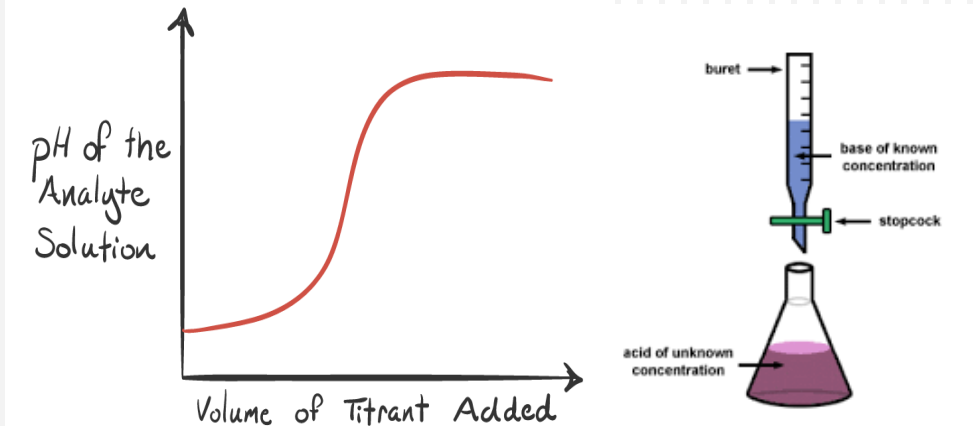


Titration Of A Weak Acid With Strong Base



Weak Acid :

- **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 it's value is always very low, Ka is usually expressed as pKa , where:

$$\text{pKa} = -\log \text{Ka}$$

- 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.

- **CH₃COOH** is a weak acid , it has 1.76×10^{-5} **Ka** value and **4.75 pKa** value.

□ **Type of weak acid:**

- Monoprotic (contain 1 group 'hydrogen ion'). → Ex: CH_3COOH

- Diprotic (contain two group). → Ex: H_2SO_4

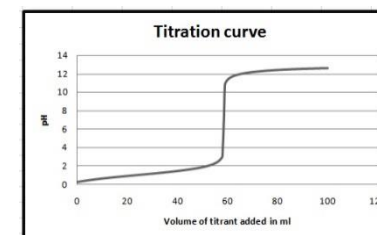
- Triprotic (contain three group). → Ex: H_3PO_4

→ each group has own K_a value.

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

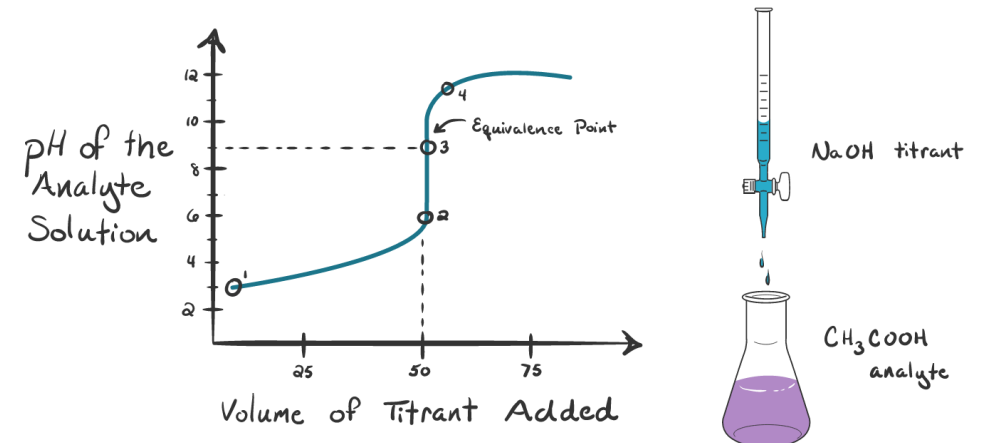
→ The group that has higher K_a value or i.e that has lower pK_a value

