

Physical Chemistry- III

UNIT 1 Electrical Conductance (16 hrs)

Mechanism of electrical conduction – Arrhenius theory – The laws of electrolysis – Faraday's law and its significance – Transference Number – True and apparent transport numbers- Determination by Hittorf's method and moving boundary method. Equivalent conductance and Molar conductance -Effect of Dilution on conductance – Effect of dielectric constants of solvents-Ionic mobilities – Kohlrausch's Law – applications – Mobilities of Hydrogen and Hydroxyl ions – Diffusion and ionic mobility. Activity and activity coefficient – standard state ionic activities and activity coefficient – ionic strength – Debye – Huckel Theory – Ionic atmosphere – Debye – Huckel limiting law – Temperature dependence of ionic conductance-Debye- Falkenhagen effect-wein effect(definition only)- determination of solubilities by conductance measurements – conductometric titrations – conductance in non-aqueous solvents.

1. Mechanism of electrical Conduction

Conductors can be divided broadly into two categories:

- (i) Metallic or electronic conduction
- (ii) Electrolytic conduction

(i) *Metallic Conduction*

Metals are the best conductor and it remains unchanged with the passage of current. A metallic conductor behaves as if it contains electrons which are relatively free to move. So electrons are considered as charge carrier in metals. Therefore, these conductors are also called *electronic conductors*. Metallic conduction or electronic conduction is the property possessed by pure metals, most alloys and certain solid salts and oxides.

(ii) *Electrolytic Conduction*

Conductors, through which passage of an electric current through them results in actual transfer of matter or brings about a chemical change in them, are called *electrolytic conductors or electrolytes*.

The electrolytic conductors which are conduct electrolytically in the pure state, such as acids, bases and salt in water. e.g. NaCl, NaNO₃, K₂SO₄ etc.

Generally electrolytic solutions are prepared by dissolving a salt, acid or base in water or other solvents. There is a special class of conductors, which conduct partly electronically and partly electrolytically, are

known as *mixed conductors*. For example, solution of the alkali and alkaline earth metals in liquid ammonia are mixed conductors. Fused cuprous sulphide conducts electronically, but a mixture with sodium or ferrous sulphide also shows electrolytic conduction.

1.1 Conduction in Electrolyte Solutions

The passage of current through solutions of salts of metals such as zinc, iron, nickel, cadmium, lead, copper, silver and mercury results in the liberation of these metals at the cathode and from solutions of salts of the metals. If the anode consists of an attackable metal, the flow of the current is accompanied by the passage of the metal into solution. When the anode is made of an inert metal, e.g., platinum, an element is generally set free at this electrode; from solutions of nitrates, sulphates, phosphates, etc., oxygen gas is liberated, whereas from halide solutions, other than fluorides, the free halogen is produced. The decomposition of solutions by the electric current, resulting in the liberation of gases or metals, is known as *electrolysis*.

1.2 Strong and Weak Electrolytes

Solutes giving conducting solution in a suitable solvent are called electrolytes. On the basis of degree of ionization, these electrolytes have been divided into two categories.

(i) Strong electrolytes

(ii) Weak electrolytes

1.2.1 Strong Electrolytes

Substances, which are highly dissociated and give solutions with high conductance in water, are called *strong electrolytes*. Due to the high degree of dissociation of strong electrolytes these substances are good conductor of electricity i.e., aqueous solutions of these substances have high value of molar conductance and on dilution the increase in their molar conductance is very small. This is due to the fact that such electrolytes are completely ionized at all dilutions therefore on further dilution the number of current carrying particles does not increase in the solution. Thus, solutions of electrolytes that have high molar conductance, and increases very slowly on dilution has a high degree of dissociation is called *strong electrolyte*.

During the passage of an electric current through solutions, flow of electricity is associated with the movement of particles, which are called *ions*. The ions carrying positive charges and moving in the direction of the current, i.e., towards the cathode, are referred to as *cations* and those carrying a

negative charge and moving in the opposite direction, i.e., towards the anode, are called *anions*.

1.2.2 Weak Electrolytes

Weak acids and weak bases, e.g., amines, phenols, most carboxylic acids and some inorganic acids and bases, such as hydrocyanic acid and ammonia, and a few salts, e.g., mercuric chloride and cyanide, are dissociated only to a small extent at reasonable concentration; this group of compounds in general are called as *weak electrolytes*.

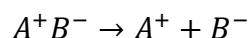
The molar conductance of the solutions of these electrolytes increases rapidly on dilution. The reason of this is that more molecules ionize on dilution in spite of this they are never completely ionized. For these electrolytes, the nature of the solvent is also important; a particular compound maybe strong electrolyte, being dissociated to large extent, in one solvent, but may behave as weak electrolyte in other solvent due to low degree of dissociation.

1.3. Arrhenius theory of electrolytic dissociation

The Arrhenius theory was first introduced by the Swedish scientist Svante Arrhenius in the year 1887. To conduct electricity, one must have free moving ions. Svante Arrhenius noticed that the solution of acid conducts electricity by dissolving the substance in the solution, which dissociates into ions. Water is a neutral substance, which does not conduct electricity. By dissolving some substance in water, it conducts electricity. These substances are called electrolytes and the process is known as “Electrolytic dissociation.”

Postulates of Arrhenius Theory:

1. When dissolved in water, neutral electrolyte molecules are split up into two types of charged particles. These particles were called ions and the process was termed ionisation. The positively charged particles were called cations and those having negative charge were called anions. The theory assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic force. When placed in water, these neutral molecules dissociate to form separate anions and cations.



2. The ions present in solution constantly reunite to form neutral molecules. Thus there is a state of equilibrium between the undissociated molecules and the ions.

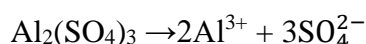


Applying the Law of Mass Action to the ionic equilibrium we have,

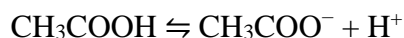
$$\frac{[A^+][B^-]}{[AB]} = K$$

Where K is called the dissociation constant.

3. The charged ions are free to move through the solution to the oppositely charged electrode. This is called the migration of ions. This movement of the ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis. There are two types of electrolytes. Strong electrolytes are those when dissolved in water are completely dissociated (ionised) into ions of positive and negative charges. The total number of cations and anions produced are equal to those in the formula of the electrolyte.



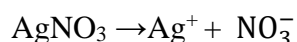
NaCl, KCl, AgNO₃, NaCl, KCl, AgNO₃ etc., are few examples of strong electrolytes. In the case of weak electrolytes, there is partial dissociation into ions in water and an equilibrium exists between the dissociated ions and the undissociated electrolyte. E.g,



Acetic acid is a weak electrolyte in water and unionised acetic acid molecules are in equilibrium with the acetate anions and protons in solution.

4. The electrical conductivity of an electrolyte solution depends on the number of ions present in solution.

Thus the degree of dissociation of an electrolyte determines whether it is a strong electrolyte or a weak electrolyte. We know that electrolytes dissociate in solution to form positive ions (cations) and negative ions (anions).



As the current is passed between the electrodes of the electrolytic cell, the ions migrate to the opposite electrodes. Thus in the electrolytic solution of AgNO₃, the cations (Ag⁺) will move to the cathode and anions (NO₃⁻) will move to the anode. Usually different ions move with different rates. The migration of ions through the electrolytic solution can be demonstrated by the following experiments.

5. The properties of solution of electrolytes are the properties of ions. The solution of electrolyte as a whole is electrically neutral unless an electric field is applied to the electrodes dipped into it. Presence of hydrogen ions (H⁺) renders the solution acidic while presence of hydroxide ions (OH⁻) renders the solution basic.

1.4. Faraday's Laws of Electrolysis

Faraday's laws of electrolysis are based on the electrochemical research of Michael Faraday which he published in 1833. These show the quantitative relationship between the substance deposited at electrodes and the quantity of electric charge or electricity passed.

Faraday's First Law of Electrolysis

Faraday's First Law of Electrolysis states that "The mass of a substance deposited at any electrode is directly proportional to the amount of charge passed." Mathematically it can be expressed as follows

$$m \propto Q \quad (1)$$

Where: m = mass of a substance (in grams) deposited or liberated at an electrode. Q = amount of charge (in coulombs) or electricity passed through it. On removing the proportionality in equation (1)

$$m = ZQ$$

Where Z is the proportionality constant. Its unit is grams per coulomb (g/C). It is also called the electrochemical equivalent. Z is the mass of a substance deposited at electrodes during electrolysis by passing 1 coulomb of charge.

Faraday's Second Law of Electrolysis

Faraday's Second Law of Electrolysis states that "the mass of a substance deposited at any electrode on passing a certain amount of charge is directly proportional to its chemical equivalent weight." Or "when the same quantity of electricity is passed through several electrolytes, the mass of the substances deposited are proportional to their respective chemical equivalent or equivalent weight".

Mathematically it can be represented as follows

$$w \propto E$$

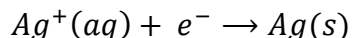
Where w = mass of the substance E = equivalent weight of the substance

It can also be expressed as

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

The equivalent weight or chemical equivalent of a substance can be defined as the ratio of its atomic weight and the number of electrons required to reduce the metal. Equivalent weight = Atomic weight/ n

Q is the quantity of electricity passed is given by $Q = It$ when I is in ampere and t is in seconds. The amount of electricity required for oxidation or reduction depends on the stoichiometry of the electrode reaction. One mole of the electron required for the reduction of one mole of silver ions.



We know that charge of electron is 1.6021×10^{-19} C therefore charge on one mole of electron is $6.023 \times 10^{23} \text{ mol}^{-1} \times 1.6021 \times 10^{-19} \text{ C} = 96487 \text{ C mol}^{-1}$. This quantity of electricity is called Faraday (F).

2. Conductance, Specific Conductance and Molar Conductance

Consider a uniform bar of conductor of length ' l ' cm and cross-sectional area ' a ' sq. cm and the cross section is rectangular and that the whole body is placed into cubes of one cm. side, as shown in Figure 1.

