Chapter 4

ELECTROCHEMISTRY Lecture/Lession Plan -2

ELECTROCHEMISTRY

4.1 Kohlrausch's law

Kohlrausch observed that the difference in equivalent conductance of a pair of electrolyte is same when the pair of electrolyte consists of same counter ion at same temperature and when same solvent is being used.

   Thus from the table we can see that difference in equivalent conductance at infinite dilution between K and Li salt is always almost same as the anion counter part is same for the pair. This can be explained as at infinite dilution, there exists no other attraction between ions, the conductance of any particular ion of different electrolyte will be same. The ionic conductance of chloride ion will be same for a sodium chloride solution as well as for a potassium chloride solution at infinite dilution. Hence the difference of conductance between NaCl and KCl will be the difference between Na^+ and K^+ as the value of chloride ion will cancel out. Thus it can be said that the attraction among ions at infinite dilution will be almost negligible.

The equivalent conductance of an electrolyte will be equal to the sum of the ionic conductances of the corresponding ions created by that electrolyte at infinite dilution.

If equivalent conductance of an electrolyte at infinite dilution is Λ_0 and ion conductance of cation and anion are λ_c and λ_a respectively then according Kohlrausch's law-

$$\Lambda_0 \quad = \quad n_c\lambda_c + n_a\lambda_a$$

; where n_c and n_a are number of cation and anion respectively. Thus according to this law the equivalent conductance of $Ca_3(PO_4)_2$ at infine dilution will be

$$\Lambda_0{}_{Ca_3(PO_4)_2} \quad = \quad 3\lambda_c{}_{Ca^{+2}} + 2\lambda_a{}_{PO_4{}^{-3}}$$

   By using Kohlrausch's law, we can determine the equivalent conductance of an weak electrolyte at infinite dilution which can not be determined experimentally. If we need to determine the equivalent conductance of benzoic acid (an weak electrolyte) at infinite dilution then we can write logically that-

$$
\begin{aligned}
\Lambda_0(\text{PhCOONa}) &= l^0_{\text{Na}^+} + l^0_{\text{PhCOO}^-} \\
\Lambda_0(\text{NaCl}) &= l^0_{\text{Na}^+} + l^0_{\text{Cl}^-} \\
\Lambda_0(\text{HCl}) &= l^0_{\text{H}^+} + l^0_{\text{Cl}^-} \\
\Lambda_0(\text{PhCOONa}) + \Lambda_0(\text{HCl}) - \Lambda_0(\text{NaCl}) &= l^0_{\text{Na}^+} + l^0_{\text{PhCOO}^-} + l^0_{\text{H}^+} + l^0_{\text{Cl}^-} - l^0_{\text{Na}^+} - l^0_{\text{Cl}^-} \\
&= l^0_{\text{PhCOO}^-} + l^0_{\text{H}^+} \\
&= \Lambda_0(\text{PhCOOH})
\end{aligned}
$$

4.2 Conductometric titration

Conductance is being measured in this type of titration method, a graph is generally plotted (conductance vs titrant) and from graph we generally determine the equivalent point of the titration. No indicator needed in these type of titrations; the plotted graph itself will indicate the end point of the reaction. Depending upon the dissociation in aqueous solution and ionic mobility, the nature of different conductometric titration graph can be predicted. Generally an acid is being titrated against a base

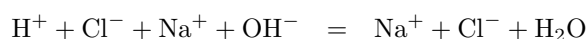### 4.2.1 Titration of a strong acid and strong base

An example of a strong acid and strong base are HCl and NaOH respectively as they dissociate completely in aqueous medium. Generally an acid is being titrated against a base and hence acid solution is taken in a beaker and the base is taken in burette. As the acid is a strong acid it will dissociate into H^+ and OH^- ion completely and hence number of ions will be maximum in the solution. Furthermore as H^+ ion has very large ionic mobility and hence ionic conductance, the solution will show high conductance.

