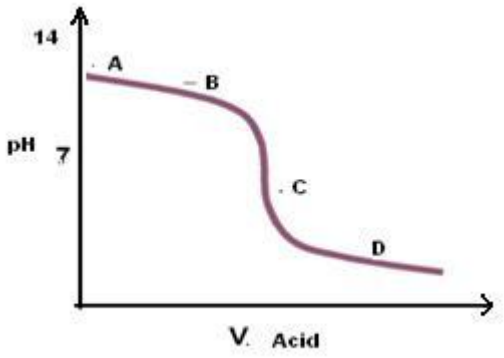
Titration curves

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

pH = -log [acid] = -log [H+] = -log 0.025= -(-1.6) = 1.6

2-After addition of 10.0ml of NaOH

No.mmols acid = 0.025 mmol/ml × 100 ml =2.5 mmol

No.mmols acid(reacted)=n.moles NaoH =10.0 ml × 0.1 mmole/ml=1.0 mmol

No.mmols acid (unreacted) =2.5 – 1.0 = 1.5 mmol

Volume (solution) =100+10 = 110 ml

[acid] unreacted =$[H^+]$ = 1.5mmol/110mmol =0.0136 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}

$n_{HCl} - n_{NaOH} = 0$ → eq.point

PH=7 → 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 ml ×0.1 mmol/ml = 3.0 mmol

no.mmols(NaOH) unreacted (excess) =3.0 -2.5 = 0.5 mmol

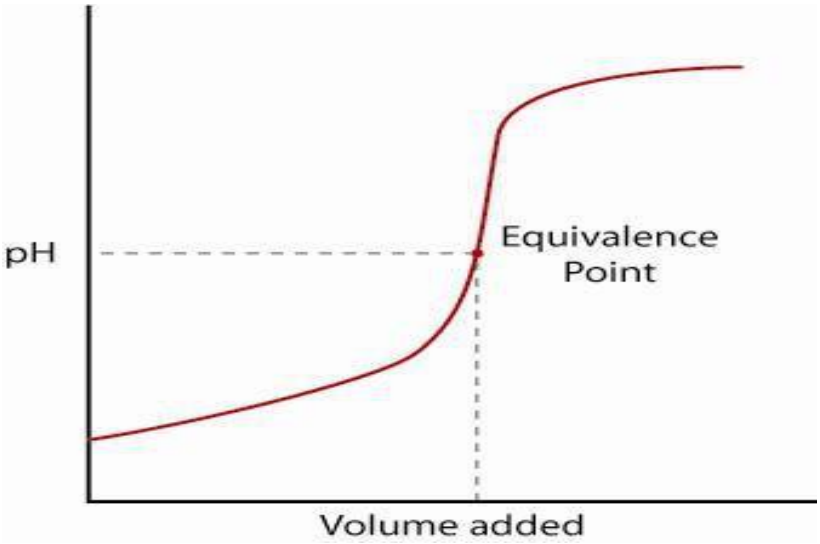
volume of solution = 100 +30 =130 ml

[base]excess =$[OH^-]$ = 0.5mmol/130ml = 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 ? ka =1.8× 10^{-5} , pka =4.76

Solution /

1-before added any NaOH or initial pH

pH= 1/2 (pka –log Ma)

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 = pka – log mmoles acid (unreacted) + log mmoles salt/NaOH

No.mmoles HCl = 25.0 ml ×0.1 mmol/ml =2.5 mmol

No.mmoles NaOH = 5.0 ml × 0.1 mmol/ml = 0.5 mmol

No.mmoles HCl (unreacted) = 2.5 – 0.5 = 2.0 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

No.mmoles HCl = 25 ml × 0.1 mmol/ml = 2.5 mmol

No.mmoles NaOH (salt) = 12.5 ml × 0.1 mmol/ml = 1.25 mmol

No.mmol HCl (unreacted) =2.5 – 1.25 = =1.25 mmol

pH = pka – log mmoles acid unreacted + log 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)

No.mmoles acid = 2.5 mmol

No.mmoles NaOH = 25.0 ml × 0.1 mmol/ml = 2.5 mmol

No .mmoles acid (unreacted) = 2.5 – 2.5 = 0 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 خلات الصوديوم فقط لذلك يمكن حساب pH بالشكل التالي :

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

pkw = 14 from kw= 1×10^{-14}

pka = 4.76 from ka = 1.8×10^{-5}

Ms = [salt] = (no.mmols NaOH)/(total volume) = (25.0ml ×0.1 M)/ 25+25

= 2.5 / 50 = 0.05 M

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

= 1/2 (14 +4.76 – 1.30)

= 8.73 → phenolphthalein

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

No.mmoles HCl = 25 ml × 0.1 mmol/ml = 2.5 mmol

No.mmoles NaOH = 25.1 ml × 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

$[OH^-]$ = 0.01 mmol /50.1 ml = 0.0001996M

pOH = - log $[OH^-]$ = - log 1.996 x 10^{-4} = 3.7

pH = 14 – 3.7 = 10.3