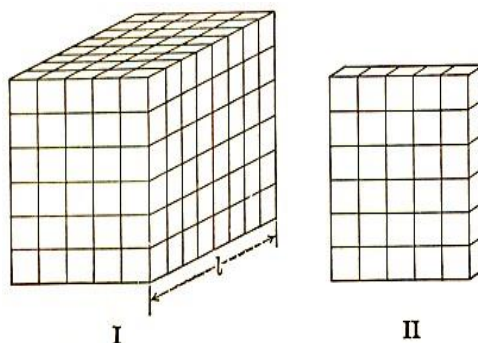


Fig. 1 Ohm's law states that 'The magnitude of current (I) passing through a conductor is directly proportional to the potential difference (E) applied across it and inversely proportional to the resistance (R) of the conductor'.

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

Thus metallic conductor and electrolytes obey Ohm's law. Conductance is the reciprocal of resistance and is expressed in Siemen (S)

$$\text{Conducantance} = \frac{1}{R} \quad (2)$$

Unit is $\frac{1}{\Omega} = \frac{1}{ohm} = moh$ or Ω^{-1} is called Siemen

2.1 Specific Conductance or Conductivity

The resistance of the bar (Fig.1) to the passage of electricity through it is proportional to its length ' l ' (cm) and inversely proportional to the area of cross section ' a ', therefore, the resistance ' R ' is given by the

relationship.

$$R \propto \frac{l}{a}$$

Or

$$R = \rho \frac{l}{a} \quad \text{also} \quad \rho = \frac{Ra}{l} = \frac{\Omega \text{cm}^2}{\text{cm}} = \Omega \text{cm} \quad (3)$$

Where, ‘ ρ ’ is a constant known as specific resistance or resistivity. If $l = 1 \text{ cm}$, $a = 1 \text{ cm}^2$. Then, $\rho = R \text{ ohm cm}^{-1}$. **Specific conductance of any conducting material is defined as the reciprocal of its specific resistance.** It is given the symbol ‘ κ ’ and is stated in reciprocal ohm cm^{-1} , nowadays called “ Scm^{-1} ” (Siemens per centimeter). The reciprocal of specific resistance is called conductance (G)

Conductance ‘G’ is then defined as reciprocal of the resistance R of the solution

$$G = \kappa \frac{a}{l} \quad \text{where} \quad \frac{1}{\rho} = \kappa$$

The SI unit of conductance is Siemens represented by the symbol S and equal to ohm^{-1} (also known as mho) or Ω^{-1} . Inverse of the resistivity called conductivity (specific conductance) is represented by the symbol κ (Greek, kappa). IUPAC has recommended the use of the term conductivity over specific conductance and hence we shall use the term conductivity.

$$G = \kappa \frac{a}{l}$$

The SI unit for the conductivity are S m^{-1} but κ is expressed in S cm^{-1} . The conductivity of a material in S m^{-1} is its conductance when it is 1m long and its area of cross section is 1 m^2 . It may be noted that $1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1}$.

2.1 Molar Conductivity

The conductivity of solutions of different electrolyte in the same solvent and at a given temperature differs due to charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under a potential gradient. It is therefore become necessary to define a physically more meaningful quantity called molar conductivity denoted by the symbol Λ_m . It is related to the conductivity of the solution by equation

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

In the above equation κ is expressed in $S\ m^{-1}$ and concentration c in $mol\ m^{-3}$ then the units of Λ_m are in $S\ m^2\ mol^{-1}$. Suppose concentration is expressed in mol/L

$$1L = \frac{1m^3}{1000}, \frac{mol}{L} = \frac{mol \times 1000}{1m^3} = 1000\ mol\ m^{-3}$$

$$\text{Molar conductivity} = \Lambda_m (S\ m^2\ mol^{-1}) = \frac{\kappa S\ m^{-1}}{1000\ c\ mol\ m^{-3}} = \frac{\kappa}{1000c} S\ m^2\ mol^{-1}$$

If we want to express the molar conductivity $\Lambda_m (S\ cm^2\ mol^{-1})$

$$1L = 1000\ cm^3$$

$$\frac{mol}{L} = \frac{mol}{1000\ cm^3} = \frac{1\ mol\ cm^{-3}}{1000}$$

$$\Lambda_m (S\ cm^2\ mol^{-1}) = \frac{1000\ \kappa\ S\ cm^{-1}}{c\ mol\ cm^{-3}} = \frac{1000\ \kappa\ S\ cm^2\ mol^{-1}}{c} \quad (7)$$

$$1\ S\ m^2\ mol^{-1} = 10^4\ S\ cm^2\ mol^{-1}$$

$$1\ S\ cm^2\ mol^{-1} = 10^{-4}\ S\ m^2\ mol^{-1}$$

$$\Lambda = \kappa v \quad (6)$$

Where v is the “dilution” of the solution in cc. containing one gram equivalent of the electrolyte. It is also called Λ_{eq}

3. Measurement of Molar Conductivity

Conductivity is the reciprocal of resistance and the resistance can be determined by a Wheatstone bridge circuit in which the conductivity cell forms one arm of the bridge, this method is known as **Null Method (Kohlrausch conductance bridge)**.

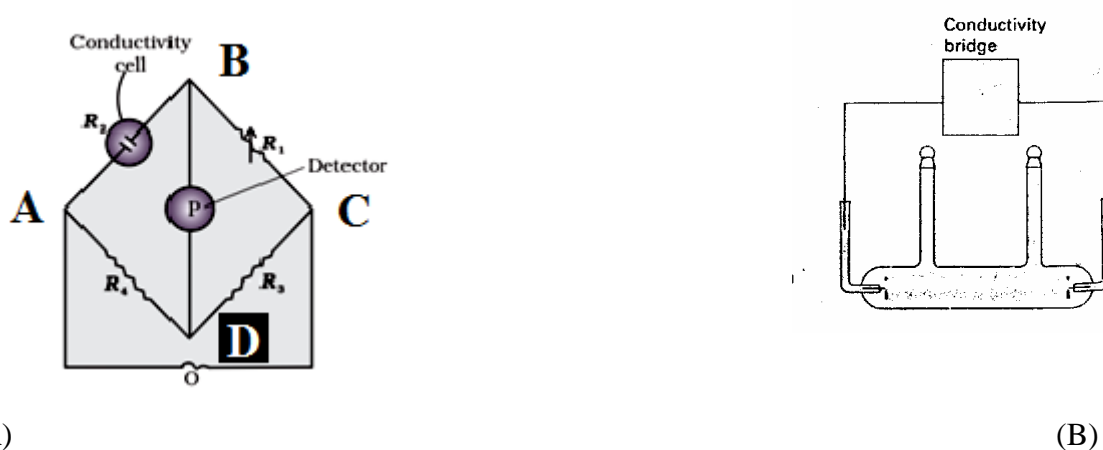


Fig. 2: (A) Wheatstone bridge circuit for measurement of conductivity, (B) Conductivity cell with one arm of a resistance bridge for measurement of conductivity of an electrolyte.

The arms AB and BC represented by resistance R_1 and R_2 are usually in the form of a single calibrated slide wire resistor with a sliding contact connected to the null detector. The solution whose conductance is to be determined is placed in conductivity cell. When the bridge is balanced, assuming that the conductivity cell behaves as a pure resistance, then the voltage between 'B' and 'D' is equal to zero.

$$R_2 = \frac{R_1 R_4}{R_3}$$

By adjustment of the ratio R_1/R_2 , a wide range of resistances can be measured. However, whenever possible, this ratio should not deviate too far away from unity. The cell capacitance is balanced out by providing a variable capacitor in parallel with resistance R_3 . It is so adjusted that the detector gives a sharply defined balance point. The null detector is not an ordinary galvanometer as it is not sensitive to alternating current at the frequency, which is employed to excite the bridge. The most popular detector in use is the magic eye, or the cathode ray oscilloscope.

The problem in determining the resistance of the solution of an electrolyte by the above method is that electrolysis of the solution also occurs simultaneously with the conduction of the current and due to this: -

- a) Polarisation sets in and causes the resistance to vary.
- b) The concentration of the solution changes.

In order to avoid these complications an alternating source of power with frequency ~ 1000 Hz is used.

3.1 Determination of Cell Constant

The electrodes in the cell are not exactly 1 cm apart and may not have surface area of 1 sq. cm (1cm²). Thus the value of observed conductivity is not equal to specific conductance but is proportional to it.

$$R = \rho \frac{l}{a}$$

$$R = \rho x$$

$$\text{Where } x = \frac{l}{a} \text{ and } \frac{R}{\rho} = \frac{\kappa}{G} = x \quad (9)$$

Where $x = \frac{l}{a} = \text{cell constant}$.

Taking an example of N/50 KCl solution, the specific conductance at 25°C is 0.002765 Scm⁻¹. We know that, Cell constant, $x = 0.002765/\text{observed conductance (G)}$. By putting the value of observed conductance in the above expression, one can calculate cell constant. Once the value of cell constant has been determined, great care must be taken not to change the distance between the electrodes during further measurements in any way.

4. Variation of Molar and Specific Conductivity with Dilution

4.1 Effect of Dilution on Molar Conductivity

With dilution following variations on molar conductivity are observed:

(i) The value of molar conductivity increases on dilution. The increase is due to the fact that molar conductivity is the product of specific conductance (κ) and the volume (V) of the solution containing 1 mole of the electrolyte. As the decreasing value of specific conductance is more than compensated by the increasing value of ' V ', thus the value of molar conductance (Λ_m) will increase with dilution. The variation of molar conductivity at different dilutions of some common electrolytes are shown Table 1:

Table 1: Molar Conductance of some common electrolytes at 25°C in Scm².