Titration curve: Strong acid vs strong base
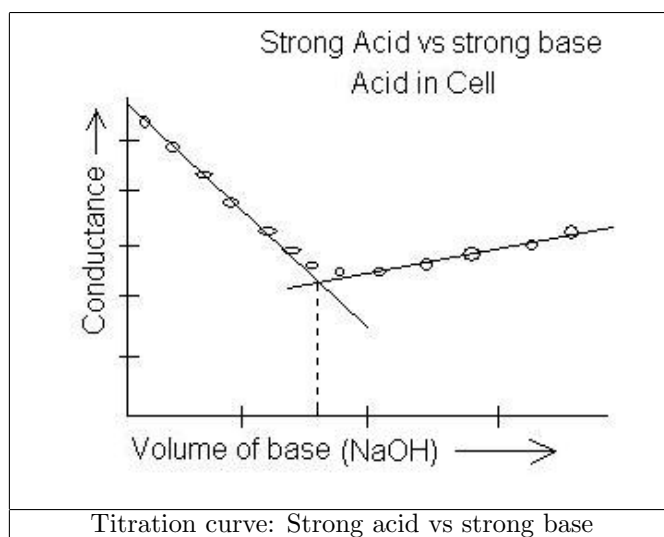
Now as we add base drop by drop from burette, acid-base reaction will take place. As the base is strong one also, it will also dissociate into Na^+ and OH- ion completely. During the acid-base
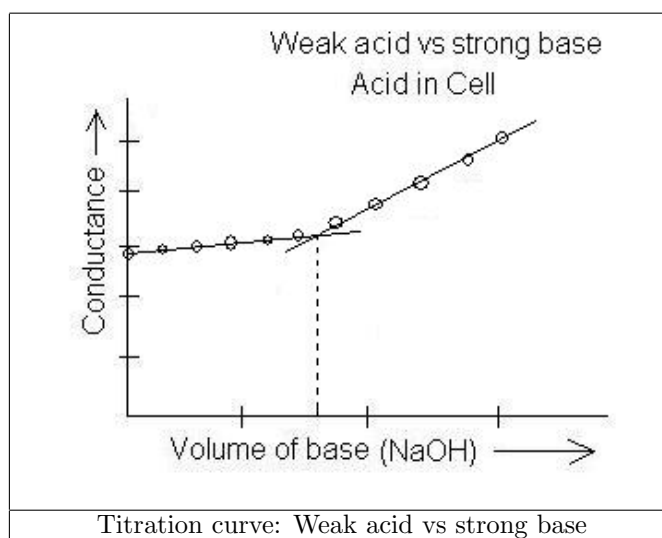
reaction, the OH^- ion will consume H^+ to form water. So, we can say as drops of NaOH will be added, H^+ ion will be consumed by OH- and Na^+ ion will be added in solution. So, we can say that as titration will proceed each Na^+ is being replaced by Na^+. Now ionic conductance of Na^+ is less compared to H^+ and hence conductance will decrease as the titration will proceed.

After reaching equivalent point when all the H^+ ion is consumed, additional addition of NaOH will simply add more Na+ and OH^- in solution and hence conductance will increase again. If will plot a conductance vs drops of base, we will get a graph like this. Now in first half the decrease of conductance is due to removal of H^+ and in second half of the graph the increase of graph is due to addition of OH^-. As ionic conductance of H^+ is higher than OH^-, the rate of decrease will be more faster than the rate of increase or the decrease line will be much more steeper than the increase line.

$$H^+ + Cl^- + Na^+ + OH^- \quad = \quad Na^+ + Cl^- + H_2O$$

4.2.2 Titration of a weak acid and strong base

An example of a weak acid and strong base are CH_3COOH and NaOH respectively. As the acid is a weak acid it will dissociate partially into H^+ and CH_3COO^- ions and hence number of ions will be few in the solution and hence the solution will show low conductance value. Now as we add few drops of base from burette, acid-base reaction will take place.


Titration curve: Weak acid vs strong base

As the base is strong one also, it will also dissociate into Na^+ and OH- ion completely. During the acid-base reaction, the OH^- ion will consume H^+ to form water. So, we can say by addition of few drops of base at first conductance will decrease slightly. Now as we move further wilh addition of more drops of base, all H^+ will be consumed and hence the dissociation of the weak acid will increase which will be reflected by gradual increase in conductance value.