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



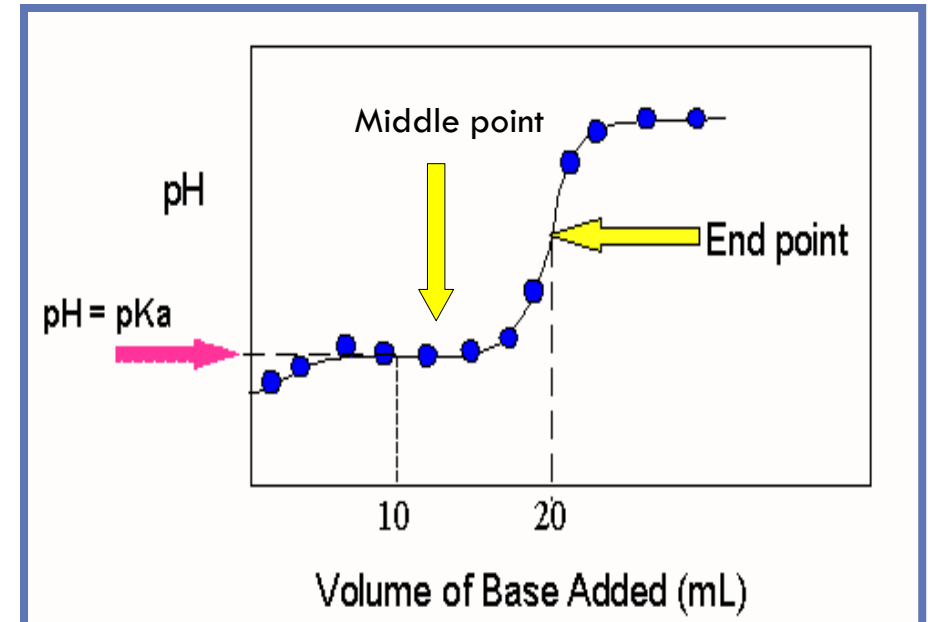
Titration Curve:

- **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.



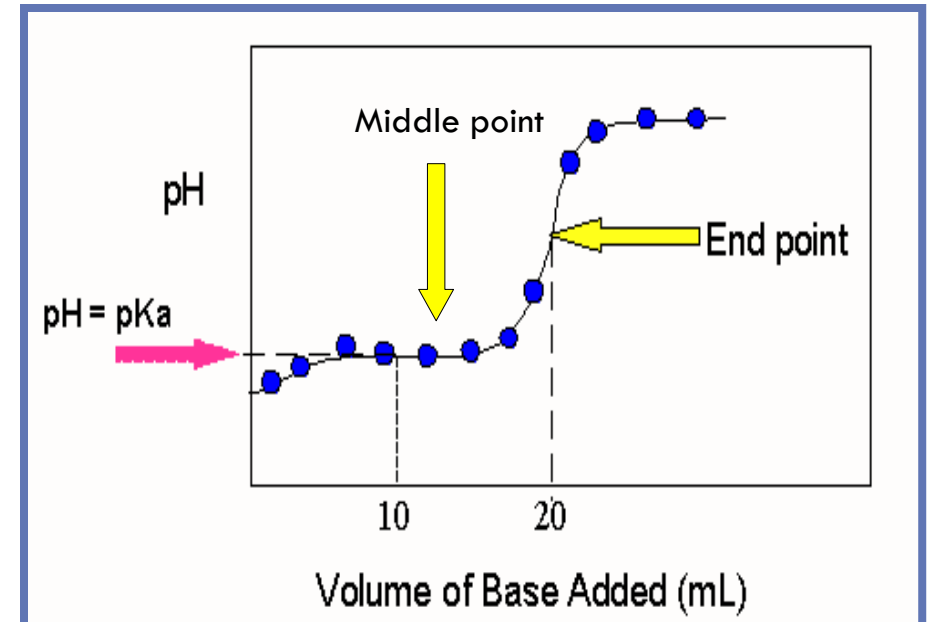
Titration curve of a weak acid with strong base:

- [1] Before any addition of strong base the (starting point):
 - ALL the weak acid is in the **full protonation** form [CH₃COOH] (electron donor) .
 - In this point pH of weak acid < pKa.
 - We can calculate the pH from:
$$\text{pH} = (\text{pKa} + \text{p[HA]}) / 2$$