Concentration (mole/L)	NaOH	KCl	HCl	CH ₃ COOH	AgNO ₃
0.0005	246	147.81	422.74	-	131.36
0.001	245	146.95	421.36	48.63	130.51
0.005	240	143.55	415.80	22.80	127.20

0.01	237	141.27	412.00	16.20	124.76
0.02	233	138.34	407.24	11.57	121.41
0.05	227	133.37	399.09	7.36	115.24
0.10	221	128.96	391.32	5.20	109.14

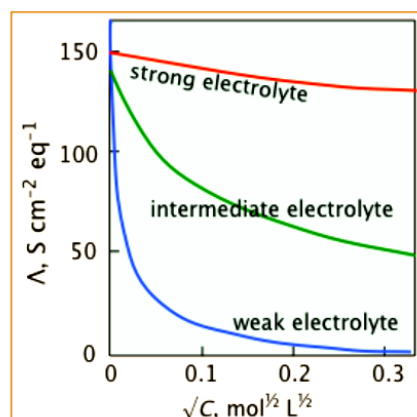


Fig. 3: Variation of molar conductivity with concentration

(i) Effect of dilution on molar conductivity is shown in the Figure.3, where the molar conductivity at different dilutions is plotted against concentration (M). From Figure 3 it is clear that strong electrolytes such as KCl, can have limiting value at zero concentration obtained by extrapolation (i.e. at infinite dilution) whereas for weak electrolyte such as acetic acid, there is no indication that a limiting value can be obtained by the extrapolation of the graph to zero concentration. It means we cannot experimentally determine molar conductivity of weak electrolytes at infinite dilution.

(ii) The maximum value of the molar conductivity is termed as the molar conductivity at zero concentration (or infinite dilution) and is termed Λ_m^∞

(iii) The specific conductance depends on the number of ions present per unit volume of the solution. Since on dilution the degree of dissociation increases but the number of ions per unit volume decreases, therefore it is expected that the specific conductance of a solution decrease on dilution

(Table.2).

Table 2: Specific Conductance of NaCl Solution at 25⁰ C:

Concentration	Molar Conductance (Scm ²)
0.000	0.012645
0.0005	0.012450
0.001	0.012374
0.01	0.011851
0.100	0.010674

For strong electrolytes, Λ_m increases slowly with dilution and can be represented by the equation

$$\Lambda_m = \Lambda_m^0 - A\sqrt{c}$$

If we plot \sqrt{c} vs Λ_m the slope is equal to $-A$ and intercept is Λ_m^0 .

5. Kohlrausch's Law of Independent Migration of Ions

It has been observed that the conductivity of solution increases with dilution until it reaches its limiting value at infinite dilution is represented as Λ_m^∞ . Kohlrausch made a systematic study of Λ_m^∞ for different electrolytes and concluded that each ion contributes a characteristic value of its own to molar conductivity at infinite dilution irrespective of the nature of the other ion present. Consider the values in Table.3 to appreciate the law:

Electrolytes in set I and II have a common anion so that the difference can only be due to the difference in contribution to Λ by K^+ and Na^+ ions. In the same way in sets III and IV the constant difference may be attributed to the difference in contribution to Λ_m^∞ made by the Cl^- and NO_3^- ions. These observations can be explained by Kohlrausch's law of independent migration of ions which states that: At infinite dilution, where the electrolytes are fully dissociated and free from interionic effects, each ion migrates independently of its co-ion. As such each ion contributes its definite share to the total equivalent conductivity of the electrolyte, which depends only on the nature of the contributing ions and not at all on the ion with which it is associated as a part of the electrolyte. In other words, the molar conductivity at infinite dilution of an electrolyte is equal to the sum of the ionic conductances of the ions composing it, provided the solvent and temperature are the same.

$$\Lambda_m^\infty = \nu_+ \lambda_+ + \nu_- \lambda_- \quad (10)$$

Where, λ_+ and λ_- are the ionic conductances of the cation and anion respectively at infinite dilution and ν_+ and ν_- is the number of cations and anions in which one molecule of the electrolyte. For anion and cation this value is constant at a fixed temperature and in a given solution. It is expressed in $\text{Scm}^2\text{mol}^{-1}$ or $\text{Sm}^2\text{mole}^{-1}$.

Applications of Kohlrausch Law

5.1.1 Calculation of molar conductivity of a weak electrolyte at infinite dilution

It is not possible to determine the value of molar conductivity at infinite dilution for weak electrolytes since we cannot obtain the limiting value of the molar conductivity for a weak electrolyte. This is done indirectly by the molar ionic conductance for the individual ions of the weak electrolyte as follows: For e.g. molar conductance of acetic acid at infinite dilution can be calculated from the molar conductance at infinite dilution of hydrochloric acid, sodium acetate and sodium chloride as follows:

$$\Lambda_m^\infty \text{HCl} = \Lambda_m^\infty \text{H}^+ + \Lambda_m^\infty \text{Cl}^- \quad (11)$$

$$\Lambda_m^\infty \text{CH}_3\text{COONa} = \Lambda_m^\infty \text{Na}^+ + \Lambda_m^\infty \text{CH}_3\text{COO}^- \quad (12)$$

$$\Lambda_m^\infty \text{NaCl} = \Lambda_m^\infty \text{Na}^+ + \Lambda_m^\infty \text{Cl}^- \quad (13)$$

Add eq. 11 and 12 and subtract 13 we get:

$$\begin{aligned} \Lambda_m^\infty \text{HCl} + \Lambda_m^\infty \text{CH}_3\text{COONa} - \Lambda_m^\infty \text{NaCl} \\ = \Lambda_m^\infty \text{H}^+ + \Lambda_m^\infty \text{Cl}^- + \Lambda_m^\infty \text{Na}^+ + \Lambda_m^\infty \text{CH}_3\text{COO}^- - \Lambda_m^\infty \text{Na}^+ - \Lambda_m^\infty \text{Cl}^- \\ = \Lambda_m^\infty \text{H}^+ + \Lambda_m^\infty \text{CH}_3\text{COO}^- = \Lambda_m^\infty \text{CH}_3\text{COOH} \end{aligned}$$

5.1.2 Calculation of Degree of Dissociation of Weak Electrolytes

The degree of dissociation of weak electrolyte such as NH_4OH , acetic acid can be determined by measuring the molar conductivity Λ_m of the solution of the electrolyte at any given dilution. For e.g. the degree of dissociation (α_c) of a weak electrolyte at the concentration c mole per liter may be given by the following relation:

$$\alpha_c = \frac{\Lambda_m}{\Lambda_m^\infty}$$

Where, Λ_m is the molar conductivity of electrolyte at concentration 'c' and Λ_m^∞ is the molar conductivity of the same electrolyte at infinite dilution. Hence, measurement of Λ_m permits evaluation of ' α_c ' if Λ_m^∞ is known. But we also know that for weak electrolyte like acetic acid α is related to K_a by Ostwald dilution law ie by the following relation.

$$K_a = \frac{c\alpha^2}{1-\alpha} = \frac{c\Lambda_m^2}{\Lambda_m^\infty \left(1 - \frac{\Lambda_m}{\Lambda_m^\infty}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^\infty (\Lambda_m^\infty - \Lambda_m)}$$

5.1.3 Determination of Solubility and solubility product of Sparingly Soluble Salts

Another application of conductance measurements is in the determination of the solubility of a slightly soluble salt. Salts like AgCl, BaSO₄, CaCO₃, Ag₂CrO₄, PbSO₄, PbS, Fe(OH)₃ etc are ordinarily regarded as sparingly soluble and have a very small but definite solubility in water. The solubility of such sparingly soluble salts is obtained by determining the specific conductivity (κ) of a saturated salt solution.

For example, a saturated solution of silver chloride in water has a conductivity which is given by

$$\kappa = \tilde{c}_{Ag^+} \lambda_{Ag^+} + \tilde{c}_{Cl^-} \lambda_{Cl^-} + \tilde{c}_{H^+} \lambda_{H^+} + \tilde{c}_{OH^-} \lambda_{OH^-}$$

$$\kappa = \tilde{c}_{Ag^+} \lambda_{Ag^+} + \tilde{c}_{Cl^-} \lambda_{Cl^-} + \kappa_w$$

$$\kappa - \kappa_w = \tilde{c}_{Ag^+} \lambda_{Ag^+} + \tilde{c}_{Cl^-} \lambda_{Cl^-}$$

If \tilde{s} is the solubility in moles per m³ then $\tilde{s} = \tilde{c}_{Ag^+} = \tilde{c}_{Cl^-}$ then

$$\kappa - \kappa_w = \tilde{s} (\lambda_{Ag^+} + \lambda_{Cl^-})$$

$$\tilde{s} = \frac{\kappa - \kappa_w}{\lambda_{Ag^+} + \lambda_{Cl^-}}$$

If the solution is very dilute, the values of λ^∞ may be used from the standard table.

$$\tilde{s} = \frac{\kappa - \kappa_w}{\Lambda_{AgCl}^\infty}$$

The solubility product constant is given by

$$K_{SP} = a_{Ag^+} a_{Cl^-}$$

If the solution is dilute enough to regard the activity coefficients as unity, then

$$K_{SP} = \left(\frac{\tilde{s}}{\tilde{c}_0}\right)^2$$

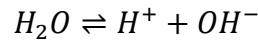
$$K_{SP} = \left(\frac{\kappa - \kappa_w}{\tilde{c}_0 \Lambda_{AgCl}^\infty} \right)^2$$

In the case of silver chloride $\kappa - \kappa_w = 1.802 \times 10^{-4} \text{ Sm}^{-1}$ and $\Lambda_{AgCl}^\infty = 138.27 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$ so that

$$K_{SP} = \frac{1.802 \times 10^{-4} \text{ Sm}^{-1}}{(1000 \text{ molm}^{-3})(138.27 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1})} = 1.698 \times 10^{-10}$$

5.1.4 Determination of ionic product of water

With the help of specific conductivity of water, the ionic product of water can be determined. The ionization of water may be represented as,



The product of the concentrations of H^+ and OH^- ions expressed in mol/L is called ionic product of water and is represented by K_w .

$$K_w = a_{H^+} a_{OH^-}$$

Since in pure water the concentrations of the ions are exceedingly small, we may set the activities equal to the concentrations of the species present.

$$K_w = \frac{\tilde{c}_{H^+} \tilde{c}_{OH^-}}{\tilde{c}_0^2}$$

In pure water $\tilde{c}_{H^+} = \tilde{c}_{OH^-} = (K_w)^{1/2} \tilde{c}_0$ where \tilde{c}_{H^+} and \tilde{c}_{OH^-} are the concentrations of H^+ and OH^- in molm^{-3} and \tilde{c}_0 is the concentrations of those ions at standard state.

