

Study Notes on Conductometric Titrations



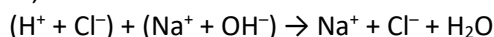
Conductometric Titration

The determination of the end point of a titration by means of conductance measurements is known as conductometric titration. The conductance readings corresponding to various added amounts of titrant are plotted against the latter.

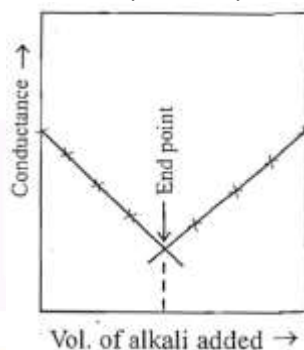
Note: (i) The titrant should be at least ten times as concentrated as the solution being titrated, in order to keep the volume change small.

(ii) Conductance due to weak acid, weak base or H₂O is very small because of their low value of dissociation constant.

(a) Strong acid with strong base: When a strong alkali e.g., sodium hydroxide is added to a solution of a strong acid, e.g., hydrochloric acid, the reaction.



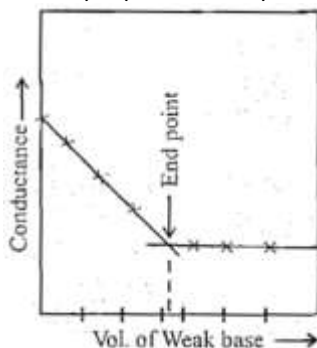
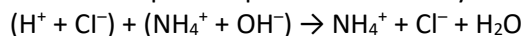
- During the reaction, highly conducting H⁺ are replaced by Na⁺ which has much lower conductance, so addition of alkali to acid solution is accompanied by a decrease of conductance.



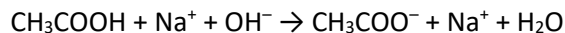
- When neutralization is complete then the further addition of alkali results in an increase of conductance since the sodium ion and hydroxyl ion are no longer used up in the chemical reaction.
- At the neutral point the conductance of the system will have a minimum value.

(b) Strong acid with weak base:

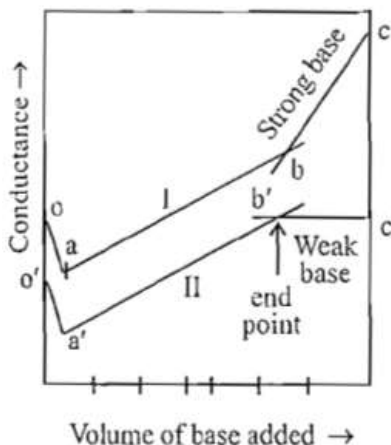
When the strong acid is titrated with a weak base, e.g., an aqueous solution of NH₃, the first part of the conductance titration curve representing the neutralization of the acid and its replacement by a salt is very similar to previous case since both NaCl and NH₄Cl are strong electrolytes. However, the conductance will remain almost constant when the end point is passed due to very low dissociation of NH₄OH.



(c) Weak acid with strong base:

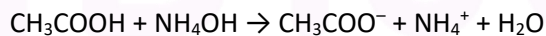


- Weak acid (CH_3COOH) has lower conductance than its salt (CH_3COONa), due to its lower dissociation w.r.t. salt, so addition of base increases conductance (region **ab** in graph).
- The reason for initial decrease in conductance (region **oa**) is because small addition of base leads to common anion, i.e., CH_3COO^- ion formation which represses the dissociation of CH_3COOH which gives highly conducting H^+ ions.



- After the end point there is a higher rate of increase in conductance because $\text{Na}^+ + \text{OH}^-$ has higher conductance than $\text{Na}^+ + \text{CH}_3\text{COO}^-$ (region **bc** in Graph-I).

(d) Weak acid with weak base:



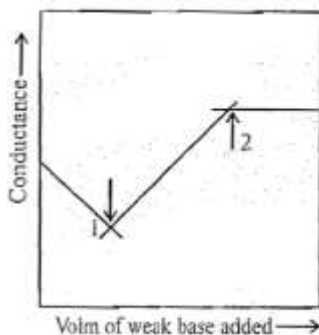
- Graph II, shows the titration of weak acid with weak base.
- First two points of the explanation are the same as the above case.
- The region **b'c'** of the graph is due to the weak nature of base, so conductance remains almost constant with the addition of weak base after end-point.

Note: (i) End point determination in case of weak acid with weak base is easier than titration of weak acid with strong base because region **ab** and **bc** of the graph may have almost the same slope (due to closeness in conductance value of salt of weak acid and conductance of strong base).

