Titration of a weak acid with strong base

Weak Acid:

- **Type of weak acid:**
- **Monoprotic** (contains 1 group 'hydrogen ion'). ➔ Ex: $CH_3COO\underline{H}$
- **Diprotic** (contains two group). ➔ Ex: $\underline{H_2}SO_4$
- **Triprotic** (contains three group). ➔ Ex: $\underline{H_3}PO_4$

➔ **each group has it own Ka value.**

- **Which dissociation group will dissociate first?**

➔ The group that has <u>higher Ka</u> value or i.e that has <u>lower pKa</u> value

- **pKa values** of weak acids can be determined **mathematically** or **practically** by the use of **titration curves.**

***Review the calculation of pH of weak acid/base*

Weak Acid con':

- Weak acids or bases do not dissociate completely, therefore an equilibrium expression with **Ka must be used.**

- **The Ka is a quantitative measure of the strength of an acid in solution.**

➔ since its value is always very low, Ka is usually expressed as pKa , where:

$$pKa = -\log Ka$$

- As an acid/base get **weaker**, its Ka/Kb gets smaller and pKa/pKb gets **larger.**

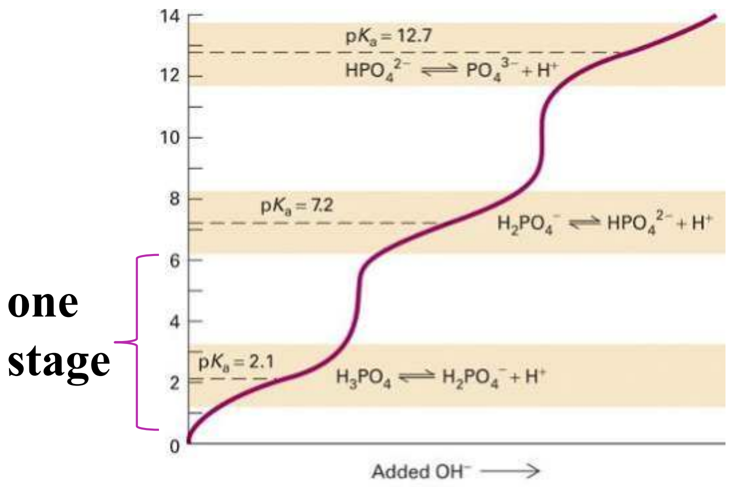
- **For example:**

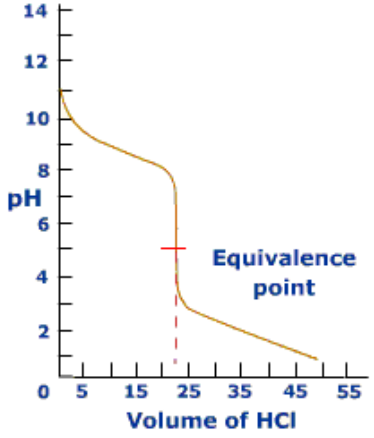
- HCl is a strong acid, it has **1×10^{7} Ka** value and **-7 pKa value**.

- CH_3COOH is a weak acid, it has **1.76×10^{-5} Ka** value and **4.75 pKa value.**

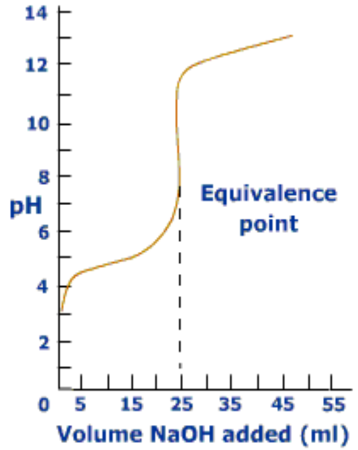
Titration Curves:

- **Titration curves** are produced by monitoring the pH of a given volume of a sample solution after successive **addition of acid or alkali**.
- The curves are usually plots of **pH** against the **volume of titrant added (acid or base).**
- There are many uses of titration, one of them is to indicate the pKa value of the **weak acid** by using the **titration curve**.
- Each dissociation group represent **one stage** in the **titration curve**.





