

2. Conductometry

Introduction

This is a method of analysis based on measuring electrolytic conductance

Conductance: is the ability of the medium to carry the electric current.

Electric current passes through metallic conductors, e.g. wires of iron or copper in the form of electron flow. But conduction of electricity through an electrolyte solution involves migration of positively charged species towards the cathode and negatively charged ones through the anode, i.e. current is carried by all ions present in solution.

The conductance of the solution is a reciprocal of its resistance and has the units of ohm^{-1} (seimen). That is,

$$G = \frac{1}{R}$$

From Ohm's law

E is the potential difference, i is the current intensity.

$$R = \frac{E}{i}$$

The conductance of the solution depends on:

1. Temperature:

It is increased by increase of temperature. An increase of temperature by 1°C is accompanied by 2 % increase in conductance for this response the measurements must be carried out at constant temperature using thermostatically controlled water bath or the conductometer used has special device which continuously calibrates for the temperature increase during measurements.

2. Nature of ions

The velocity by which ions move towards the electrodes carrying the electric current varies according to their nature, i.e. size, molecular weight, number of charges the ion carries and other factors.

3. The concentration of ions:

The electrical conductance of a solution is a summation of contribution from all ions present. It depends on the number of ion/unit volume of solution and their nature i.e. each ion presents itself independently. As the number of ions increases the conductance of the solution increases.

4. The size of the electrodes

Conductance is directly proportional to the cross sectional area A and inversely proportional to the length L of a uniform conductor.

$$G = K \frac{A}{L}$$

The conductance of electrolyte solution can be calculated from :

$$K = G \frac{L}{A}$$

K is the specific conductance or conductivity, it is the conductance of a cube of liquid on centimeter on a side.

If A and L are measured by centimeter, or of cubic meter if A and L are taken by meter. The dimensions of K is $1/\text{ohm}\cdot\text{cm}$ or $\text{ohm}^{-1}\text{cm}^{-1}$ or seimen/cm. ($\Omega^{-1}\text{m}^{-1}$)

L/A is known by the cell constant, K , is a constant value for specific solution it changes if we change the concentration of the solution it decreases by dilution as fewer ion will be present per cubic centimeter.

Equivalent conductance Λ

It is defined as the conductance of one gram equivalent of solute contained between electrodes spaced one centimeter apart.

$$\text{For a substance} = \frac{1000 K}{C}$$

Where C is the concentration in gram equivalent per liter.

Equivalent ionic conductance:

At infinite dilution, interactions become nil; the overall conductance of the solution consists of the sum of the individual equivalent ionic conductance

$$\Lambda_o = \lambda_{+^o} + \lambda_{-^o}$$

Table. Equivalent Conductivity at Infinite Dilution at 25°C

Cation	A $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$	Anion	A $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$
H ⁺	350	OH ⁻	198
Li ⁺	38.7	Cl ⁻	76.3
Na ⁺	50.1	Br ⁻	78.4
K ⁺	73.5	NO ₃ ⁻	71.4
Rb ⁺	76.4	CH ₃ COO ⁻	40.9
Cs ⁺	76.8	ClO ₄ ⁻	68
		½ SO ₄ ²⁻	80

Where λ_{+^o} and λ_{-^o} are equivalent ionic conductance of the cation and anion of the salt at infinite dilution. Individual ionic conductance can be determined from other electrolytic measurements.

Instrumentments used in conductometric determination

To carry out conductometric measurement it is necessary to measure the resistance of the solution and the conductance is i/r .

The instrument consists of two parts:

1. A mean to measure the resistance and then converts it to conductivity unit this called **conductivity bridge**.
2. **Conductance cell**; in which the solution to be measured is filled.

1. Conductivity bridge (Kohlrausch Bridge)

It is formed of:

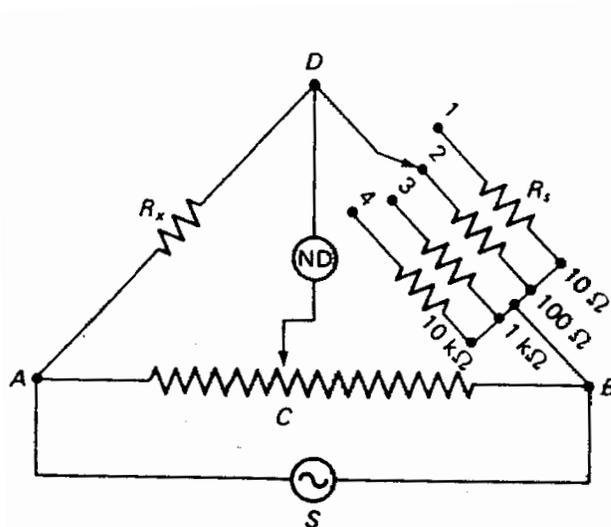
- a- Whetstone Bridge.
- b- An oscillator.

