

$$\lambda_{\text{OH}^-} = 198.5 \text{ mhos}$$

According to Kohlrausch's Law

$$\begin{aligned}\lambda_{\text{H}_2\text{O}} &= \lambda_{\text{H}^+} + \lambda_{\text{OH}^-} \\ &= 349.8 + 198.5 = 548.3 \text{ mhos}\end{aligned}$$

One molecule of water gives one H^+ ion and one OH^- ion



Assuming that ionic concentration is proportional to conductance, we have

$$[\text{H}^+] = [\text{OH}^-] = \frac{5.5 \times 10^{-5}}{548.3} = 1.01 \times 10^{-7} \text{ g ion litre}^{-1}$$

The ionic product of water is then

$$K_w = [\text{H}^+][\text{OH}^-] = 1.02 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

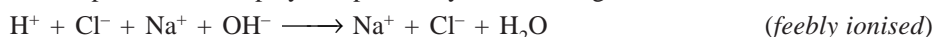
For most purposes, the value of K_w is taken to be 10^{-14}

CONDUCTOMETRIC TITRATIONS

Titration in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called **Conductometric titrations**. In these titrations, advantage is taken of the fact that the **conductance of a solution at a constant temperature depends upon the number of ions present in it and their mobility**. For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant. In this way two linear curves are obtained, the point of intersection of which is the **end-point**. Several phenomena like hydrolysis of reactants or products or partial solubility of a precipitated product give rise, however to a curvature in the curves. The shapes of curves obtained in certain types of titration are discussed below :

(1) Titration of a Strong acid against a Strong base

Consider the reaction in which hydrochloric acid solution is titrated against a solution of sodium hydroxide. Take 20 ml of the acid solution in the conductance cell placed in a thermostat and determine its conductance. Now add 1 ml sodium hydroxide solution from the burette at a time. After each addition, determine the conductance of the solution after thorough mixing and plot the conductance of the solution against the volume of the alkali added. It will be observed that the points lie on two lines which are almost straight. The point of intersection of the interpolated lines will be the end point and the volume of alkali corresponding to this point is the volume of alkali required to neutralise 20 ml of the acid (Fig. 25.9). The reason for this is that before the addition of alkali, the conductance of the solution is due to presence of H^+ and Cl^- ions. Since hydrogen ions possess the greatest mobility of any ion, the greater part of the conductance is due to it. As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions forming feebly ionised water molecules and their place is taken up by comparatively slow moving Na^+ ions.

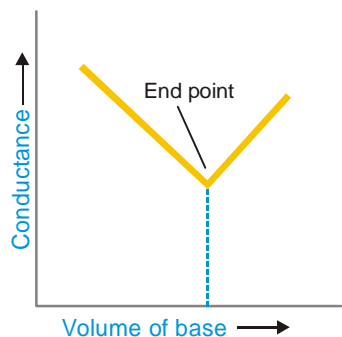


As a result of this, the conductance of the solution decreases and continues to fall with every subsequent addition of alkali till the end-point is reached. After the equivalence point, the further addition of sodium hydroxide solution results in an increase of conductance since the hydroxyl ions are no longer removed in the chemical reaction in the form of feebly ionised water. **The point of minimum conductance, therefore, coincides with the end-point of the titration.**

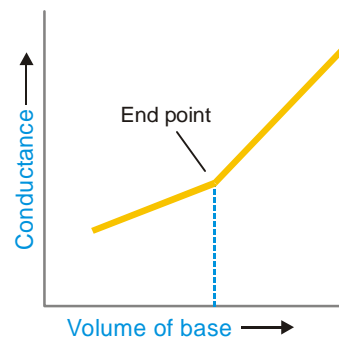
In order to get accurate results, the volume change during titration should be as little as possible. The titrant should, therefore, be about 10 times as strong as the acid solution in the conductance cell in order to keep the volume change small. If this is not so, a correction to the readings has to be applied viz,

$$\text{actual conductance} = \left(\frac{v + V}{V} \right) \times \text{observed conductance}$$

where v is the volume of the titrant and V is the original volume of the solution to be titrated.



■ **Figure 25.9**
Conductometric titration curve
for strong acid and strong base.



■ **Figure 25.10**
Curve for titration of a weak
acid against a strong base.

(2) Titration of a Weak acid against a Strong alkali

When a weak acid like acetic acid is titrated against a strong alkali like sodium hydroxide, we get a curve of the type shown in Fig. 25.10. The initial conductance of the solution is low because of the poor dissociation of the weak acid. On adding alkali, highly ionised sodium acetate is formed. The acetate ions at first tend to suppress the ionisation of acetic acid still further due to *Common Ion Effect* but after a while the conductance begins to increase because the conducting power of highly ionised salt exceeds that of the weak acid.



Immediately after the end point, further addition of sodium hydroxide introduces the fast moving hydroxyl ions. Thus, the *conductance value shows a sharp increase*. The point of intersection of the two curves, gives the end-point.



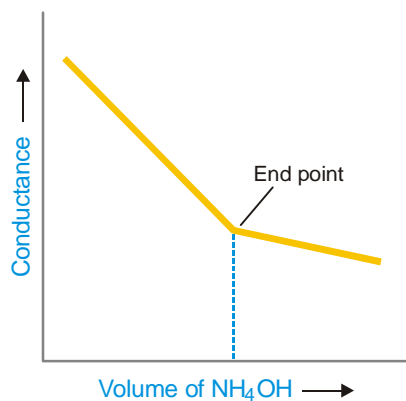
After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small compared with that of the acid or its salt. The shape of this part of the curve will, therefore, be as shown in the figure.