The conductivity of pure water κ_w is related to the concentrations by the equation.

$$\kappa_w = \tilde{c}_{H^+} \lambda_{H^+} + \tilde{c}_{OH^-} \lambda_{OH^-}$$

$$\kappa_w = (K_w)^{1/2} \tilde{c}_0 (\lambda_{H^+} + \lambda_{OH^-})$$

$$\lambda_{H^+} + \lambda_{OH^-} = 548.1 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

The value of κ_w at 25°C obtained by Kohlrausch law is $5.5 \times 10^{-6} \text{ Sm}^{-1}$. Using these values we obtain K_w .

$$K_w = \left(\frac{\kappa_w}{\tilde{c}_0 (\lambda_{H^+} + \lambda_{OH^-})} \right)^2$$

$$= \left[\frac{5.5 \times 10^{-6} \text{ Sm}^{-1}}{(1000 \text{ molm}^{-3})(548.1 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1})} \right]^2$$

$$= 1.01 \times 10^{-14}$$

The best values of K_w are obtained from measurements of electrochemical cell potentials, and these agree well with the best values from conductivity measurements.

Ionic Activity

Our next task is to learn to write chemical potentials of electrolytes in solution. First, we shall discuss ideal electrolyte solutions in which the concentrations are expressed on the molality scale. For an ideal NaCl solution, the chemical potential

For an ideal NaCl solution, the chemical potential μ_{NaCl} is given by

$$\mu_{NaCl} = \mu_{Na^+} + \mu_{Cl^-}$$

Because cations and anions cannot be studied individually, μ_{Na^+} and μ_{Cl^-} are not measurable. Nevertheless, we can express the chemical potentials of the cation and anion as

$$\mu_{Na^+} = \mu_{Na^+}^0 + RT \ln(m_{Na^+})$$

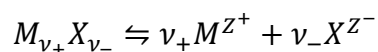
$$\mu_{Cl^-} = \mu_{Cl^-}^0 + RT \ln(m_{Cl^-})$$

Where $\mu_{Na^+}^0$ and $\mu_{Cl^-}^0$ are the standard chemical potential of ions. So we can rewrite the equation for μ_{NaCl} as

$$\mu_{NaCl} = \mu_{NaCl}^0 + RT \ln(m_{Na^+} m_{Cl^-})$$

$$\mu_{NaCl}^0 = \mu_{Na^+}^0 + \mu_{Cl^-}^0$$

In general a salt with the formula $M_{v_+} X_{v_-}$ dissociate as follows



The chemical potential is given by

$$\mu = v_+ \mu_+ + v_- \mu_-$$

$$\mu_+ = \mu_+^0 + RT \ln(m_+) \text{ and } \mu_- = \mu_-^0 + RT \ln(m_-),$$

The molalities of the cation and anion are related to the molality of the salt originally dissolved in solution, m , as follows:

$$m_+ = v_+ m \text{ and } m_- = v_- m$$

Substituting the expressions for μ_+ and μ_-

$$\mu = (v_+\mu_+^0 + v_-\mu_-^0) + RT \ln(m_+)^{v_+}(m_-)^{v_-}$$

We can define mean ionic molality (m_{\pm})

$$m_{\pm} = (m_+^{v_+}m_-^{v_-})^{1/\nu}$$

Where $\nu = v_+ + v_-$

On taking ν power on both sides

$$(m_{\pm})^{\nu} = m_+^{v_+}m_-^{v_-}$$

$$\mu = (v_+\mu_+^0 + v_-\mu_-^0) + \nu RT \ln m_{\pm}$$

In majority of cases we can replace mean ionic molality with mean ionic activity

$$a_{\pm} = \gamma_{\pm}m_{\pm}$$

At infinite dilution the mean ionic activity coefficient $\gamma_{\pm} = 1$

So

$$\mu = (v_+\mu_+^0 + v_-\mu_-^0) + RT \ln(a_{\pm})^{\nu}$$

$$\mu = (v_+\mu_+^0 + v_-\mu_-^0) + RT \ln(a)$$

$$(a_{\pm})^{\nu} = a$$

Mean ionic molality can also be expressed in terms of the molality of the solution, m because

$$m_+ = v_+m \quad \text{and} \quad m_- = v_-m$$

$$m_{\pm} = [(v_+m)^{v_+} + (v_-m)^{v_-}]^{1/\nu}$$

$$m_{\pm} = m(v_+^{v_+}v_-^{v_-})^{1/\nu}$$

Write the expression for the chemical potential of $\text{Mg}_3(\text{PO}_4)_2$ in terms of the molality of the solution.

A N S W E R

For $\text{Mg}_3(\text{PO}_4)_2$, we have $\nu_+ = 3$, $\nu_- = 2$, and $\nu = 5$. The mean ionic molality is

$$m_{\pm} = (m_+^3 m_-^2)^{1/5}$$

and the chemical potential is given by

$$\mu_{\text{Mg}_3(\text{PO}_4)_2} = \mu_{\text{Mg}_3(\text{PO}_4)_2}^{\circ} + 5RT \ln m_{\pm}$$

From Equation 7.19,

$$\begin{aligned} m_{\pm} &= m(3^3 \times 2^2)^{1/5} \\ &= 2.55m \end{aligned}$$

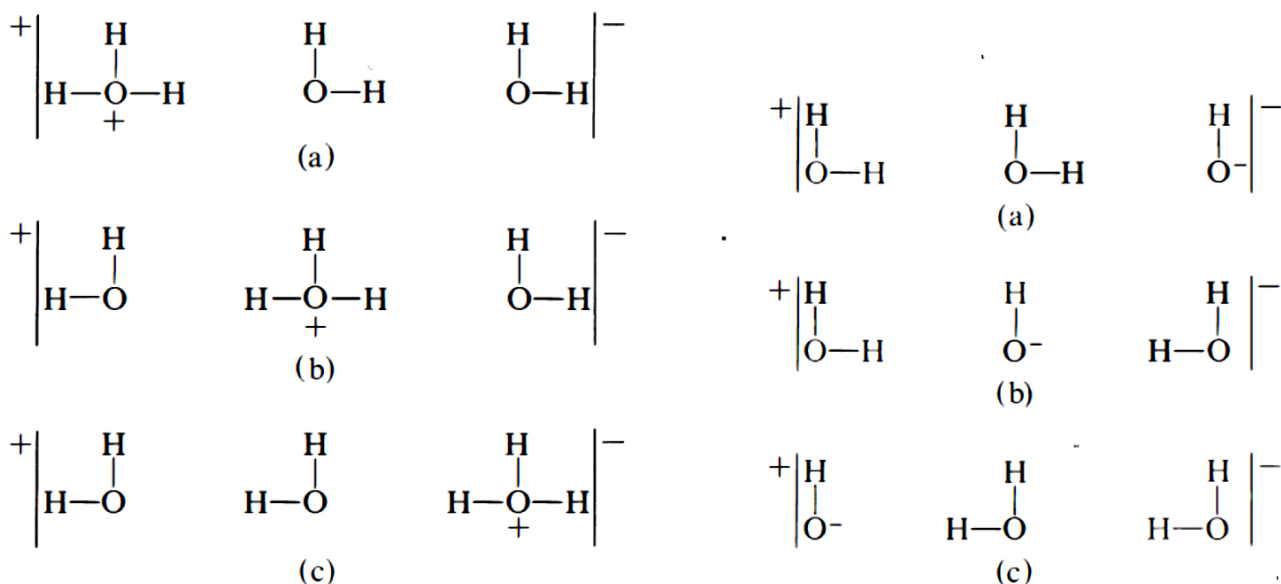
so that

$$\mu_{\text{Mg}_3(\text{PO}_4)_2} = \mu_{\text{Mg}_3(\text{PO}_4)_2}^{\circ} + 5RT \ln 2.55m$$

Conductivities of hydrogen and hydroxyl ions

The molar conductivities of the hydrogen ion and the hydroxyl ion are much larger than those of other ions. While the other ions move like a sphere pushing through a viscous medium, the very large values of the molar ionic conductivity observed for H^+ and OH^- have been explained on the basis of a proton jump from one species to another. For conduction by H^+ ion, we have the scheme shown in Fig. below. A proton is transferred from the H_3O^+ ion to an adjacent water molecule, thereby converting the water molecule to an H_3O^+ ion. The process is repeated, the newly formed H_3O^+ ion handing on a proton to the next water molecule, and so on. The occurrence of this process leaves the water molecules in an unfavorable orientation; for the process to happen again, they must rotate through 90° . The initial stage is shown in Fig.(a), an intermediate stage in Fig. (b), and the final stage in Fig. (c). The analogous process for the hydroxyl ion is shown in Fig.

The process of proton transfer results in a more rapid transfer of positive charge from one region of the solution to another than would be possible if the ion H_3O^+ has to push its way through the solution as other ions must. For this reason also the conductivities of H^+ and OH^- ions are not related to the viscosity of the solution.



Ionic mobility

Although at infinite dilution all electrolytes are completely dissociated their molar conductance differ vastly from one another. This has been attributed to the differences in the speed of the ions. For example molar conductivity at infinite dilution of HCl is more than three times that of sodium chloride. Since chloride ion is common it follows that the speed of ion is more than three times the speed of sodium ion.

Since the speed of an ion varies with the potential applied it is better to use the term ionic mobility which is defined as the distance travelled by an ion per second under a potential gradient of 1 volt per meter.