The whetstone bridge shown in the next figure used here to measurement of resistance. The power source S provides an ac current at a potential of 6 to 10 V.

The unknown resistance R_x is placed in the upper-left arm of the bridge.

A null detector ND (ac galvanometer) is employed to indicate an absence of current between D and C .

To measure R_x the position of C is adjusted to a minimum as indicated by the null detector (the position of C will change rapidly and automatically till the balance point, where no current is detected). At balance



A Wheatstone bridge for resistance measurements.

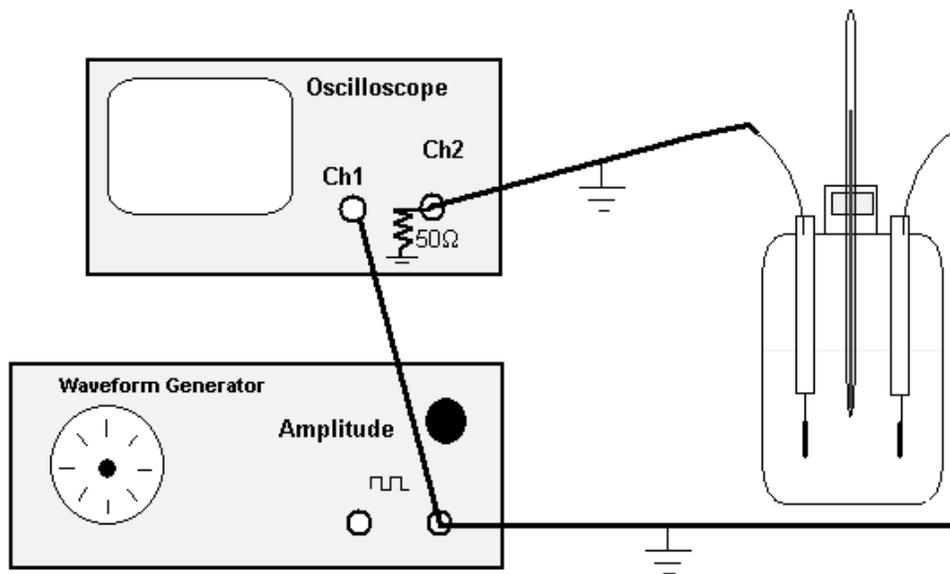
$$\frac{R_s}{R_{CB}} = \frac{R_x}{R_{AC}} \quad R_x = \frac{R_s R_{AC}}{R_{CB}} \quad R_x = R_s \frac{AC}{BC}$$

$$G = \frac{1}{R} \cdot \frac{BC}{AC} \quad AB = 100 \quad BC = X$$

$$\left[\therefore G = \frac{1}{R_1} \cdot \frac{x}{100 - x} \right]$$

2. Cells used in conductometric measurements:

The cell is formed of two parallel sheets of platinum. Fixed in position by being sealed into the sides of the measuring cell. The distance between the two electrodes must be constant during the determination.



For a given cell with fixed electrodes the ratio of L/A . cm is a constant known as cell constant. It is determined for each cell

using solutions of known conductivity. The cell must be dipped in thermostatically controlled water bath or the instrumental has a temperature calibration device.

Application of conductivity

1. Direct or absolute measurements:

This is used in industry for checking purity of distilled water or other chemicals. Also for determination of physical constants such as ionisation constant.

In this method a series of standard solutions of extra pure grade of the substance to be determined is prepared, the conductivity is determined and a calibration curve is plotted representing conductivity against concentration.

A solution of the substance to be tested is prepared and checked from conductivity calibration curve.

2. Conductometric titrations

A conductometric titration involves measurement of the conductivity after successive addition of the reagent. The end point is obtained from a plot of conductivity against ml of titrant. Here it is the change of conductivity of the solution during the course of reaction which is important.

The most important advantages of this method are that it can be used for determination of:

- a- Turbid and highly coloured solutions.
- b- Very dilute solutions.
- c- Reaction which is not complete and where there is no suitable indicator, e.g. reaction between weak acid and weak base.

Precaution to be considered in conductometric titrations:

1. Upon carrying on titration the titrant used should be at least 10 times concentrated as the solution to be determined, e.g. on determination of 0.01 N hydrochloric acid the titrant sodium hydroxide should be at least 0.1 N. By this way dilution that takes place during titration is minimum and this is necessary because conductivity decrease with dilution. However a correction factor must be used to compensate for this dilution.

$$\text{Correction factor} = \frac{V_i + V_t}{V_i}$$

Where; V_i = initial volume of the solution

V_t = titrant volume added.