Beyond the equivalent point when all the H^+ ion is consumed, additional addition of NaOH will simply add more Na+ and OH^- in solution and hence conductance will increase again sharply. If will plot a conductance vs drops of base, we will get a graph like this. Now in first half the increase of conductance is due to more dissociation of actic acid and in second half of the graph the increase of graph is due to addition of OH^-.

$$CH_3COOH + Na^+ + OH^- \quad = \quad CH_3COO^- + Na^+ + H_2O$$
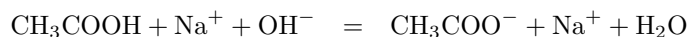
4.2.3   Titration of a strong acid and weak base

An example of a strong acid and weak base are HCl and NH_4OH respectively. As the acid is a strong acid it will dissociate into H^+ and OH^- ion completely and hence number of ions will be maximum in the solution. Furthermore as H^+ ion has very large ionic mobility and hence ionic conductance, the solution will show high conductance.
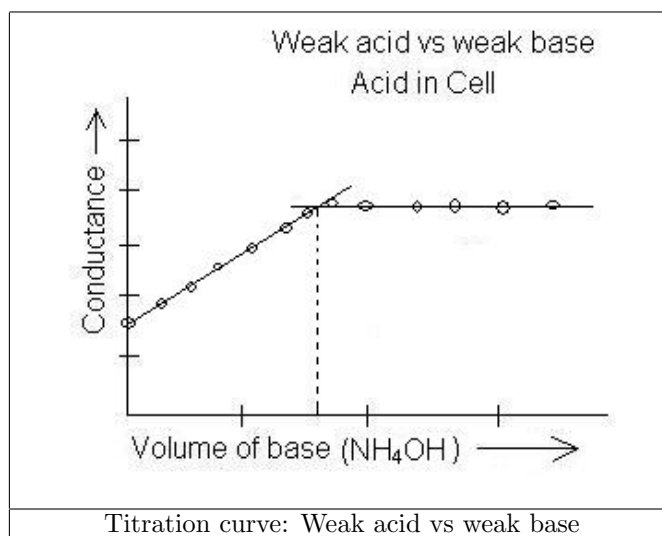

Titration curve: Strong acid vs weak base
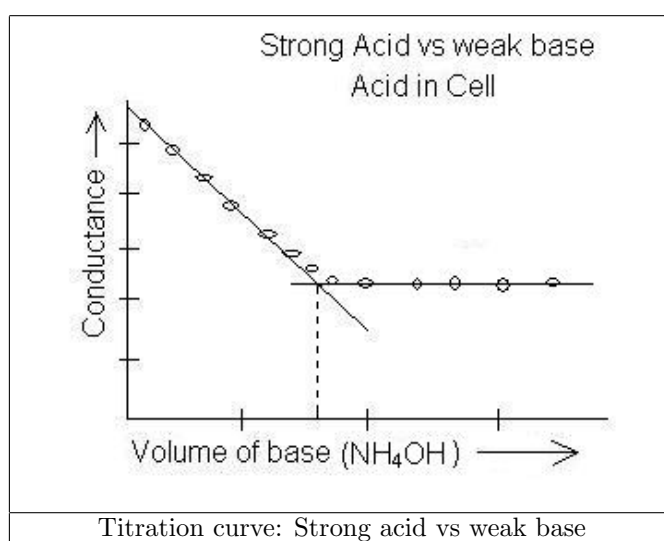
Now as we add base drop by drop from burette, acid-base reaction will take place. During the acid-base reaction, the OH^- ion will consume H^+ to form water. So, we can say as drops of NH_4OH will be added, H^+ ion will be consumed by OH^- and NH_4^+ ion will be added in solution. So, we can say that as titration will proceed each Na^+ is being replaced by NH_4^+. Now ionic conductance of NH_4^+ is less compared to H^+ and hence conductance will decrease as the titration will proceed. After reaching equivalent point when all the H^+ ion is consumed, additional addition of NH_4OH will have no effect. This is due to the fact that NH_4OH will not dissociated further as it is weak base and due to common ion effect. So, the conductance value will be unchanged or we will get a parallel line to X-axis.

$$H^+ + Cl^- + (NH_4^+OH) \quad = \quad NH_4^+ + Cl^- + H_2O$$
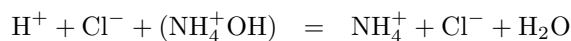
4.2.4   Titration of a weak acid and weak base

An example of a weak acid and strong base are CH_3COOH and NH_4OH respectively. As the acid is a weak acid it will dissociate partially into H^+ and CH_3COO^- ions and hence number of ions will be few in the solution and hence the solution will show low conductance value.