The pH titration curve of weak base(NH_4OH) and strong acid (HCl)



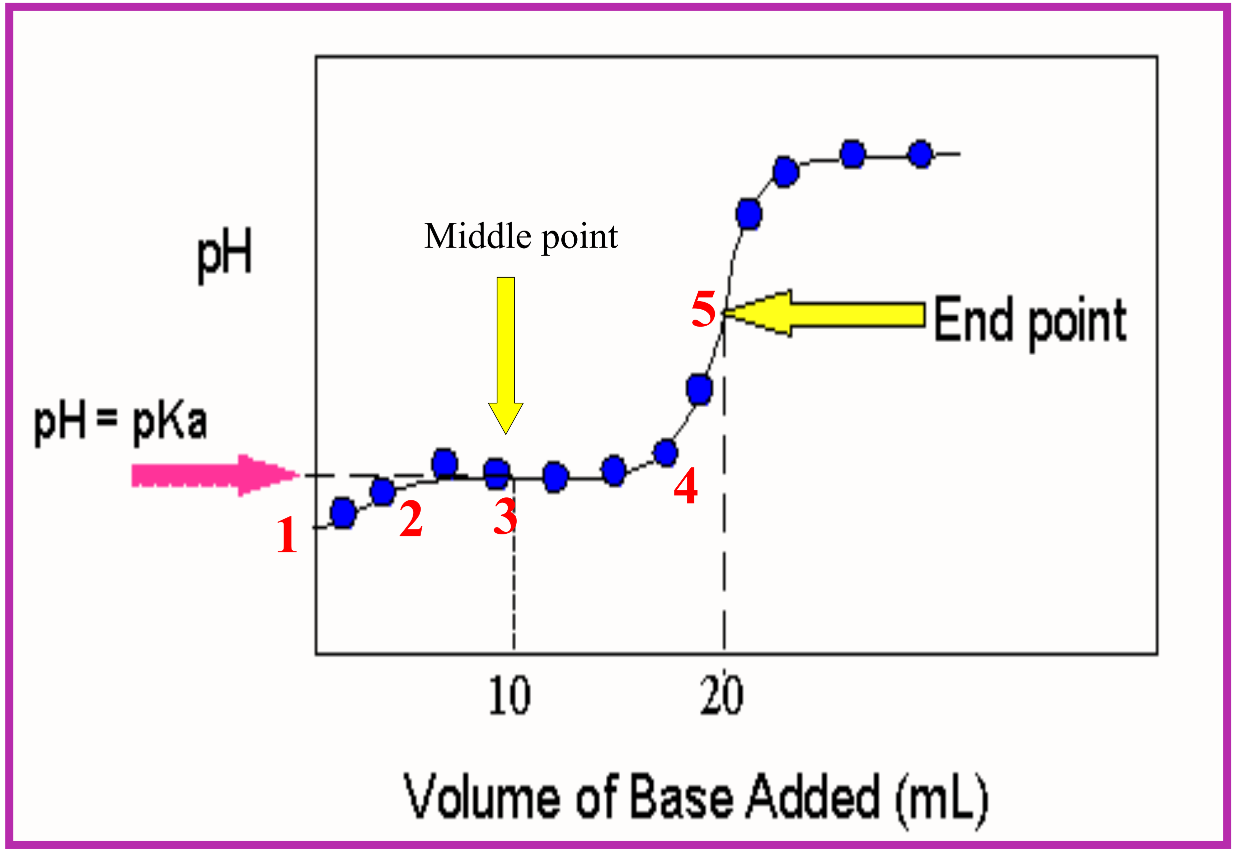
The pH titration curve of weak acid (CH_3COOH) and strong base (NaOH)

Titration curve of a weak acid with strong base:

[1] Before any addition of strong base the (starting point):