Diffusion

Electrical conductance is a consequence of a motion of ions in an applied electric field. If the electric field is absent the ions and solvents molecules in solution move in random manner as a result of thermal energy. If there exist concentration gradient for a given electrolyte at constant temperature and pressure then there is a tendency for diffusion of the electrolyte from a region of higher concentration to a region of lower concentration so as to reach an equilibrium condition wherein the concentration gradient is smoother out. Diffusion is thus a process which involves the migration of a component in solution down the gradient of its own concentration.

An ion in a solution possess diffusion coefficient D , which measures the mobility of ion due its thermal energy kT . Ionic mobility u of the ion on other hand measures the mobility of the ion due to the kinetic energy imparted to its by the applied electric field. The parameter D and u are related by the Nernst-Einstein equation

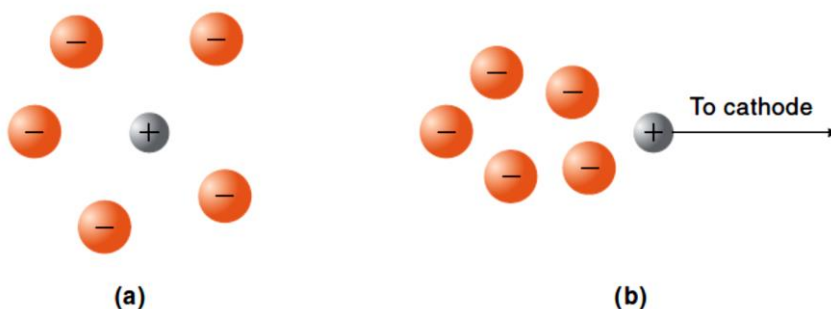
$$D = \frac{u kT}{ez}$$

Where e is the electronic charge and z is the charge number of the ion.

Debye–Huckel Theory of Electrolytes

Our treatment of deviations from ideality by electrolyte solutions has been empirical: Using the ionic activities obtained from the activity coefficient and the known concentration, we calculate chemical potential, the equilibrium constant, and other properties. Missing in this approach is a physical interpretation of ionic behavior in solution. In 1923, Debye and the German chemist Erich Hückel (1896–1980) put forward a quantitative theory that has greatly advanced our knowledge of electrolyte solutions. Based on a rather simple model, the Debye–Hückel theory enables us to calculate the value of γ_{\pm} from the properties of the solution.

The mathematical details of Debye’s and Hückel’s treatment are too complex to present here. Instead, we shall discuss the underlying assumptions and final results. Debye and Hückel began by assuming the following: (1) electrolytes are completely dissociated into ions in solution; (2) the solutions are dilute, with a concentration of 0.01 m or lower; and (3) on average, each ion is surrounded by ions of opposite charge, forming an ionic atmosphere in the figure below. Working from these assumptions, Debye and Hückel calculated the average electric potential at each ion caused by the presence of other ions in the ionic atmosphere.



The Gibbs energy of the ions was then related to the activity coefficient of the individual ion. Because neither γ_+ nor γ_- could be measured directly, the final result is expressed in terms of the mean ionic activity coefficient of the electrolyte as follows

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| \sqrt{I}$$

Where $||$ sign denotes magnitude not sign of the product $z_+ z_-$, The quantity I is the ionic strength is defined as

$$I = \frac{1}{2} \sum_i m_i z_i^2$$

m_i and z_i are the molality and charge of the i th ion. The above equation for $\log \gamma_{\pm}$ is called Debye-Hückel limiting law. The left side of the equation is unit less so I also should be unit less and it is assumed to be divided by $m^0 [1 \text{ mol } (H_2O)^{-1}]$

Calculate the mean activity coefficient (γ_{\pm}) of a 0.010 *m* aqueous solution of $CuSO_4$ at 298 K.

ANSWER

The ionic strength of the solution is given by Equation 7.25:

$$\begin{aligned} I &= \frac{1}{2} [(0.010 \text{ m}) \times 2^2 + (0.010 \text{ m}) \times (-2)^2] \\ &= 0.040 \text{ m} \end{aligned}$$

From Equation 7.26,

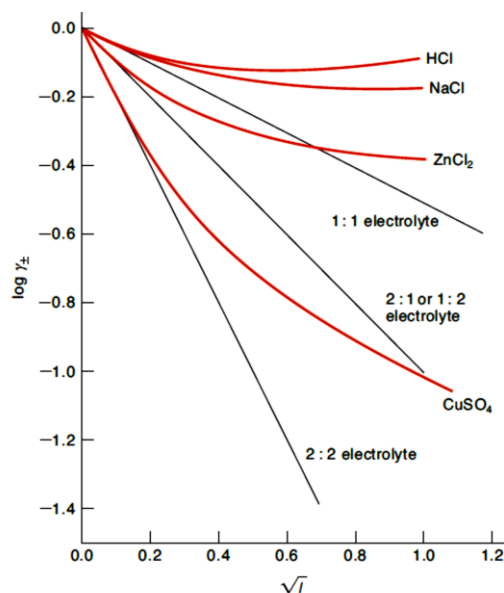
$$\begin{aligned} \log \gamma_{\pm} &= -0.509(2 \times 2)\sqrt{0.040} \\ &= -0.407 \end{aligned}$$

or

$$\gamma_{\pm} = 0.392$$

Experimentally, γ_{\pm} is found to be 0.41 at the same concentration.

Figure below shows calculated and measured values of $\log \gamma_{\pm}$ at various ionic strengths. We can see Equation for γ_{\pm} holds quite well for dilute solutions but must be modified to account for the drastic deviations that occur at high concentrations of electrolytes.



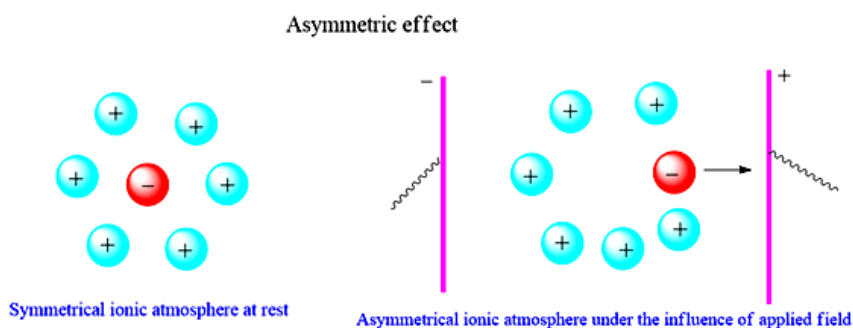
Debye-Huckel-Onsagar Equation

In order to explain the abnormal behaviour of strong electrolytes number of scientists worked in this field viz. Noyes (1904), Sutherland (1906), Bjerrum (1909) and Milner (1912), Debye and Huckel in 1923, and Onsagar in 1926 put forward the modern theory of strong electrolytes known as ***Debye- Huckel- Onsagar theory of strong electrolyte.***

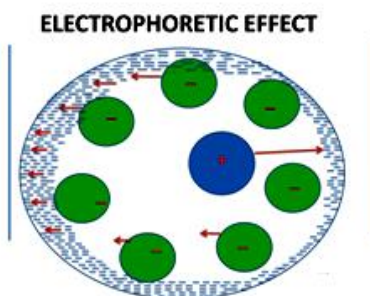
Debye-Huckel treatment deals with the distribution of ions around a given ion and the net effects of these neighbouring ions have on the central ion. Debye and Huckel derived an equation based on the quantitative treatment of inter ionic attraction. This equation was later on modified by Onsagar and is known as Debye-Huckel-Onsagar (DHO) equation for strong electrolyte. It shows how the potential energy of an ion in solution depends on the ionic strength of the solution. In the case of strong electrolytes the value of molar conductance at infinite dilution is much less than unity due to following effects:

(i) *Assymmetric effect/Relaxation effect*

Interionic forces are present and each ion has a tendency to be surrounded on the time average by ions of opposite charge called the ionic atmosphere. A negative ion is surrounded by the ions of opposite charge called the ionic atmosphere. When an EMF is applied, the negative ions migrate towards the anode where the ionic atmosphere of positive ions is left behind to disperse, at this time a new ionic atmosphere is under formation. The rate of formation of new ionic atmosphere is not the same at which the previous ionic atmosphere disperses and the later takes more time. This time is called the 'relaxation time'. In the case of the moving ion there will always be an excess of ions of opposite charge. The ions will always be dragged back. This effect will decrease the mobility of the ions and is known as 'relaxation effect or asymmetric factor'



(ii) ***Electrophoretic effect***



The solvent molecules attach themselves to ionic atmosphere and the ions move in the direction opposite to that of central ion. It produces friction due to which the mobility of the central ion is retarded. This effect is called the electrophoretic effect. The electrophoretic effect reduces the mobility of the ions and hence also reduces their conductivities. The quantitative formulation of these effects is far from simple, but the Debye-Huckel-Onsager theory is an attempt to obtain quantitative expression at about the same

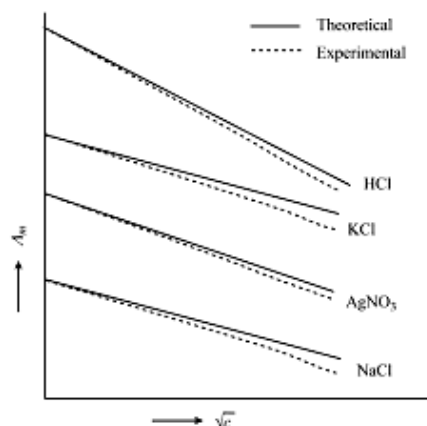
level of sophistication as the Debye-Huckel-theory itself.

The theory leads to a Kohlrausch like expression in which

$$\Lambda_m = \Lambda_m^\infty - (A + B\Lambda_m^\infty)\sqrt{c}$$

$$\Lambda_m = \Lambda_m^\infty - \left(\frac{82.4}{(\epsilon_r T)^{1/2} \eta} + \frac{8.20 \times 10^5}{(\epsilon_r T)^{3/2}} \Lambda_m^\infty \right) \sqrt{c}$$

ϵ_r is the dielectric constant, η is the coefficient of viscosity, T is the temperature of the medium and c is the concentration of the solution in moles per liter. The first term in the bracket gives a measure of the electrophoretic effect while the second term gives asymmetric effect. A and B are called Debye-Hückel constants.