(3) Titration of a Strong acid against a Weak base

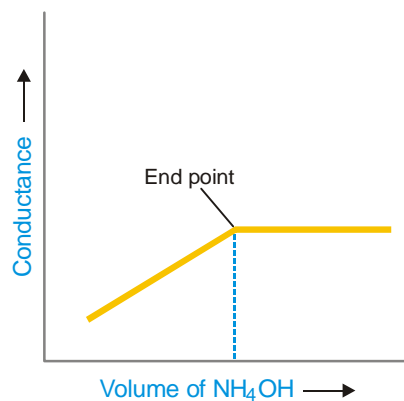
The curve obtained for the titration of a strong acid against a weak base is shown in Fig. 25.11. In this case, the conductance of the solution will first decrease due to the fixing up of the fast moving H^+ ions and their replacement by slow moving NH_4^+ ions.

(4) Titration of a Weak acid against a Weak base

The conductometric method is particularly suitable as such titrations do not give a sharp end-point with indicators. Consider the titration of acetic acid with ammonium hydroxide. The complete titration curve is shown in Fig. 25.12. The initial conductance of the solution in this case is also low due to the poor dissociation of the weak acid. But it starts increasing as the salt $\text{CH}_3\text{COONH}_4$ is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte. The end-point is quite sharp.



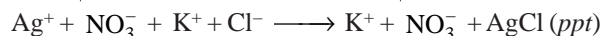
■ **Figure 25.11**
Curve for titration of a strong acid against a weak base.



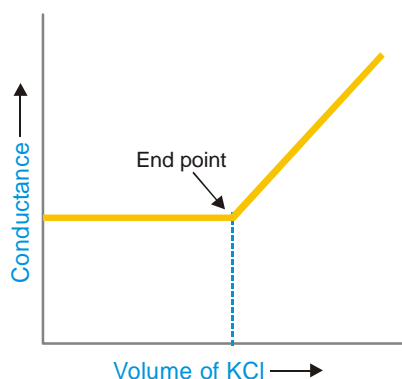
■ **Figure 25.12**
Curve for titration of acetic acid against ammonium hydroxide.

(5) Precipitation reactions

The end-point in precipitation reactions can be accurately determined by conductometric titration. The accuracy is further increased by working with fairly dilute solutions and addition of alcohol which reduces the solubility of the precipitate and prevents adsorption. In the titration of potassium chloride against silver nitrate, for example, the change in conductance on the addition of silver nitrate is not much since the mobility of the potassium ion and the silver ion is of the same order. Thus the curve is nearly horizontal.



After the end-point, there is a sharp increase in conductance due to an increase in the number of free ions in solution.



■ **Figure 25.13**
Titration of potassium chloride against silver nitrate.

Advantage of Conductometric Titrations

- (1) Coloured solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.
- (2) This method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indicators in ordinary volumetric analysis.
- (3) More accurate results are obtained because the end -point is determined graphically.

Precautions. (i) It is necessary to keep the temperature constant throughout the experiment. (ii) In acid-alkali titrations, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

DIFFERENCES BETWEEN CONDUCTOMETRIC AND VOLUMETRIC TITRATIONS

Conductometric Titrations	Volumetric Titrations
<ol style="list-style-type: none"> 1. Conductance measurements are done to check end points. 2. Titrations can be carried out even with coloured solution. 3. Accurate results are obtained. 4. End point is determined graphically. 5. In case of polybasic acids conductometric titrations can be used. 6. These are successful even in weak acids and strong bases. 	<ol style="list-style-type: none"> 1. Volume measurements are done to check end points. 2. These titrations fail in coloured solutions as suitable indicators are not available some times. 3. Results are not so accurate. 4. End point is determined by change in colour of indicator. 5. In case of polybasic acids volumetric titrations do not give correct end points. 6. These are not successful in weak acids and strong bases.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
 - (a) Arrhenius theory
 - (b) Transport number
 - (c) Hittorf's method
 - (d) Moving boundary method
 - (e) Kohlrausch's law
 - (f) Degree of dissociation
2. (a) Explain ionic conductance, transport number of an ion, and absolute ionic velocity.
 (b) The absolute velocity of Ag^+ is $0.00057 \text{ cm sec}^{-1}$ and of the NO_3^- is $0.00069 \text{ cm sec}^{-1}$. Assuming complete dissociation, calculate the specific conductivity of 0.01 M solution of silver nitrate.
Answer. (b) 0.00012 mhos
3. Describe Hittorf's method for the experimental determination of the transference number. The speed ratio of silver and nitrate ions in AgNO_3 electrolysed between silver electrodes was found to be 0.89. Calculate the transference number of silver and nitrate ions.
Answer. $\text{Ag}^+ = 0.4708$; $\text{NO}_3^- = 0.5292$
4. (a) What do you understand by the transport number of an ion? Does it vary?
 (b) In a moving boundary experiment with 0.1 N KCl using 0.65 N LiCl as indicator solution, a constant current of 0.006 amp was passed for 1900 secs and the boundary was observed to move through 5 cm in a tube of 0.1142 cm^2 cross-section. Calculate the transport number of K^+ and Cl^- ions.
Answer. (b) $\text{K}^+ = 0.4833$; $\text{Cl}^- = 0.5167$
5. (a) What is meant by transport number of ions? Describe Hittorf's method for the determination of transport number of silver ions.
 (b) A dilute solution of silver nitrate was electrolysed using platinum electrodes. After passing small