2. Avoid the presence of extraneous ions which will not enter the reaction such as the presence of buffer or concentrated acids. These ions will increase the initial conductivity and the

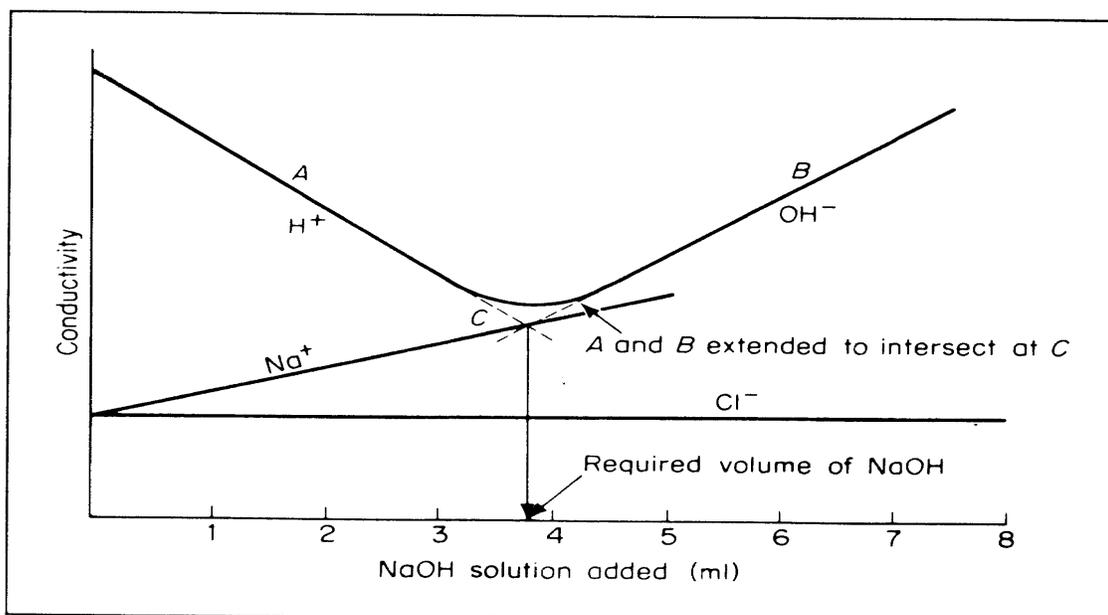
change in it during the titration will be comparatively small and cannot be accurately observed.

3. The method is suitable for detection of end point in neutralization, complexation and precipitation reactions but not redox reaction, as there is no electron transfer at the electrode surface.

Neutralization titrations:

a- Titration of strong acid with strong base:

The reaction is represented by the following equations



*Conductivity of the solution during an HCl-NaOH titration
(C is the neutralization point).*

Initial conductivity is high as it is that of $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$ (mobility, for $\text{H}^+ = 350$ and for $\text{Cl}^- = 76$) upon addition of NaOH ($\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$) water, which is weakly ionized is formed, hydrogen ion is removed from the medium and sodium ions added, i.e. hydrogen ions are replaced with sodium ions which has 43 mobility so decrease in conductivity occurs this will continue till the end point. Beyond the end point there is excess sodium and hydroxide ions with 43 and 198 mobility. So, there is a continuous increase in conductivity and the curve will have a V shape the end point is the minimum of the curve.

In ideal condition the two arms are straight and end point is the point of intersection. The slope of the curve depends on the ratio of mobility of sodium to hydrogen ions and on the initial concentration of the sample the higher the concentration the sharper the curve.

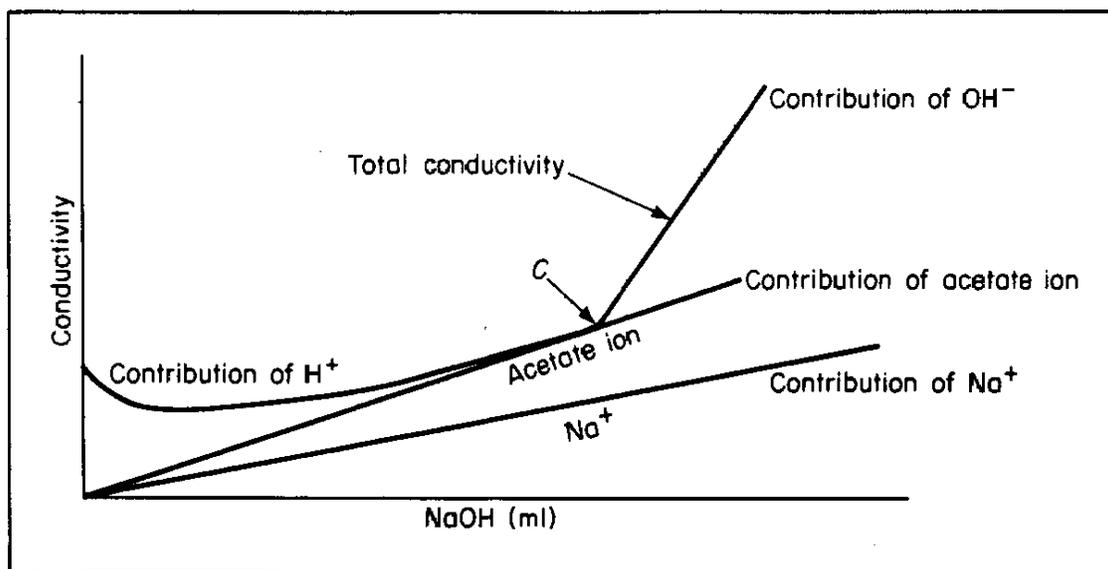
In many cases the curve minimum is blunt and the end point is obtained by extrapolation of the curve, this curvature increases with dilution and a usage of correction factor. The more concentrated the solution the sharper will be the change.