Titration curve: Weak acid vs weak base

Now, as we add few drops of base from burette, acid-base reaction will take place. During the acid-base reaction, the OH^- ion will consume H^+ to form water. So, we can say by addition of few drops of base at first conductance will decrease slightly. Now as we move further wilh addition of more drops of base, all H^+ will be consumed and hence the dissociation of the weak acid will increase which will be reflected by gradual increase in conductance value.

After reaching equivalent point when all the H^+ ion is consumed, additional addition of NH_4OH will have no effect. This is due to the fact that NH_4OH will not dissociated further as it is weak base and due to common ion effect. So, the conductance value will be unchanged or we will get a parallel line to X-axis.

$$CH_3COOH + (NH_4OH) \quad = \quad CH_3COO^- + NH_4^+ + H_2O$$
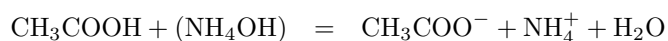
4.2.5 Precipitation titration of KCl with AgNO$_3$

KCl and $AgNO_3$ both are strong electrolyte and hence they dissociate completely in aqueous medium. KCl is being titrated against $AgNO_3$ and hence KCl solution is taken in a beaker and $AgNO_3$ is taken in burette.

Titration curve: Precipitation titration
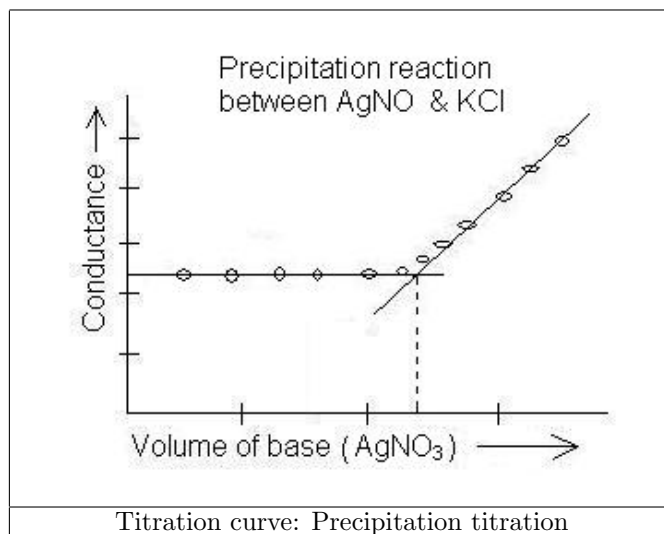
As KCl is strong electrolyte it will dissociate into K^+ and NO_3^- ion completely and hence number of ions will be maximum in the solution and hence the solution will show high conductance. Now as we add $AgNO_3$ drop by drop from burette, a precipitation of AgCl will occur.

$$K^+ + Cl^- + Ag^+ + NO_3^- \quad = \quad AgCl \Downarrow + K^+ + NO_3^-$$
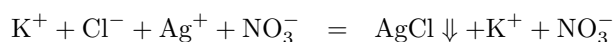
Now, as AgCl precipitated, chloride ion is removed from the solution and nitate ion is introduced in the solution. So, we can say that as titration will proceed each chloride is being replaced by a nitrate ion. The ionic conductance value of chloride and nitrtate is comparable and hence there will not be any effective change of conductance.

After reaching equivalent point when all the Cl^- ion is consumed, additional addition of $AgNO_3$ will simply add more Ag^+ and NO_3^- in solution and hence conductance will increase again. If will plot a conductance vs drops of base, we will get a graph like this. Now in first half there will be no chnage in conductance and hence we will observed a straight line parllel to X-axis and then in the second half an increase of conductance will be observed. The point where two line intersect will be the equivalent point.