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

- The weak acid is starting to dissociate $[\text{CH}_3\text{COOH}] > [\text{CH}_3\text{COO}^-]$
- (Donor > Acceptor).
- In this point pH of weak acid < pKa.
- We can calculate the pH from:
$$\text{pH} = (\text{pKa} + \log [\text{A}^-] / [\text{HA}])$$

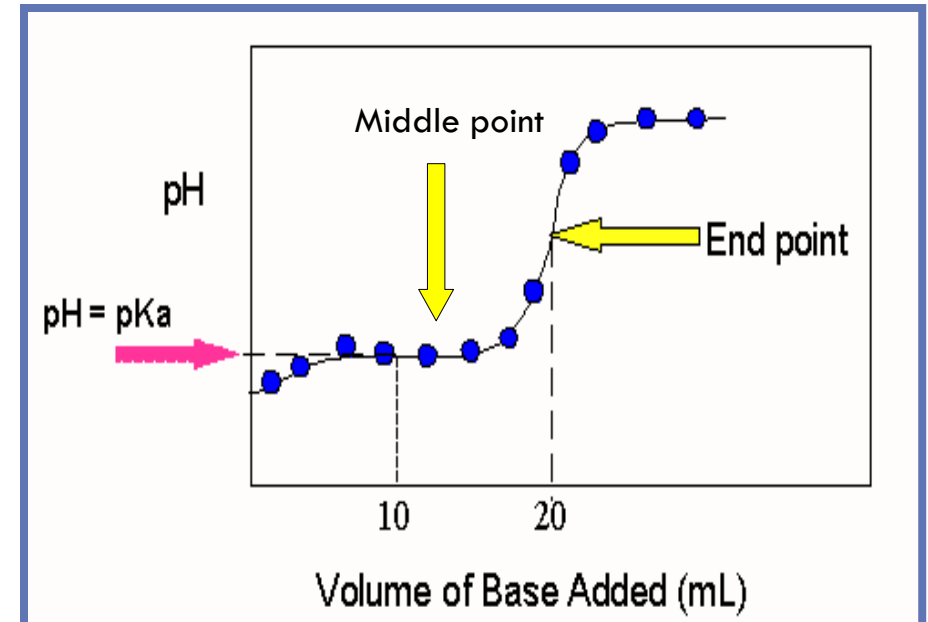


□ [3] At middle of titration:

- $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^-]$.
- (Donor=Acceptor).
- In this point $\text{pH} = \text{pKa}$.
- The component of weak acid work as a **Buffer** (A solution that can resistant the change of pH) .
- Buffer capacity= $\text{pKa} \pm 1$
- **pKa is defined as** the pH value at middle of titration at which they will be $[\text{donor}] = [\text{acceptor}]$.

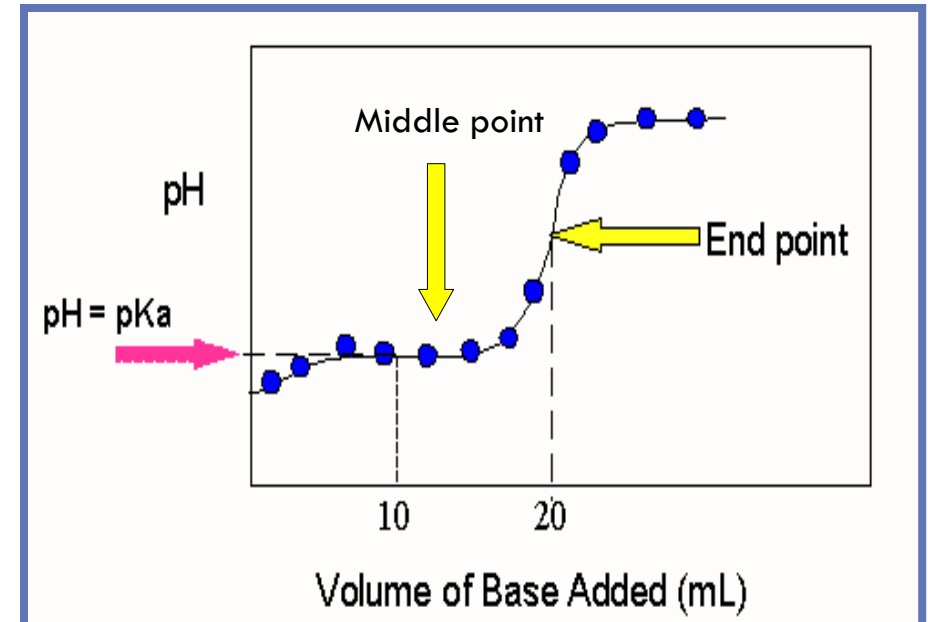
- We can calculate the pH from:

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



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

- $[\text{CH}_3\text{COOH}] < [\text{CH}_3\text{COO}^-]$.
- (Donor < Acceptor) .
- In this point $\text{pH} > \text{pKa}$.
- We can calculate the pH from:
$$\text{pH} = (\text{pKa} + \log [\text{A}^-] / [\text{HA}])$$



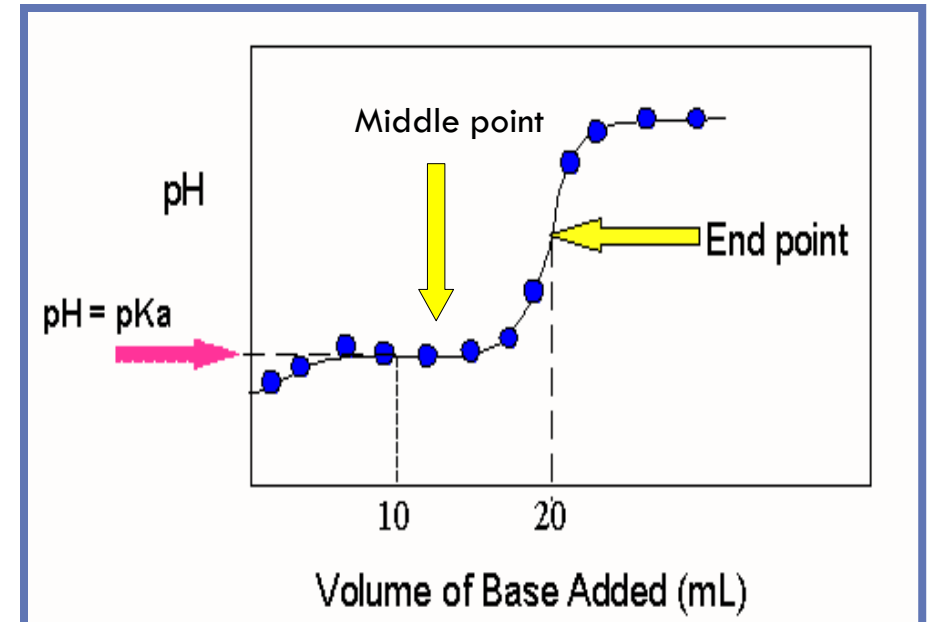
□ [5] At the end point :

- The weak acid is **fully dissociated** $[\text{CH}_3\text{COO}^-]$.
- (electron acceptor).
- In this point $\text{pH} > \text{pKa}$.
- Approximately, all the solution contains CH_3COO^- , so we first must calculate pOH , then the pH :

$$\text{pOH} = (\text{pKb} + \text{p}[A^-]) / 2$$

$$\text{pH} = \text{pKw} - \text{pOH}$$

$$*\text{pKb} = \text{pKw} - \text{pKa}$$



Calculating the pH at different point of the titration curve :

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

$$\text{pH} = (\text{pK}_a + \text{p}[\text{HA}]) / 2$$

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

$$\text{pH} = (\text{pK}_a + \log [\text{A}^-] / [\text{HA}]) \quad \text{-Henderson-Hasselbalch equation-}$$

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

$$\text{pOH} = (\text{pK}_b + \text{p}[\text{A}^-]) / 2 \rightarrow \text{pH} = \text{pK}_w - \text{pOH}$$

- 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.

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

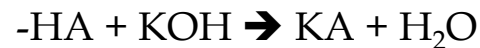
Example: Determine the pH value of 500 ml of monoprotic weak acid (0.1M) , titrated with 0.1M KOH (pKa=5), after addition of:

(1) 100 ml. (2) 250 ml (3) 375 (4) 500 ml of KOH?

