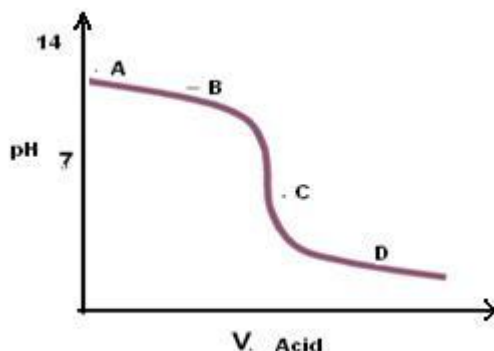


## Titration curves

Graphs of PH versus the volume of reagent added in a titration are known as titration curves.



### Strong acid- strong base:

Note the following features of the titration:

1-The PH changes slowly at first ,until the equivalence point is approached.

2-In the region of the equivalence point there is a rapid change in PH. There is a nearly vertical rise in the region from pH 4 to 10.

3- After the equivalence point is passed, the curve flattens out, as excess of NaOH is added.

The curve will become as :

EX/ compute the pH for additions of 0,10,20, and 30ml 0.1M NaOH to 100 ml 0.025 M HCl . Use the computed values and the pH of 7.00 at the equivalence point to plot the titration curve.

Solution /

1-Before any NaoH added or initial pH

[acid] = 0.025 M

$\text{pH} = -\log [\text{acid}] = -\log [\text{H}^+] = -\log 0.025 = -(-1.6) = 1.6$

2-After addition of 10.0ml of NaOH

No.mmols acid =  $0.025 \text{ mmol/ml} \times 100 \text{ ml} = 2.5 \text{ mmol}$

No.mmols acid(reacted)=n.moles NaOH =  $10.0 \text{ ml} \times 0.1 \text{ mmole/ml} = 1.0 \text{ mmol}$

No.mmols acid (unreacted) =  $2.5 - 1.0 = 1.5 \text{ mmol}$

Volume (solution) =  $100 + 10 = 110 \text{ ml}$

[acid] unreacted =  $[H^+] = 1.5 \text{ mmol} / 110 \text{ mmol} = 0.0136 \text{ M}$

pH =  $-\log [H^+] = -\log 0.0136$

$$= -(-1.866) = 1.866$$

3- At equivalence point after addition 25 ml of NaOH

At the equivalence point:

$[H_3O]^+ = [OH^-] = 10^{-7}$

$n_{HCl} - n_{NaOH} = 0 \rightarrow \text{eq. point}$

pH=7  $\rightarrow$  Bromothymol blue

4- After addition excess of NaOH , 30 ml NaOH added

no.mmols NaOH (react) = no.mmols acid = 2.5 mmol

no.mmols NaOH (added) =  $30.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 3.0 \text{ mmol}$

no.mmols(NaOH) unreacted (excess) =  $3.0 - 2.5 = 0.5 \text{ mmol}$

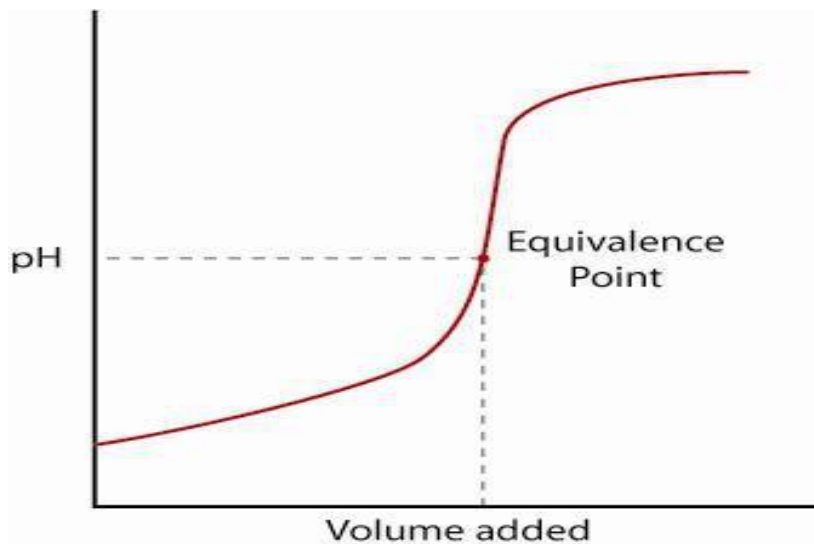
volume of solution =  $100 + 30 = 130 \text{ ml}$

