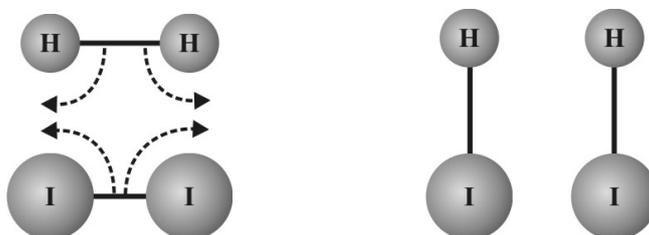


1

Electrochemistry and Batteries

1.1 Introduction-Concept of Electrochemistry

All matter is electrical in nature. An atom, the basic particle is made up of subatomic particles, viz., electrons, protons, neutrons, etc., where the positively charged nuclei is surrounded by the revolving cloud of electrons. Any chemical change may be considered as rearrangement of atoms and their electron clouds. Thus the formation of HI by the combination H_2 and I_2 may be represented as



Here the atoms rearrange themselves by changing partners with simultaneous rearrangement of covalent bonds. This suggests that a chemical change and an electrical change are two faces of the same coin.

Electrochemistry is the branch of physical chemistry that is concerned with the inter-relationship of electricity and chemistry. It has a two pronged coverage, firstly, with the nature and properties of substances containing ions and charged particles and, secondly, with the relationship between electric currents and chemical reaction. The former is sometimes called **ionics** and the latter **electrodics**.

1.2 Electrical Conduction

The substances of this universe can fall into four different categories depending upon their capability of flow of electrons, viz., electrical conductors, insulators, semiconductors and super-conductors.

A. Electrical Conductors (or Simply Conductors)

With few exceptions like mica, generally all the good thermal conductors are good electrical conductors. They allow electrons to pass through them with minimum resistance, and show no preference of direction of flow. Some examples of this class are metals, metal sulphides, acids, bases, ionizable aqueous and nonaqueous salt solutions and fused salts. The electrical conduction of a solid depends on the spacing and state of occupancy of the energy bands. Their valence and conduction bands are placed closely and side by side.

B. Insulators or Non-Conductors

Substances of this category do not allow the electricity to pass through them. Some examples of this class are pure water, majority of the substances of plant origin (dry wood, rubber, paper, etc.), many synthetic organic compounds (benzene, CCl₄, ether, etc.), mica and all non-metals except carbon. In an insulator, the gap between the valence band and conduction band is considerably large making the flow of electrons difficult.

C. Semiconductors

Elements of 4A group, especially Si and Ge have properties that are intermediate between those of metals and nonmetals and therefore are called semiconductors. Their conducting properties are considerably enhanced by the addition of certain impurities, called doping elements. Addition of impurities like phosphorus (P) that have more valence electrons than Si generally called donor impurities give ***n*-type semiconductors**. Similarly acceptor impurities like boron (B) Aluminium (Al) that have lesser number of valence electrons produce ***p*-type semiconductors**. In addition to conducting properties these impurities also restrict the electron movement in the crystal.

The most valuable property derived out of doping and unidirectional flow of electrons is replacement of cumbersome valve versions with small semiconductor pieces of thickness of a pencil eraser called "**Chips**". This led to invention of solid state devices like calculators, mini computers, pocket radios, etc. Further, variation of conducting property of a semiconductor with temperature is exploited by making temperature measuring and controlling devices.

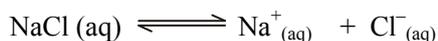
D. Superconductors

Electrical conductivity decreases with decrease in temperature. Lead was found to conduct electricity with zero resistance below 7.3 K. In 1987, physicists found that certain mixtures of copper, barium and rare earth metal oxides exhibit this zero resistance to or at high as 130 K. The property of certain metals, alloys and compounds by virtue of which they conduct electricity with zero or negligible resistance is known as **super conductivity**. The characteristic temperature at which a metal becomes superconducting is called transition temperature T_c .