The Debye –Falkenhagen effect

The Debye and Falkenhagen examined the conductance behavior of a solution of a strong electrolyte by applying alternating currents of a strong electrolyte by applying alternating currents of different frequencies. They predicted that if the frequency of alternating current is high so that the time of oscillation is small in comparison with the relaxation time of the ionic atmosphere, the asymmetry effect will be virtually absent. In other words the ionic atmosphere around the central ion will remain symmetric. The retarding effect due to the asymmetry may therefore be entirely absent and the conductance may be higher. The conductance of a solution therefore should vary with the frequency of alternating current used. The higher the frequency the higher will be the conductance evidently. This effect also known as dispersion of conductance has been verified experimentally. The conductance remain independent of the frequency of alternating current up to 10 cycles per second. But with the further increase in frequency, the conductance starts increasing towards a certain limiting value indicating complete absence of asymmetric effect.

The Wien effect

The speed of an ion in an electric field varies with the applied potential gradient. Thus in very high fields $E > 10^7$ V/m an increase in conductivity is observed resulting from the fact that a finite time (the relaxation time) is required for the atmosphere to form about an ion. In very high fields the ion moves so quickly that it effectively loses its atmosphere; the atmosphere does not have time to form and so cannot slow the ion. The asymmetry effect disappears and the conductance increases. This effect is called Wien effect. The moving ion is therefore almost free from the effect of the oppositely charged ionic atmosphere. Thus the conductance of a strong electrolyte in aqueous solution increases to a certain limiting value with the increase in the potential gradient applied.

Transport number

The measurement of the conductivity yields the sum of the positive and negative ion conductivities. To obtain the individual ion conductivities, an additional independent measurement is necessary. Even before Kohlrausch demonstrated the law of independent migration of ions, it was commonly supposed that each ion contributed to the flow of current. In 1853 Hittorf devised a method to measure the contribution of the individual ions. The transport number of an ion is defined as the fraction of the current carried by that ion. By the following equation, the conductivity of a solution containing any number of electrolytes is $\kappa = \sum_i c_i \lambda_i$ then the definition of the transport number of the kth ion is

$$t_k = \frac{c_k \lambda_k}{\kappa} = \frac{c_k \lambda_k}{\sum_i c_i \lambda_i}$$

The transport number of an ion is not a simple property of the ion itself; it depends on which other ions are present and on their relative concentrations. It is apparent that the sum of the transference numbers of all the ions in the solution must equal unity.

In a solution containing only one electrolyte, it follows from the above equation that the transference numbers, t_+ and t_- are defined by

$$t_+ = \frac{v_+ \lambda_+}{\Lambda_m} = \frac{v_+ \lambda_+}{v_+ \lambda_+ + v_- \lambda_-} \quad t_- = \frac{v_- \lambda_-}{\Lambda_m} = \frac{v_- \lambda_-}{v_+ \lambda_+ + v_- \lambda_-}$$

We know that $\lambda_+ = z_+ F u_+$ and $\lambda_- = z_- F u_-$ where u_+ and u_- are motilities of ions

$$t_+ = \frac{v_+ z_+ u_+}{v_+ z_+ u_+ + v_- z_- u_-} \text{ and } t_- = \frac{v_- z_- u_-}{v_+ z_+ u_+ + v_- z_- u_-}$$

But the electrical neutrality of the compound requires that $v_+ z_+ = v_- z_-$ thus we see that

$$t_+ = \frac{u_+}{u_+ + u_-} \text{ and } t_- = \frac{u_-}{u_+ + u_-}$$

$$t_+ + t_- = 1$$

Hittorf method

To illustrate the Hittorf method for measuring the contribution of the individual ions to the current, we consider the electrolysis cell shown in Fig. Suppose that the solution contains copper sulfate and that the anode is copper. We examine the changes that occur in each compartment if one mole of electricity passes. These changes are summarized in Table. If a quantity of electricity Q passes, this is Q/F moles, so all of the changes are multiplied by Q/F . In this experiment, the amount of CuSO_4 in the cathode compartment decreases by $\left(\frac{t_-}{z^+}\right)\left(\frac{Q}{F}\right)$ moles, while in the anode compartment the number of moles increases by $\left(\frac{t_-}{z^+}\right)\left(\frac{Q}{F}\right)$. The concentration in the middle part of the cell is unchanged by the passage of the current. By arranging the apparatus properly, the boundaries indicated at A and B in Fig. 1 can be replaced by stopcocks (Fig. 2), so that the three portions of the solution can be drawn off separately after the experiment. The weight and concentration of electrolyte in each portion is measured after the experiment. Knowing the original concentration, we can calculate the changes in number of moles of electrolyte in each compartment. Analysis of the middle compartment is used as a check to determine if any interfering effects have occurred. The changes in numbers of moles of electrolyte in the compartments can be related to the transference numbers of the ions by a procedure such as the one given above

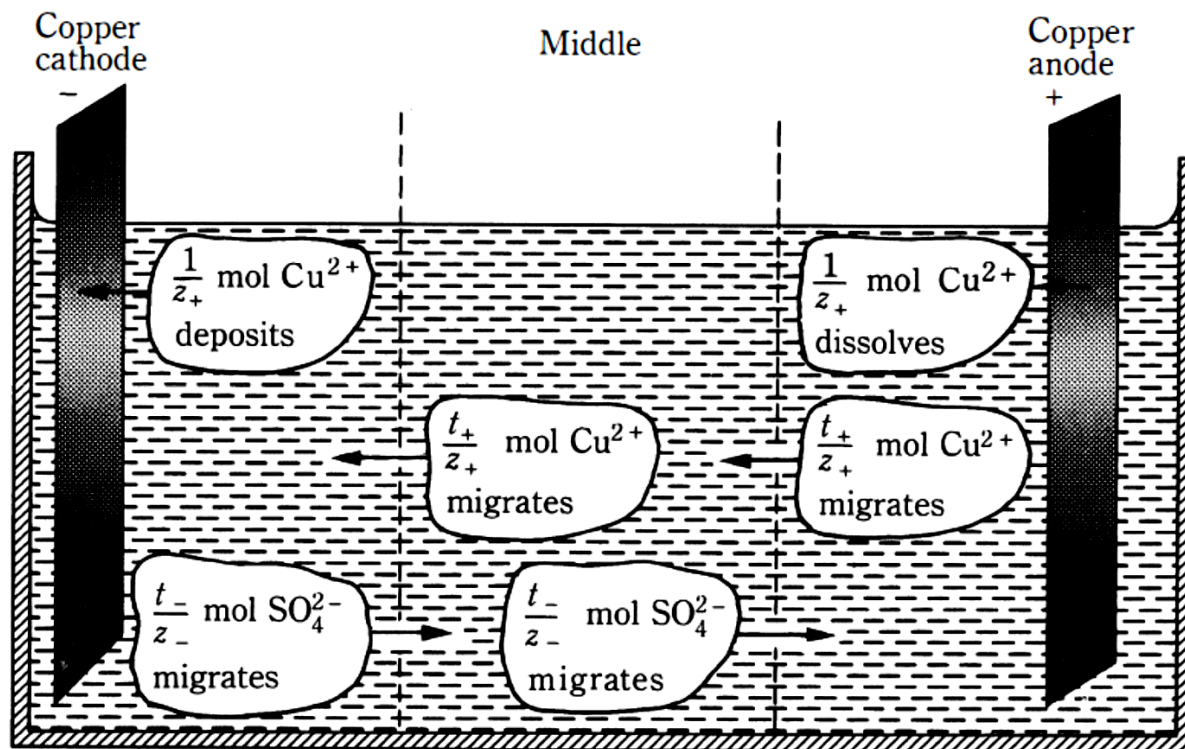


Figure 1. Transport of copper sulphate solution by using copper electrode

Cathode compartment	Middle compartment	Anode compartment
$(1/z_+)$ mol Cu^{2+} plate out on cathode (t_+/z_+) mol Cu^{2+} migrate in (t_-/z_-) mol SO_4^{2-} migrate out	(t_+/z_+) mol of Cu^{2+} migrate out at A (t_+/z_+) mol of Cu^{2+} migrate in at B (t_-/z_-) mol of SO_4^{2-} migrate in at A (t_-/z_-) mol of SO_4^{2-} migrate out at B	$(1/z_+)$ mol Cu^{2+} dissolve from anode (t_+/z_+) mol Cu^{2+} migrate out (t_-/z_-) mol SO_4^{2-} migrate in
Net change	Net change	Net change
$(\Delta n_{\text{Cu}^{2+}})_c = (t_+/z_+) - (1/z_+)$ mol $= -(t_-/z_-)$ mol $(\Delta n_{\text{SO}_4^{2-}})_c = -(t_-/z_-)$ mol	$\Delta n_{\text{Cu}^{2+}} = 0$ $\Delta n_{\text{SO}_4^{2-}} = 0$	$(\Delta n_{\text{Cu}^{2+}})_a = (1/z_+) - (t_+/z_+)$ mol $= (t_-/z_-)$ mol $(\Delta n_{\text{SO}_4^{2-}})_a = (t_-/z_-)$ mol