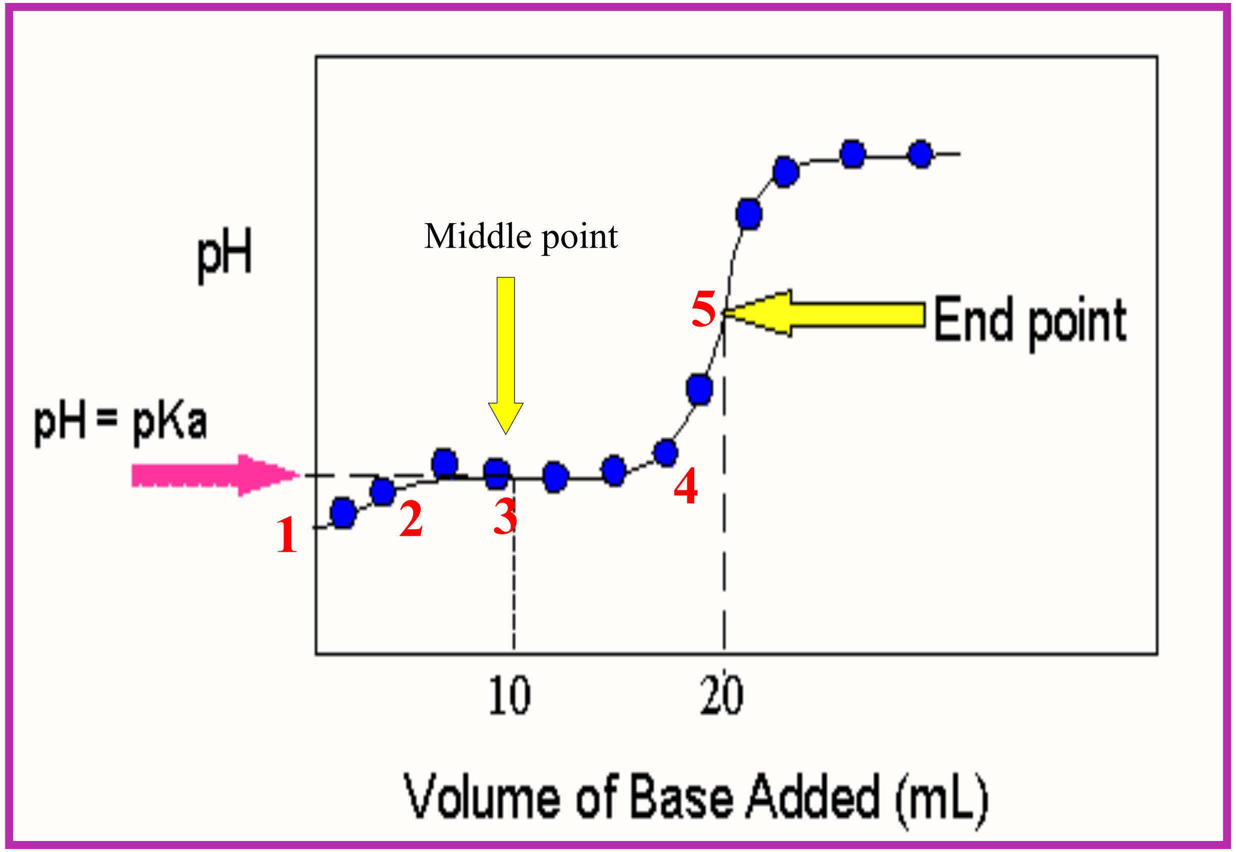
- ALL the weak acid is in the full protonation form [CH_3COOH]
- (Electron donor) .
- In this point **pH** of weak acid < **pKa**.
- We can calculate the pH from:

  pH = (pKa + p[HA]) / 2



Titration curve of a weak acid with strong base:

[2] When certain amount of strong base added (any point before the middle of titration):



- The weak acid is starting to dissociate **$[CH_3COOH] > [CH_3COO^-]$**

(Donor > Acceptor).

- In this point **pH** of weak acid < **pKa**.

- We can calculate the pH from:

$pH = (pKa + \log [A^-] / [HA])$

Titration curve of a weak acid with strong base:

[3] At middle of titration:

- **$[CH_3COOH] = [CH_3COO^-]$**

(Donor=Acceptor).

- In this point **pH = pKa**.

