0.0125 \text{ M}$	$[\text{H}^+] = 8.0 \times 10^{-13} \text{ M}$	12.10





Titration Curve for Strong Acid and Weak Base: (similar to BOP #37)

Consider 100 mL of 0.100 M NH_3 with 0.200 M HCl



① initial pH = pH of weak base solution

$$[\text{OH}^-] = \sqrt{K_b [\text{base}]}$$

② pH before equivalence = pH of basic buffer solution

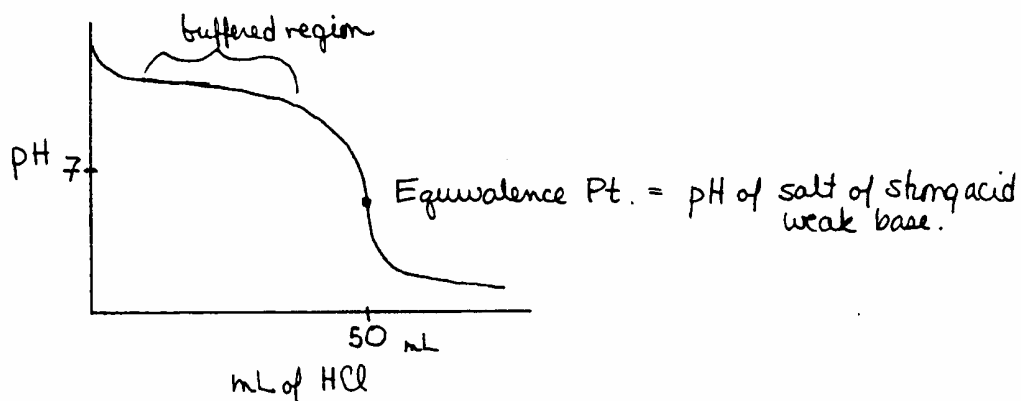
$$[\text{OH}^-] = K_b \frac{\text{mol base}}{\text{mol salt}}$$

③ pH at equivalence = pH of salt (strong acid/weak base acidic solution)

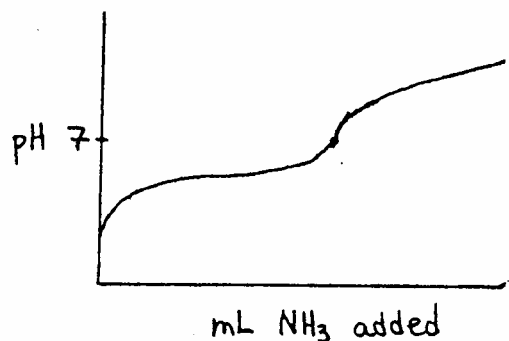
$$[\text{H}^+] = \sqrt{\frac{K_w}{K_b} [\text{salt}]}$$

④ pH after equivalence = pH of strong acid solution

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



Titration Curve for Weak Acid with Weak Base



Titration of CH_3COOH solution with NH_3

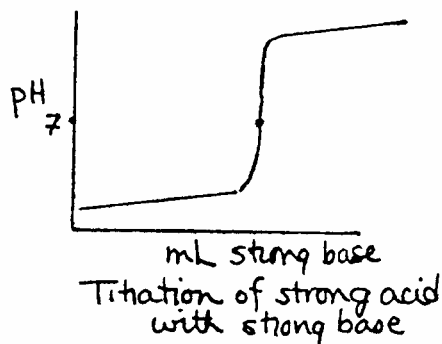
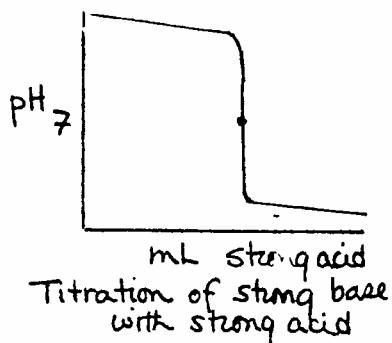
The equivalence point is at $\text{pH} = 7$

since $K_a = K_b$

(salt = $\text{NH}_4\text{CH}_3\text{COO}$ and both ions hydrolyze to the same extent)

Note that the equivalence pt is not sharp at all.

Comparison of Titration Curves :



Note:
very sharp
pH change
at equiv.