[base]excess =  $[OH^-] = 0.5 \text{ mmol} / 130 \text{ ml} = 0.0038$

pOH =  $-\log [OH^-] = -\log 0.0038$

$$= -(-2.415) = 2.415$$

pH =  $14 - 2.415 = 11.585$



### **Weak acid – strong base**

The curve will be become as :

EX/ compute the pH of 25.0 ml 0.1 M acetic acid at addition of 0,5,10,12.5,20,25,and 30 ml 0.1 M NaOH ?  $K_a = 1.8 \times 10^{-5}$  ,  $pK_a = 4.76$

Solution /

1-before added any NaOH or initial pH

$$pH = 1/2 (pK_a - \log M_a)$$

$$pH = 1/2 (4.76 - \log 0.1)$$

$$pH = 1/2 (4.76 + 1) = 1/2 (5.76)$$

$$= 2.88$$

2-After addition 5.0 ml NaOH

$$pH = pK_a - \log \text{mmoles acid (unreacted)} + \log \text{mmoles salt/NaOH}$$

$$\text{No. mmoles HCl} = 25.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No. mmoles NaOH} = 5.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 0.5 \text{ mmol}$$

$$\text{No. mmoles HCl (unreacted)} = 2.5 - 0.5 = 2.0 \text{ mmol}$$

$$pH = 4.76 - \log 2.0 + \log 0.5$$

$$= 4.76 - 0.30 - 0.30 = 4.16$$

### 3- After addition of 12.5 ml of NaOH

في هذه الحالة يتم معادلة نصف الحامض وان تركيز الحامض يصبح مساويا الى تركيز الملح لذلك فان :

$$pH = pka$$

$$pH = 4.76$$

$$\text{No. mmoles HCl} = 25 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No. mmoles NaOH (salt)} = 12.5 \text{ ml} \times 0.1 \text{ mmol/ml} = 1.25 \text{ mmol}$$

$$\text{No. mmol HCl (unreacted)} = 2.5 - 1.25 = 1.25 \text{ mmol}$$

$$pH = pka - \log \text{ mmoles acid unreacted} + \log \text{ mmoles salt (NaOH)}$$

$$= 4.76 - \log 1.25 + \log 1.25$$

$$pH = 4.76$$

### 4- At eq .point (after addition of 25.0 ml of NaOH)

$$\text{No. mmoles acid} = 2.5 \text{ mmol}$$

$$\text{No. mmoles NaOH} = 25.0 \text{ ml} \times 0.1 \text{ mmol/ml} = 2.5 \text{ mmol}$$

$$\text{No .mmoles acid (unreacted )} = 2.5 - 2.5 = 0 \quad \text{this is eq . point}$$

ملاحظة:- عندما يكون عدد مولات القاعدة المضافة مساوية لعدد مولات الحامض الاصلي فان تلك هي نقطة التكافؤ ، والمحلول في هذه الحالة يحتوي على خلاص الصوديوم فقط لذلك يمكن حساب pH بالشكل التالي :

$$pH = 1/2 (pkw + pka + \log Ms)$$

$$pkw = 14 \quad \text{from } kw = 1 \times 10^{-14}$$

$$pka = 4.76 \quad \text{from } ka = 1.8 \times 10^{-5}$$

$$Ms = [ \text{salt} ] = (\text{no. mmols NaOH}) / (\text{total volume} ) = (25.0 \text{ ml} \times 0.1 \text{ M} ) / 25 + 25$$

$$= 2.5 / 50 = 0.05 \text{ M}$$

$$pH = 1/2 ( 14 + 4.76 + \log 0.05)$$

$$= 1/2 ( 14 + 4.76 - 1.30 )$$

$$= 8.73 \rightarrow \text{phenolphthalein}$$

5- After eq . point (excess of NaOH ) addition of 25.1 of NaOH

No.mmoles HCl = 25 ml  $\times$  0.1 mmol/ml = 2.5 mmol

No.mmoles NaOH = 25.1 ml  $\times$  0.1 mmol/ml = 2.51 mmol

No.mmol NaOH excess = 2.51 – 2.5 = 0.01 mmol

Volume =( 25 + 25.1)ml = 50.1ml

$[\text{OH}^-] = 0.01 \text{ mmol} / 50.1 \text{ ml} = 0.0001996\text{M}$

$\text{pOH} = -\log [\text{OH}^-] = -\log 1.996 \times 10^{-4} = 3.7$

$\text{pH} = 14 - 3.7 = 10.3$