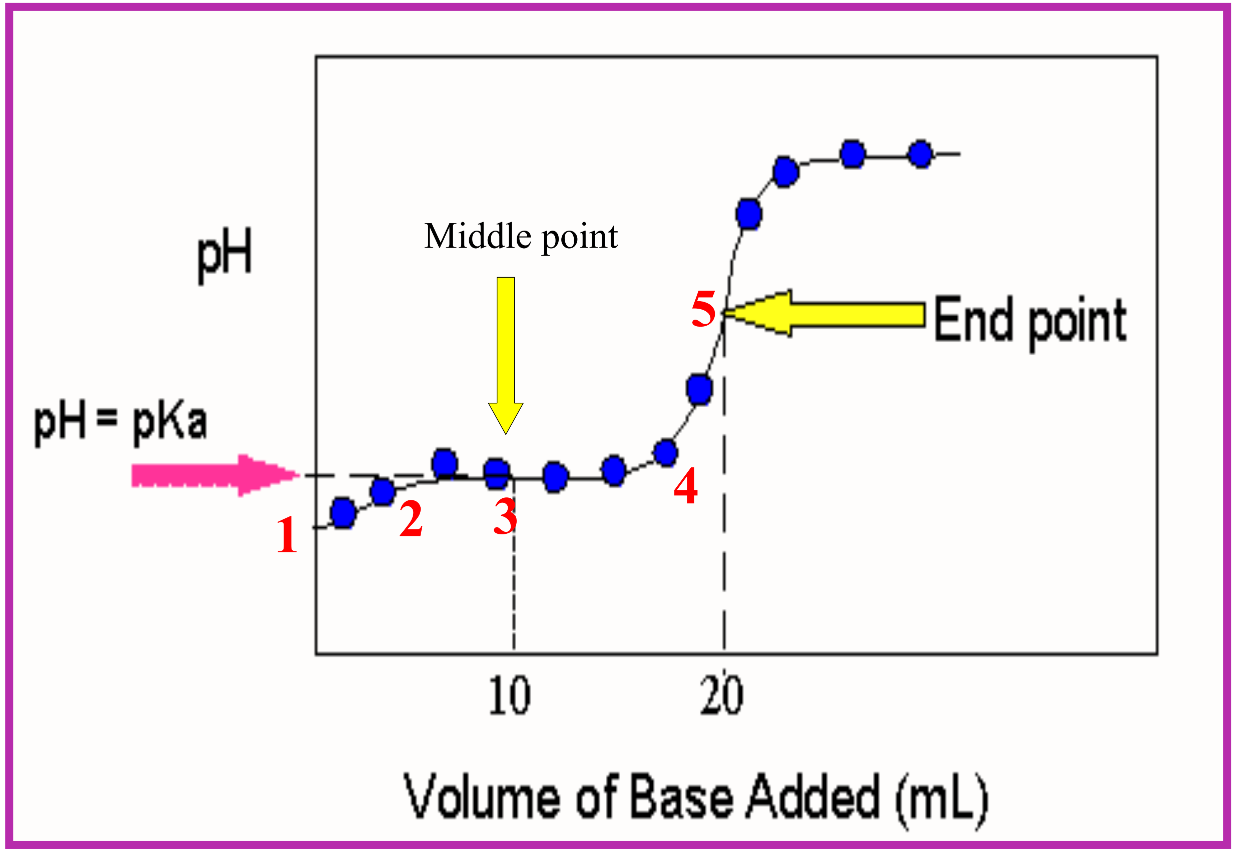
The component of weak acid work as a **Buffer** (A solution that can resistant the change of pH) .

- Buffer capacity= **pKa ± 1**

Note: pKa is defined as the pH value at middle of titration at which they will be [donor]=[acceptor].

- We can calculate the pH from:

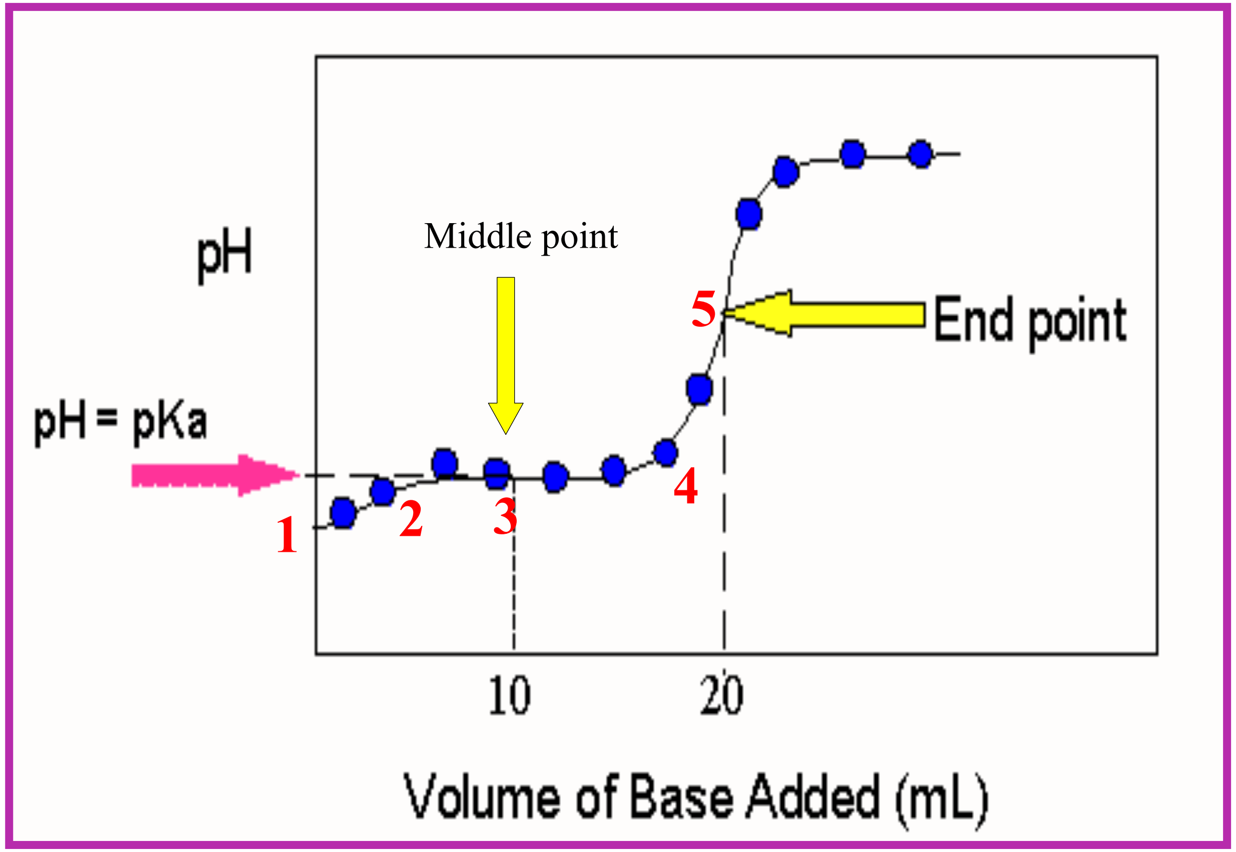
pH = (pKa + log [A-] / [HA])



Titration curve of a weak acid with strong base:

[4] At any point after mid of titration and before end point:

- **$[CH_3COOH] < [CH_3COO^-]$** (Donor < Acceptor) .
- In this point **pH > pKa.**
- We can calculate the pH from:
  $pH = (pKa + \log [A^-] / [HA])$



Titration curve of a weak acid with strong base:

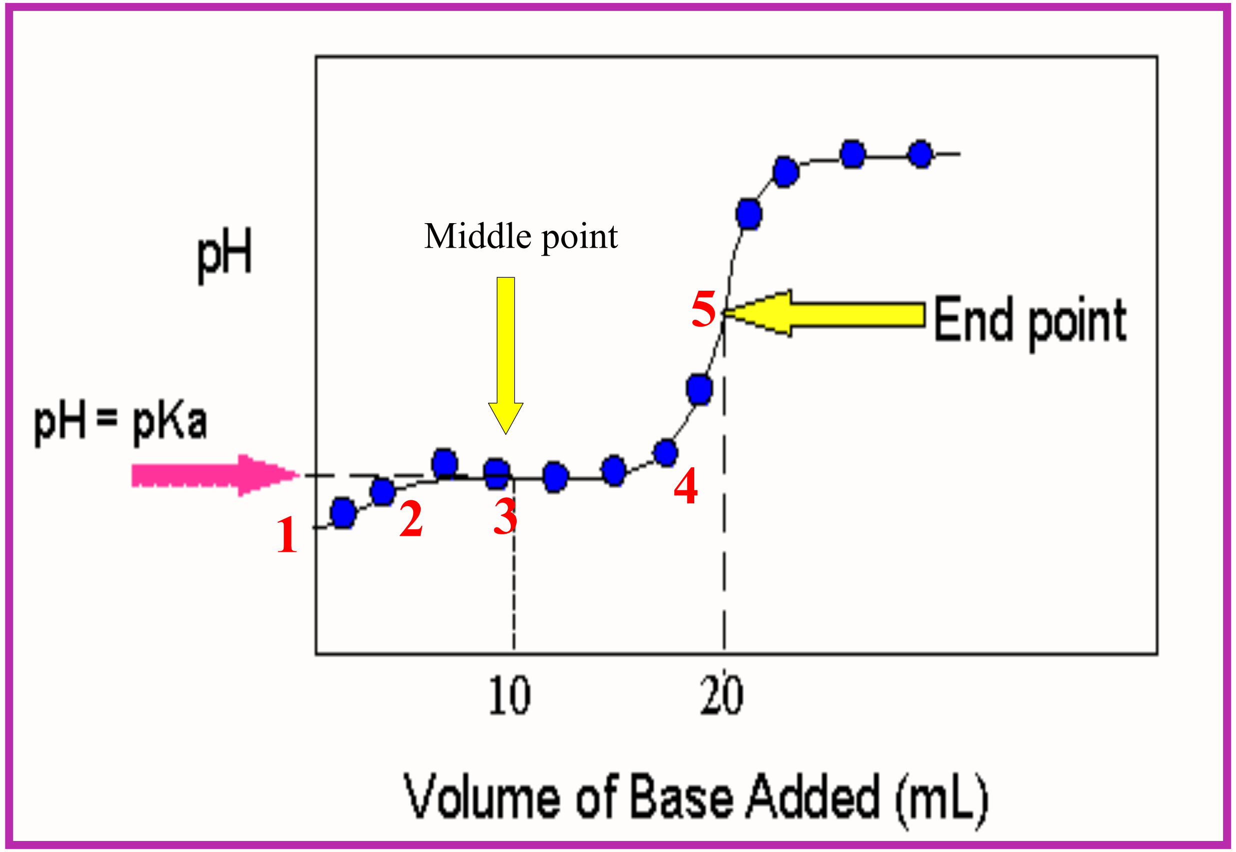
[5] At the end point :