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

→ SECOND STAGE

$$- \text{pH} = \text{pKa} + \log[\text{A}^-]/[\text{HA}]$$



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

-Mole of HA [original] - mole of KOH [added] = mole of HA remaining.

$$-\text{No. of KOH [A}^-] \text{ mole} = 0.1 \times 0.1 \text{ L} = 0.01 \text{ mole}$$

$$-\text{No. of HA mole originally} = 0.1 \times 0.5 \text{ L} = 0.05 \text{ mole}$$

$$-\text{No. of HA mole remaining} = 0.05 - 0.01 = 0.04 \text{ mole}$$

So,

$$\text{pH} = 5 + \log [0.01]/[0.04]$$

$$\text{pH}=4.4 \rightarrow \text{pH} < \text{pKa}$$

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

→ MIDDLE STAGE

$$- \text{pH} = \text{pKa} + \log[\text{A}^-]/[\text{HA}]$$

-Mole of HA [original] - mole of KOH [added] = mole of HA remaining.

$$-\text{No. of KOH [A}^-] \text{ mole} = 0.1 \times 0.25 \text{ L} = 0.025 \text{ mole}$$

$$-\text{No. of HA mole originally} = 0.1 \times 0.5 \text{ L} = 0.05 \text{ mole}$$

$$-\text{No. of HA mole remaining} = 0.05 - 0.025 = 0.025 \text{ mole}$$

So,

$$\text{pH} = 5 + \log [0.025] / [0.025]$$

pH=5=pKa → (at mid point , The component of weak acid work

as a Buffer , has a buffering capacity 5 ± 1)

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

→ FOURTH STAGE

$$- \text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

-Mole of HA **[original]** - mole of KOH **[added]** = mole of HA **remaining**.

$$-\text{No. of KOH } [\text{A}^-] \text{ mole} = 0.1 \times 0.375 \text{ L} = 0.0375 \text{ mole}$$

$$-\text{No. of HA mole originally} = 0.1 \times 0.5 \text{ L} = 0.05 \text{ mole}$$

$$-\text{No. of HA mole remaining} = 0.05 - 0.0375 = 0.0125 \text{ mole}$$

So,

$$\text{pH} = 5 + \log \frac{[0.0375]}{[0.0125]}$$

$$\text{pH} = 5.48 \rightarrow \text{pH} > \text{pK}_a \text{ "slightly"}$$

[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 $[\text{CH}_3\text{COO}^-]$).

$$- \text{pOH} = (\text{pK}_b + \text{p}[\text{A}^-]) / 2 \rightarrow \text{pK}_b = \text{pK}_w - \text{pK}_a$$

$$\rightarrow \text{pK}_b = 14 - 5 = 9$$

$$- \text{p}[\text{A}^-] = -\log [\text{A}^-] \rightarrow [\text{A}^-] = ??$$

$$\text{No. of a mole KOH} = 0.1 \times 0.5 \text{ (volume of base added)} = 0.05 \text{ mole}$$

$$-[\text{A}^-] = 0.05 / 1 = 0.05 \text{ M (total volume} = 500 + 500 = 1000 = 1\text{L)}$$

$$\text{So } \rightarrow \text{p}[\text{A}^-] = -\log 0.05 = 1.3$$

$$-\text{pOH} = (9 + 1.3) / 2 = 5.15$$

$$-\text{pH} = \text{pK}_w - \text{pOH}$$

$$\text{pH} = 14 - 5.15 = 8.85 \rightarrow \text{pH} > \text{pK}_a \text{ "slightly"}$$



Practical Part

Objectives

- To study titration curves.
- Determine the pK_a value of a weak acid.
- Calculate the pH value at a given point.

Method:

- You are provided with 10 ml of a **0.1M CH₃COOH** 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	
....	

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 after the addition of 3ml, 5ml, and 10ml of NaOH.
3. **Determine the pKa** value of weak acid.
4. **Compare** your calculated pH values with those obtained from Curve.
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	
....	