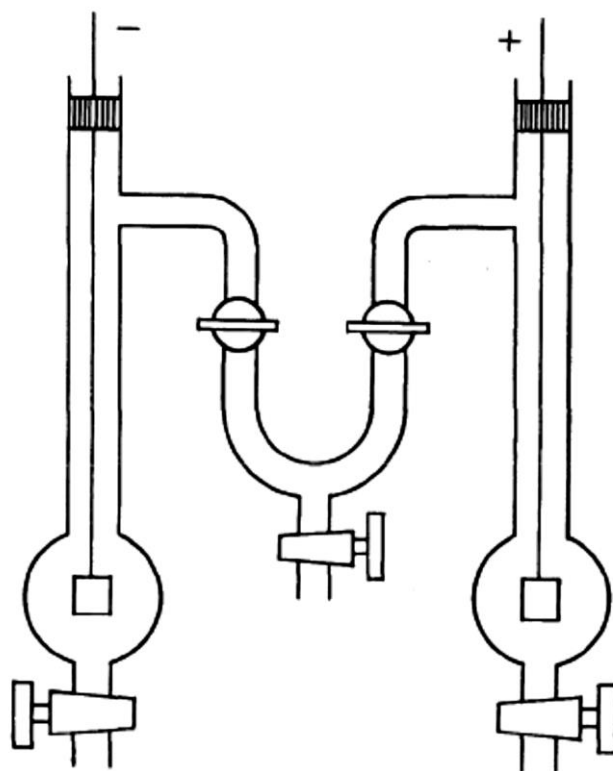
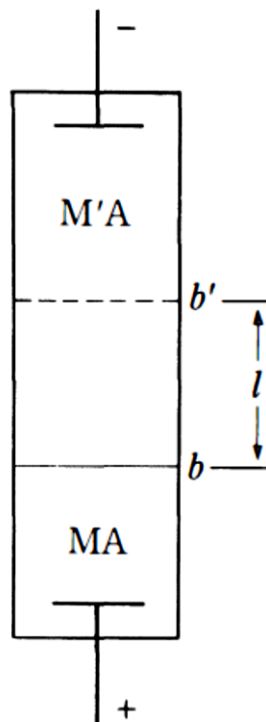


Figure 2. The Hittorf cell

The Hittorf experiment is subject to many difficulties in practice. The development of a concentration gradient by the flow of current results in diffusion of the electrolyte from the more concentrated to the less concentrated regions. To minimize the effect of diffusion the experiment must not run for long time also small currents should be used because the large currents cause heating effects which occurs unevenly and produce convection in the solution ; this mixes the solution up again.

Moving boundary method

The moving-boundary method for the measurement of transference numbers has been brought to a high state of perfection. A schematic diagram of the apparatus is shown in the figure.



A tube has two electrodes fixed at the ends and contains two solutions having an ion in common, one of a compound M'A and another of a compound MA. The system is arranged so that the boundary between the solutions is reasonably sharp; the position of the boundary is visible because of a difference in refractive index of the solutions, or in some cases a difference in color. To avoid mixing and destruction of the boundary, the denser solution is placed beneath the less dense. Suppose that the boundary between the two solutions is initially at b , and that Q/F moles of charge are passed. The M^{Z+} ion carries $\frac{t_+}{z_+} \left(\frac{Q}{F} \right)$ moles of charge past the plane at b . The boundary must move up far enough to (b') so that $\frac{t_+}{z_+} (F)$ moles of electrolyte may be accommodated in the volume between b and b' . If l is the length between b and b' and a is the cross sectional area of the tube, then the volume is displaced in la . If \tilde{c} is the concentration of MA in $\frac{\text{mol}}{\text{m}^3}$, the number of moles that contained in la is $\tilde{c}la$, but this is simply the number of moles passing the plane at b . Thus $\tilde{c}la = \frac{t_+}{z_+} \left(\frac{Q}{F} \right)$ so that

$$\frac{t_+}{z_+} = \frac{\tilde{c}laF}{Q}$$

which assumes that the volume displaced, la , is small compared with the total volume of the solution of MA ; in precise work a correction must be applied.

The moving-boundary method yields more accurate data on transference numbers than does the Hittorf method. Experimentally it is easier to handle. The difficulties lie in the establishment of a sharp boundary, the necessity of avoiding convection currents, and excessive heating by the current. However, once the boundary is established, the flow of current sharpens the boundary, making this a minor difficulty. The relative concentrations of the two solutes are important in maintaining a sharp boundary.

Conductometric Titration

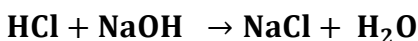
The determination of the equivalent point of a titration by means of conductance measurements is known as conductometric titration. In these titrations measurement of actual specific conductance of the solution is not required, and any quantity proportional to it is sufficient. The titrant is added by a burette and change of conductance as a function of added titrant is used to determine the equivalence point. A conductance cell, in which solution of substance to be titrated is taken, consists of two platinum electrodes of large surface area across which an alternating low-voltage potential is applied. Generally, potential in the range 5-10V at 1000 – 3000 Hz is employed. The conductance cell, therefore, is incorporated into one arm of a Wheatstone bridge type of circuit and the conductance is measured by adjustment of a calibrated resistor to balance the bridge.

Some typical examples of conductometric titration and interpretation of their curves are given in following paragraphs. In all cases, the equivalence points are located at the intersection of lines of differing slope. One of the requirements of these titrations is that the titrant should be at least ten times as concentrated as the solution being titrated, in order to keep the volume change small.

1. Acid-Base Titration

(i) Strong Acid with a Strong Base

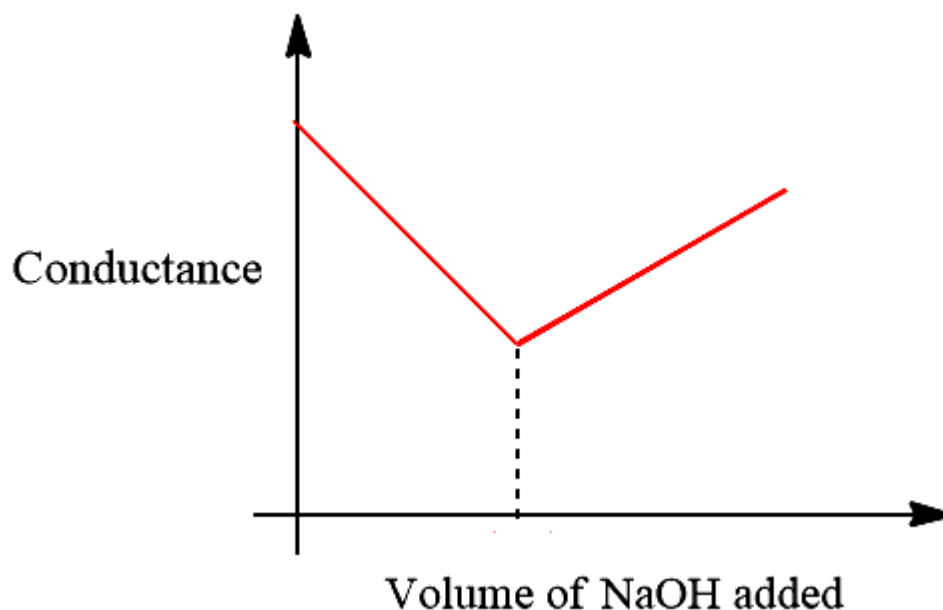
When a strong alkali, e.g., sodium hydroxide is added to a solution of a strong acid, e.g., hydrochloric acid, the following reaction occurs:



In this type of reaction, the conductance first falls, due to the replacement of the H^+ ($\Lambda_m^\infty = 350$) by the added cation Na^+ ($\Lambda_m^\infty = 40 - 80$) and after the equivalence point has been reached, the conductance rapidly rises with further addition of strong alkali due to large Λ_m^∞ value of the hydroxyl ion ($\Lambda_m^\infty = 198$). The two branches of the curve are straight lines provided the volume increase is

negligible and their intersection gives the endpoint. At the neutral point the conductance of the system will have a minimum value, from which the equivalence point of the reaction can be determined.

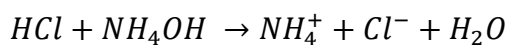
Conductometric Titration of HCl vs NaOH



In actual practice the lines may be slightly curved due to variation in temperature, heat of neutralization, interionic effect and slight increase in the volume of the solution because of the addition of titrant. In spite of this, the inflection is sharp enough to get the equivalent point.

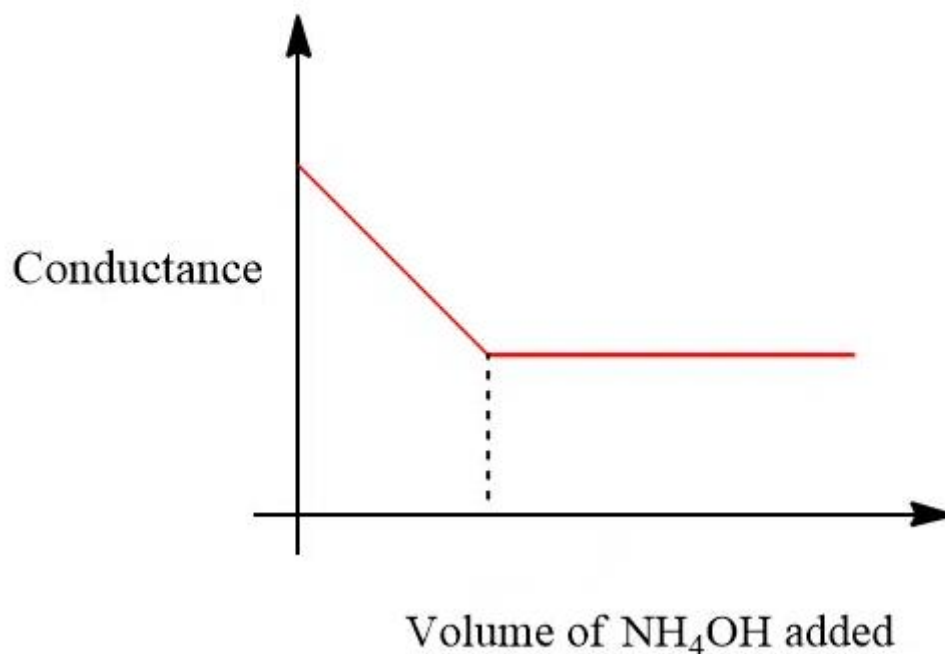
(ii) Strong Acid with a Weak Base

The titration of a strong acid with a weak base may be illustrated by the neutralization of dilute HCl by dilute NH_4OH .