- The weak acid is fully dissociated **[CH_3COO^-]** (electron acceptor).

- In this point **pH > pKa**.

- Approximately, all the solution contains CH_3COO^- , so we first must calculate pOH, then the pH:

$pOH = (pKb + p[A^-]) / 2$
$pH = pKw – pOH$
$^*pKb = pKw - pKa$



Calculating the pH at different point of the titration curve:

- **[1] At start point [Weak acid only]:**

$$pH = (pKa + p[HA]) / 2$$

- **[2] At any point within the curve [weak acid and conjugated base mix]:**

$$pH = (pKa + \log [A^-] / [HA])$$ **(Henderson-Hasselbalch equation)**

- **[3] At the end point [approximately conjugated base only]:**

$$pOH = (pKb + p[A^-]) / 2 \rightarrow pH = pKw - pOH$$

- **Henderson-Hasselbalch equation is an equation that is often used to :**

1. To calculate the pH of the Buffer.
2. To preparation of Buffer.
3. To calculated the pH in any point within the titration curve (Except starting and ending point)

Note:

- **If you start titration using 20 ml of the weak acid, In titration curve………..**

➔ The total volume of weak acid is 20 ml, we need 20 ml of strong base to full dissociate the group of weak acid.

➔ We can reach to middle titration if we add 10 ml of strong base (half the amount of 20 ml).

- **Bearing in mind that :**

1. The weak acid and the strong base (titrant) should have the same concentration (ex: 0.1 M HA and 0.1 M KOH).

2. The weak acid and strong base should have the same protonation and hydroxylation state respectively (ex: monoprotic acid (HA) and monohydroxy base (KOH)).

Example: **Determine the pH value of 500 ml of monoproteic weak acid (0.1M) , titrated with 0.1M KOH (pKa=5), at 0 ml and after the addition of:**
(1) 100 ml (2) 250 ml (3) 375 (4) 500 ml of KOH?

[1] pH at 0 ml of KOH?

➔ **FIRST STAGE**

pH= (pKa + p[HA]) / 2

At the start point, the pH depends only on the [HA] and the value of pKa

p[HA] = -log [HA]
p[HA] = -log [0.1] = 1

So,
pH = (5 + 1) / 2
pH = 3 ➔ pH<pKa

Example: Determine the pH value of 500 ml of monoproteic weak acid (0.1M) , titrated with 0.1M KOH (pKa=5), after addition of:
(1) 100 ml (2) 250 ml (3) 375 (4) 500 ml of KOH?

[1] pH after addition of 100 ml of KOH?

➔ **SECOND STAGE**
- pH= pKa + log[A-]/[HA]

-HA + KOH ➔ KA + H_2O

-we should calculate the **No. of moles of remaining [HA]** first because it is reflect the pH value at this stage.