b) Very weak acid with strong base or a very weak base with stronger acids

Very weak acids such as phenols, boric acid or those which their salts are coloured also weak bases as alkaloids, amines, xanthenes dyes can be determined by this method. The initial conductance is low as solute is weakly ionizable and minute amount of ions present to conduct electric current. An example of this type of titration, determination of boric acid ($K_a = 6 \times 10^{-10}$) with sodium hydroxide. This reaction is so incomplete that a potentiometric or visual indicator end point is unsatisfactory. Before titration the conductivity is low due to small amount of hydro-gen and borate ions obtained from ionization of boric acid, upon titration with sodium hydroxide water is formed which is less ionizable than boric acid but sodium ion will be added and slight decrease in conductivity occurs, but since a salt (sodium borate) is formed a buffer is rapidly established that imparts to the solution relatively small and nearly constant hydrogen ion concentration. The added hydroxides ions are consumed by this buffer and thus do not contribute to the conductivity.

A gradual increase in conductivity occurs due to the increase in sodium and borate ions.

At and beyond the equivalent point addition of base causes rapid increase of conductivity due to added sodium and hydroxide ions. In case of moderately weak acid such as acetic acid ($K_a = 1.8 \times 10^{-5}$) the solution initially has a moderate concentration of hydrogen ions. Addition of base results in establishment of buffer system. The decrease conductivity due to decrease of hydrogen ion concentration is balanced by its increase due to formation of sodium acetate (completely ionizable) and nearly a horizontal line is obtained. Beyond the equivalence point there is a sudden increase in conductivity due to addition of hydroxide and sodium ion from sodium hydroxide.

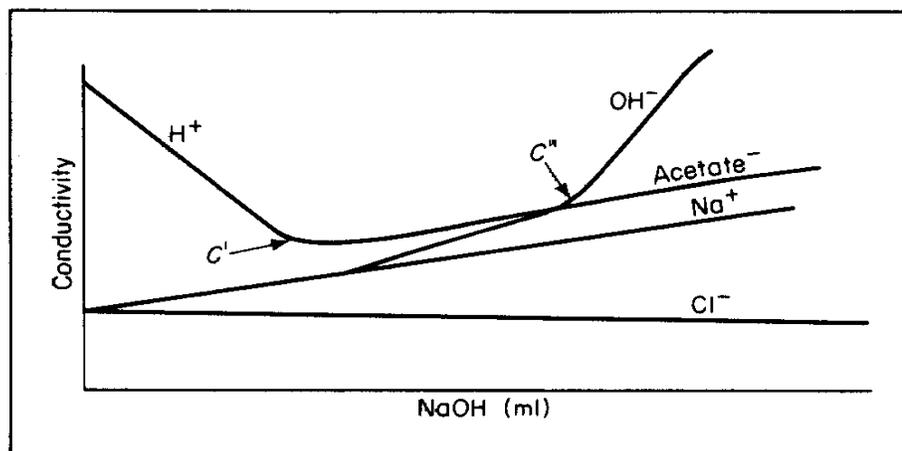


*Conductivity of the solution during an acetic acid-NaOH titration
(C is the neutralization point).*

c) Determination of mixture of hydrochloric acid (strong acid) and acetic acid (weak acid) with sodium hydroxide (strong base)

The following figure represents the titration curve obtained upon determination of a mixture of hydrochloric acid and acetic acid with sodium hydroxide:

The initial conductivity is high it is due to hydrochloric acid which by common ion effect suppress the ionization of acetic acid. So a rapid decrease in conductivity occurs upon titration due to replacement of hydrogen ions with 350 mobility by sodium ion with 43 mobility till all hydrogen ions from hydrochloric acid are neutralized. Acetic acid will thus ionize and react with sodium hydroxide and change in conductivity occurs as described in the previous paragraph.



Conductivity of a solution containing HCl and CH₃COOH during titration with NaOH. C' C'' designate points at which two abrupt changes in conductivity take place.