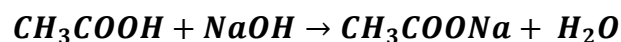
In the beginning, the conductance of the HCl solution is very high due to the liberation of fast-moving H^+ ions. But, when a weak base such as NH_4OH is added from the burette, the fast-moving H^+ ions are replaced by slow-moving NH_4^+ ions. Therefore, the conductance decreases until the endpoint is reached. After the neutralization (equivalent point) is completed, the graph becomes almost horizontal, since the excess aqueous NH_4OH is not appreciably ionized in the presence of NH_4Cl . As NH_4OH is a weakly ionized electrolyte it has a very small conductivity compared with that of the acid or its salt.

Conductometric Titration of HCl vs NH₄OH



(iii) Weak Acid with a Strong Base

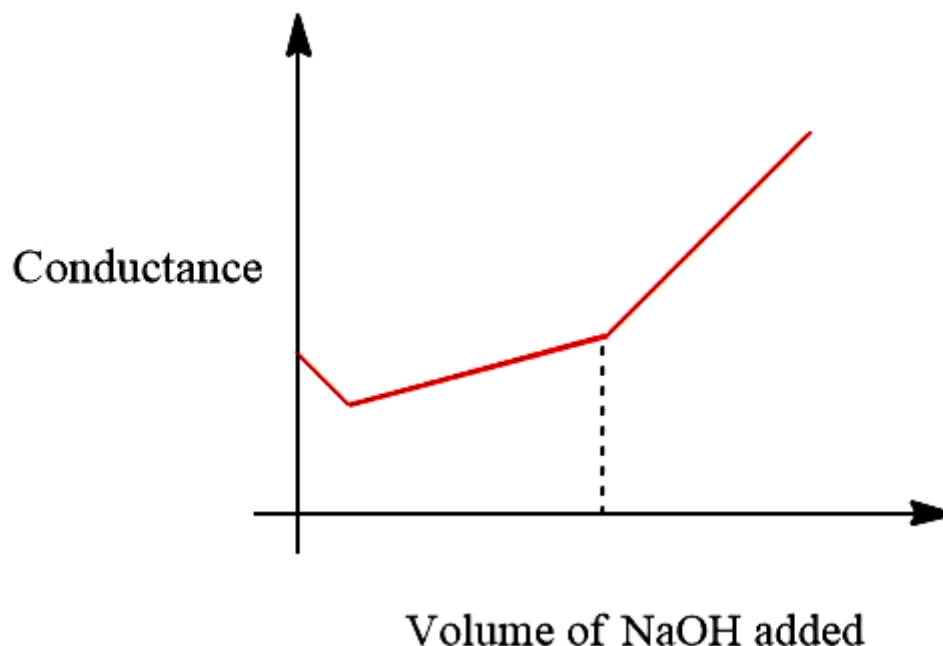
Consider the titration of the weak acid like CH₃COOH with strong base NaOH.



In this titration, the shape of the curve will depend upon the concentration and the K_a of the acid (K_a ~ 1.8 x 10⁻⁵).

Initially, the conductance of acetic acid solution is low because it is a weak acid and weakly dissociated. When we add NaOH solution from a burette, there is a slight decrease in the conductance of the solution which is due to the substitution of free H⁺ ions by slow-moving Na⁺ ions. On further addition of NaOH solution, the conductance of solution increases slightly due to the formation of highly ionized compound CH₃COONa, till endpoint. After the endpoint, the addition of NaOH further, there is an increase in the conductances of the solution sharply which is due to free OH⁻ ions. The conductometric titration graph of CH₃COOH vs NaOH is shown below.

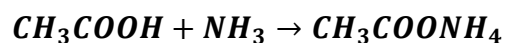
Conductometric Titration of CH₃COOH vs NaOH



(iv) Weak Acid with Weak Base

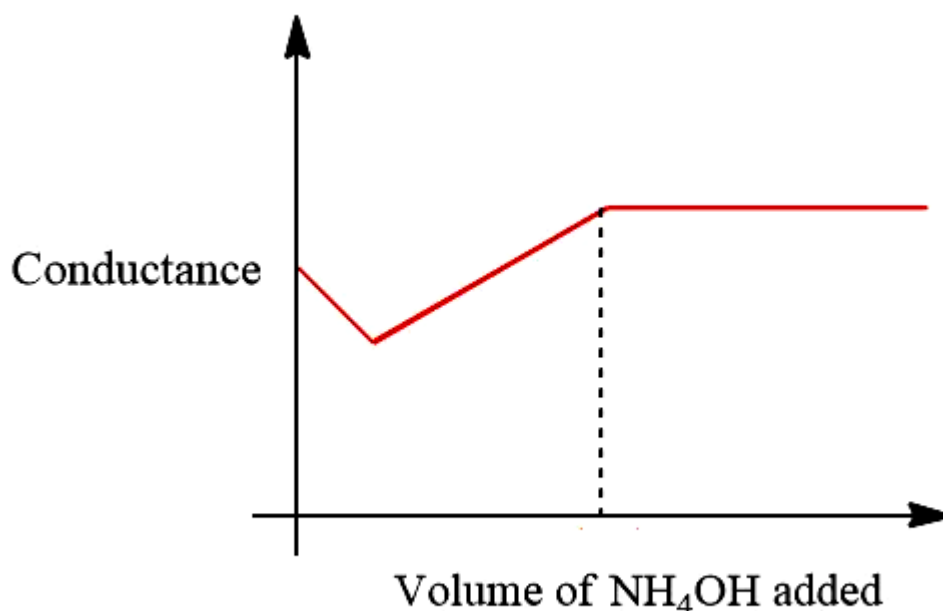
When a weak acid is titrated with a weak base the initial portion of the conductance titration curve is similar to that for a strong base, since the salt is a strong electrolyte in spite of the fact that the acid and base are weak.

Consider the titration curve of CH₃COOH and NH₃



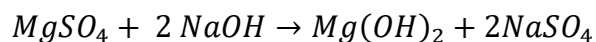
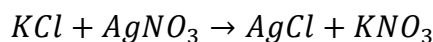
In the beginning, the conductance of weak acid solution is very low due to low ionization. But when NH₄OH is added gradually to the acid solution, the conductance slightly decreases due to the substitution of H⁺ ions by slow-moving NH₄⁺ ions. On further addition of NH₄OH solution, the conductance of solution increases till the endpoint due to the formation of highly ionized salt. After the endpoint, the further addition of NH₄OH solution does not cause to increase in conductance due to a very small extent of ionization. The conductometric titration graph of CH₃COOH vs NH₄OH is shown below:

Conductometric Titration of CH_3COOH vs NH_4OH



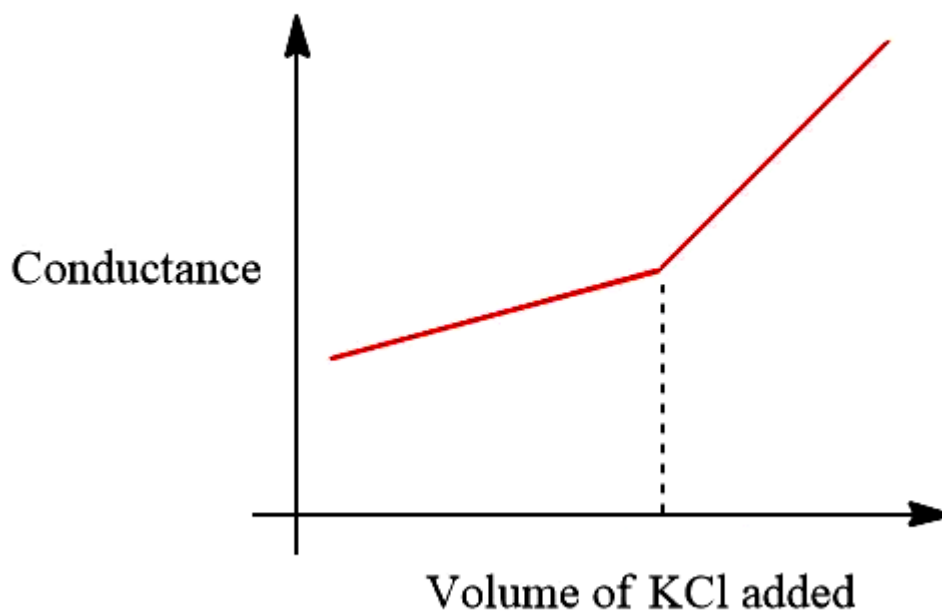
(v) *Precipitation Reactions*

Precipitation titration may also be carried out by conductometric methods. In reactions of the type,



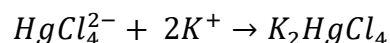
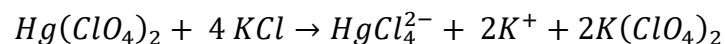
In the beginning, the AgNO_3 solution has a certain value of conductance. But when the KCl solution is added to the AgNO_3 solution, Ag^+ ions are substituted by K^+ ions. It means slow-moving Ag^+ ions are replaced by fast-moving K^+ ions. In another word, the ionic mobility of potassium ions is greater than that of silver ions. Therefore, there is a gradual increase in the conductance of the solution till the endpoint. After the endpoint, further addition of KCl produces more K^+ ions and Cl^- ions, therefore, the conductance of the solution increases sharply. The conductometric titration curve of the AgNO_3 vs KCl solution is shown below

Conductometric Titration of AgNO_3 vs KCl



(vi) Complexometric Titration Reactions

Conductometric titrations have also been employed in the determination of stoichiometry of complex compounds. For example, Job titrated roseo-cobaltic sulphate $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]_2(\text{SO}_4)_3$ with $\text{Ba}(\text{OH})_2$ and obtained two breaks in the titration curve (Figure 16). Also consider the complexometric titrations of KCl with $\text{Hg}(\text{ClO}_4)_2$, where two breaks are obtained in the curve as shown in Figure 16.



The first break is due to the formation of HgCl_4^{2-} and the second is due to the formation of K_2HgCl_4 at the end of the reaction.