Mole of HA remaining = mole of HA [original] – mole of KOH [added]
Moles of A^- = mole of KOH [added]

-No. of KOH [A^-] mole = 0.1 X 0.1 L = 0.01 mole
-No. of HA mole originally = 0.1 X 0.5 L =0.05 mole
-No. of HA mole remaining = 0.05 – 0.01 = 0.04 mole

So,
pH = 5 + log [0.01]/[0.04]
pH = 4.4 ➔ pH<pKa

[2] pH after addition of 250 ml of KOH?

➔ **MIDDLE STAGE**
- pH= pKa + log[A-]/[HA]

Mole of HA remaining = mole of HA [original] – mole of KOH [added]
Moles of A^- = mole of KOH [added]

-No. of KOH [A^-] mole = 0.1 X 0.25 L = 0.025 mole
-No. of HA mole originally = 0.1 X 0.5 L =0.05 mole
-No. of HA mole remaining = 0.05 – 0.025 = 0.025 mole

So,
pH = 5 + log [0.025] / [0.025]
pH=5 =pKa ➔ (at mid point , The component of weak acid work as a Buffer , has a buffering capacity 5 ± 1)

Note: the ratio of moles A^- / mole HA is same as [A^-]/[HA]

Example: Determine the pH value of 500 ml of monoproteic weak acid (0.1M) , titrated with 0.1M KOH (pKa=5), after addition of:
(1) 100 ml (2) 250 ml (3) 375 (4) 500 ml of KOH?

[3] pH after addition of 375 ml of KOH?

➔ **FOURTH STAGE**
- pH= pKa + log[A-]/[HA]

Mole of HA remaining = mole of HA [original] – mole of KOH [added]
Moles of A- = mole of KOH [added]

-No. of KOH [A^-] mole = 0.1 X 0.375 L = 0.0375 mole
-No. of HA mole originally = 0.1 X 0.5 L =0.05 mole
-No. of HA mole remaining = 0.05 – 0.0375 = 0.0125 mole

So,
pH = 5 + log [0.0375] / [0.0125]
pH= 5.48 ➔ pH>pKa "slightly"

[4] pH after addition of 500 ml of KOH?

➔ **END STAGE** (Note: 500 ml is the same volume of weak acid that mean the all weak acid are as [$CH3COO^-$]).

- pOH = (pKb + p[A^-])/2 ➔ pKb+pKa= 14 ➔**pKb=14-5=9**
- p[A-]= - log [A^-] ➔ [A^-]=??

[A-] = No. of a mole KOH / Total volume (L) *(Molarity formula)*
No. of a mole KOH= 0.1 X 0.5 = 0.05 mole
[A-] = 0.05/1 =0.05 M *(total volume = 500+500=1000= 1L)*

So ➔ **p[A-]= - log 0.05 = 1.3**
-pOH=(9+1.3)/2 = 5.15

pKw= pH + pOH , pKw = 14

pH=pKw-pOH

pH = 14 – 5.15 = 8.85 ➔ pH>pKa

Practical Part

Objectives:

- To study titration curves
- Determine the pKa value of a weak acid
- Calculate the pH value at a given point
- Reinforce the understanding of buffers

Method:

- You are provided with 10 ml of a **0.1M CH_3COOH** weak acid solution, titrate it with **0.1M NaOH.**
- Add the base drop wise mixing, and recording the pH after each **0.5 ml** NaOH added.
- Stop when you reach a pH=9.

ml of 0.1M NaOH	pH
0	
0.5	
1	
1.5	
….	

Results:

1. Record the values in titration table and plot a curve of pH versus ml of NaOH added.
2. Calculate the pH of the weak acid HA solution at the beginning and after the addition of **3ml**, **5ml**, and **10ml** of **NaOH** (**pKa = 4.76**)
3. Compare your calculated pH values with those obtained from the curve.
4. Determine the pKa value of weak acid, and compare its value with the theoretical value
5. At what pH-range did the acid show buffering behavior? What are the chemical species at that region, what are their proportions? What is the buffer capacity range?

ml of 0.1M NaOH	pH
0	
0.5	
1	
1.5	
….	

Results:

1. Determination of the pKa of weak acid from the curve
2. At what pH range did the acid show the best buffering behaviour? Is shown between the small brackets.
3. What are the chemical species in that region? CH_3COOH and CH_3COONa
4. What are their proportions?
5. What is the buffer capacity range? Is shown between the large brackets.