(ii) Sometimes the regions **oa** and **o'a'** are so small that they are not shown in the graph.

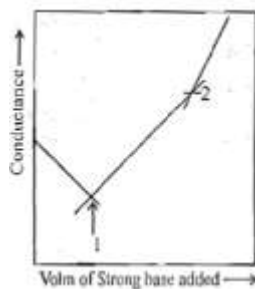
(e) Mixture of weak acid and strong acid with weak base:

- The 1st end-point is obtained when strong acid is consumed.
- The 2nd end-point is obtained when weak acid is consumed.



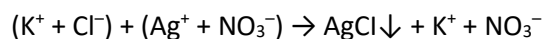
(f) Mixture of weak acid and strong acid with strong base:

Similar explanation as the above case

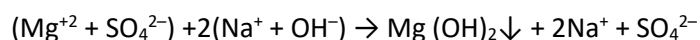


(g) Precipitation reactions:

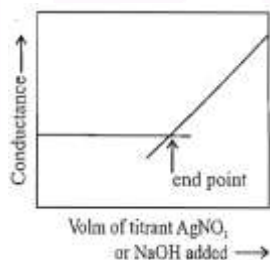
Type I: (a) Titration of KCl with AgNO₃:



(b) Titration of MgSO₄ with NaOH:



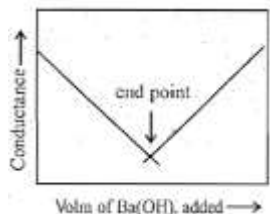
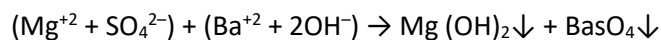
- In reaction (a) net result is placement of Cl⁻ by NO₃⁻. As both Cl⁻ and NO₃⁻ have almost the same conductance so up to end point there is no change in conductance value.
- After the end-point there is an increase in conductance due to combined conductance of Ag⁺ and NO₃⁻ ions.



For reaction (b), same explanation as above.

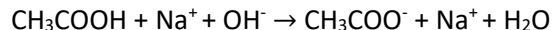
Type II: If both products of the reaction are sparingly soluble.

Example: (a) Titration of MgSO₄ with Ba(OH)₂

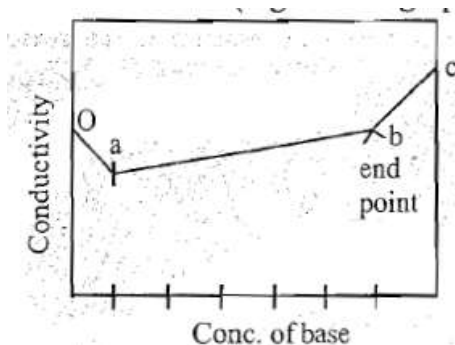


Here conductance of solution decreases right from the commencement, but increases after the end-point because of the free barium hydroxide.

(b) (1). Weak acid with strong base: CH₃COOH with NaOH

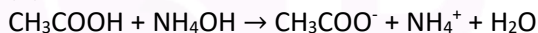


- Weak acid (CH₃COOH) has lower conductance than its salt (CH₃COONa). Due to its lower dissociation w.r.t. salt. So, addition of base increases conductance (region ab in graph).
- The reason for initial decrease in conductance [region (oa)] is because small addition of base leads to common anion, i.e., CH₃COO⁻ ion formation which represses the dissociation of CH₃COOH which gives highly conducting H⁺ ions.

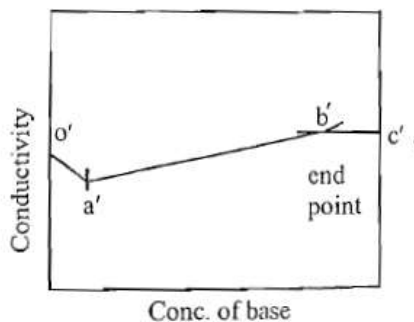


- After the end point, there's a higher rate of increase in conductance because Na⁺ + OH⁻ has higher conductance than Na⁺ and CH₃COO⁻ (region bc in graph).

(2). Weak acid with weak base:



- Weak acid (CH₃COOH) has lower conductance than its salt (CH₃COONa). Due to its lower dissociation w.r.t. salt. So, addition of base increases conductance (region ab in graph).
- The reason for initial decrease in conductance [region (oa)] is because small addition of base leads to common anion, i.e., CH₃COO⁻ ion formation which represses the dissociation of CH₃COOH which gives highly conducting H⁺ ions.



- The region b 'c' of the graph is due to the weak nature of the base. So, conductance remains almost constant with the addition of a weak base after the end point.

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