lect 23:Conductometric Titrations

Conductometry is a measurement of electrolytic conductivity to monitor a progress of chemical reaction. Conductometry has notable application in analytical chemistry, where **conductometric titration** is a standard technique.

conductometric titration: In this method we determine the point where reaction is completed with the help of a conductometer that measures the changes in conductance of solution produced by the ions in the solution.This point at which this transition occurs is called Equivalence point.

At Equivalence point we measure the volume of base used to neutralize the acid ions completely in the solution. Putting these values in formula we can get the strength of acid

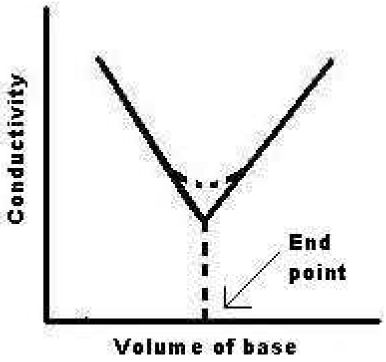
The principle of conductometric titration is based on the fact that during the titration,one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added.

1-Strong Acid with a Strong Base, e.g. HCl with NaOH:

$HCl + NaOH \rightarrow NaCl + H_2O$

$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$

Before titration the conductance is high which is due to **$HCl \rightarrow H^+ + Cl^-$** mobility of **$H^+$** is 350 and that of **$Cl^-$** ion is 73. Upon addition of **NaOH** the **H^+** ion reacts with **OH^-** ion to form the very weakly ionized water molecule. This means that the **H^+** ion is removed from the medium and replaced by **Na^+** ion which has a mobility of 43; thus a continuous abrupt decrease in conductance occurs during the titration till the end point. Beyond the end point there is **excess Na^+** and **OH^-** ions with 43 and 198 mobility due to continuous addition of **NaOH** So there is continuous increase in conductance and the curve will have a V shape , the end point is the minimum of the curve.

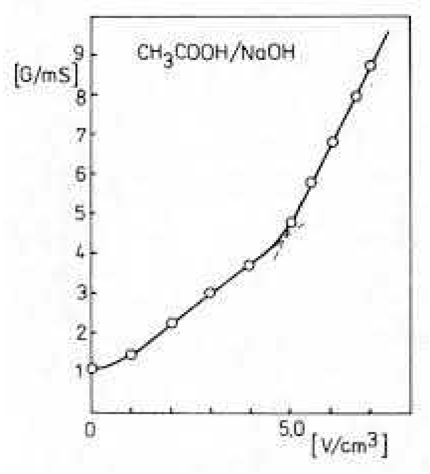


Conductometric titration of a strong acid (HCl) vs. a strong base(NaOH) .

2. **Weak Acid with a Strong Base, e.g. acetic acid with NaOH:**

$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$

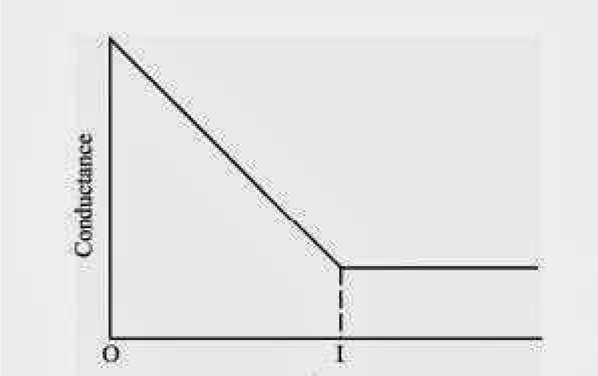
Before titration low initial conductance is observed due to low H^+ obtained during dissociation of weak CH_3COOH.During titration we can observe slight decrease of conductance due to consumption of H^+ . During progress of titration we can observe slight increase in conductancedue to the presence of CH_3COO^- &Na^+ and nearly constant H^+ due to the buffer action of the produced CH_3COONa and the remaining CH_3COOH. After end point excess NaOH will lead to increase in conductance due to increasingof Na^+ and OH^- .



Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH).

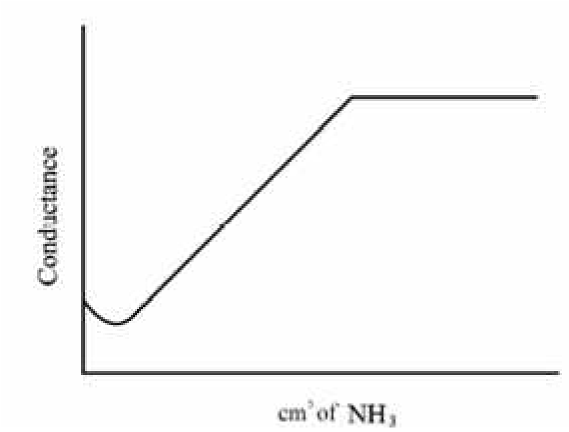
3. **Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia**:

Initially the conductance is high and then it decreases due to the replacement ofH+. But after the endpoint has been reached the graph becomes almosthorizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.



Conductometric titration of a strong acid (H_2SO_4) vs. a weak base(NH_4OH**)**.

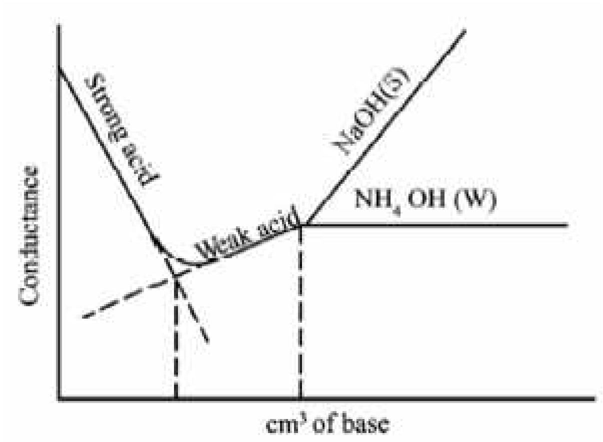
4. **Weak Acid with a Weak Base**: The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base.After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting.



Conductometric titration of a weak acid (acetic acid) vs. a weak base (NH_4OH).

❑ 5. **Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base**: The initial conductivity is high it is due to **HCl** which by common ion effect suppress the ionization of **H_3COOH**. Upon titration; decrease in conductivity occurs due to replacement of **H^+** ion with mobility 350

by **Na^+** ion with mobility 43 , till all the **H^+** ions from **HCl** are neutralized.**CH_3COOH** will thus ionize and react with **NaOH**.The change in conductivity will take place in similar way as described above.



Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH_3COOH) vs. a strong base (NaOH) or a weak base (NH_4OH).

Aggregated ions

$$M^+A^- \leftrightarrow MA \leftrightarrow M^+ + A^-$$

$$\theta C \quad C \quad \alpha C \quad \alpha C$$

$$MAM^+ \leftrightarrow MA + M^+$$

$$\acute{\alpha} C \quad \alpha C \quad C$$

$$AMA^- \leftrightarrow MA + A^-$$

$$\acute{\alpha} C \quad \alpha C \quad C$$

Where MA 1:1 elwctrolyte,A^- and M^+ are anion and cation respectively, M^+A^- is nonconducting ion pair, MAM^+ and AMA^- are conducting triple ions.

Let us consider the equilibrated reaction:

$MA \leftrightarrow M^+ + A^-$

$k_1=[M^+][A^-]/[MA^+]$

$k_1=(\alpha C)(\alpha C)/(C)$

$\alpha=(k_1/C)^{1/2}$ ……1

Where k_1 is the equilibrium constant.

For equilibrated reaction

$MAM^+ \leftrightarrow MA + M^+$

$k_2=[MA][M^+]/[MAM^+]$

$k_2=(C)(\alpha C)/(\acute{\alpha} C)$

$k_2= \alpha C/\acute{\alpha}$……….2

substitution eqn 1 into eqn 2

$k_2= =(k_1/C)^{1/2} C/\acute{\alpha}$

$k_2= =(k_1C)^{1/2} / \acute{\alpha}$

$\acute{\alpha}==(k_1/C)^{1/2}C/k_2$

$\acute{\alpha}==(k_1C)^{1/2} / k_2$

Equivalent conductance can be represented as

$\Lambda=\alpha\Lambda_0+ \acute{\alpha}\, \Lambda_0'$

$\Lambda=(k_1/C)^{1/2}\Lambda_0+ (k_1C)^{1/2} / k_2\Lambda_0$

$\Lambda= k_1^{1/2} \Lambda_0/C^{1/2}+ (k_1^{1/2}/ k_2) \Lambda_0C/ C^{1/2}$

$\Lambda\, C^{1/2}= k_1^{1/2} \Lambda_0+ (k_1^{1/2}/ k_2) \Lambda_0C$

Plotting of $\Lambda\, C^{1/2}$ versus C gives a straight line with a slope equal of $(k_1^{1/2}/ k_2)\, \Lambda_0$ and intercept equal of $k_1^{1/2}\, \Lambda_0$.The later equation can be rewritten as following:

$\Lambda = A/C^{1/2} +BC^{1/2}$

Where A equal of $k_1^{1/2}\, \Lambda_0$ and B is equal of $(k_1^{1/2}/ k_2)\, \Lambda_0$.The relationship between equivalent conductance Λ and $C^{1/2}$ is indirect as a result of formation of an ion pairs that restricted the conduction by free ions M^+ and $A^-$when the concentration is increases until the equivalent conductance reaches the minimum value. Above that, any excess increasing of concentration leads to increasing of Λ as a result of formation of conducting triple ions MAM^+ and AMA^-.