Because of zero resistance, super conductors attain the capacity to store infinite amount of current. This allows transfer of power from the place of generation to place of utility, few hundred kilometers away without any loss of power during transmission. Further superconductivity is expected to create very high field strength electromagnets that can be used for many purposes like lifting super heavy weights.

E. Solution State Equilibrium – Electrolyte-Conduction

Salt and ions are solvated (aquated)



The negatively charged ions, called anions, move towards **anode** or positive electrode i.e., electrode connected to positive terminal of the battery. The electrode connected to negative terminal of the battery is called **cathode** or negative electrode and the cations move towards it. This assembly of cathode and anode in an electrolytic medium is referred as **cell**.

Electricity or flow of electrons from a battery enters the cell through cathode and leaves through anode. Regardless of the kind of cell or battery, the cathode is defined as an electrode at which reduction occurs i.e., the species around it gain electrons and the anode is defined as an electrode at which oxidation occurs i.e., the species around it lose electrons. In the fused sodium chloride, the sodium ions are reduced at cathode to liberate sodium metal and at anode, the chloride ions are oxidized to chlorine gas. Thus the mechanism of electrolytic conduction may be summarized as follows.

1. Electrolytic conduction mainly occurs through movement of cations and anions, and therefore depends on their concentration.
2. Electrolytic conduction is always accompanied by electrochemical changes.
3. When there are no secondary reactions due to solvent or any other foreign species, there is a progressive decrease in conduction. This fall is attributed to the fall in the concentration of electrolyte on account of deposition or development of non-conducting atmosphere around electrode.
4. A rise in temperature decreases the viscosity of the medium and increases the kinetic motion of the ion. Both these factors act cumulatively and the electrolytic conduction invariably increases with increase in temperature.
5. The electrodes may participate in the electrochemical secondary reactions, in which case they are corroded and sometimes may even contribute for the rise in electrolytic conduction.

1.3 Electrical Resistance and Ohms' Law

We know that the metallic conduction increases with fall in temperature. With the approach of absolute zero the resistance will be almost equal to zero and therefore *all substances behave like perfect conductors at absolute zero*. G. S. Ohm in 1827 found that resistance (R) is related to the current passed (I) and the potential difference across the conductor (E)

$$I = \frac{E}{R} \quad \dots(1.1)$$

Ohm's law may thus be defined that the current strength flowing through a conductor at uniform temperature is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the material.

When current is measured in amperes and potential difference in volts the resistance offered is a fixed value called ohm (represented by symbol omega ' Ω ')

$$\text{Ohm} = \frac{\text{Volt}}{\text{Ampere}}$$

Thus, Ohm is the resistance offered by a body when a current of 1 ampere flows across it under an application of a potential difference of 1 volt. Ohm's law is strictly obeyed by all metallic conductors. Electrolytic conductors obey the law, when the current passed is small enough not to bring any significant concentration changes of the electrolyte.

In addition Ohm also found that the resistance of a conductor of uniform cross section is directly proportional to its length and inversely proportional to the area of cross section.

$$R \propto \frac{1}{a} \quad \text{or} \quad R = \rho \frac{1}{a} \quad \dots(1.2)$$

where ρ (rho) is a proportionality constant called **specific resistance** or **resistivity**. Specific resistance is nothing but the resistance offered by a material of unit length and unit area of cross section. The units of specific resistance are

$$\rho = \text{Ohm} \times \frac{\text{cm}^2}{\text{cm}} = \text{Ohm cm}$$

1.3.1 Conductance and Specific Conductance

Resistance and specific resistance are commonly used for metallic conductors, where the atoms are static. In case of electrolytic solutions the electricity is virtually conducted by constantly moving ions. So it was thought more meaningful to define another quantity called **conductance** (this term should not be equated to conductivity, as done in older literature, as the term conductivity is reserved by IUPAC to represent specific conductance introduced below). It gives the ease with which electricity flows through an electrolytic conductor. The conductance of an electrolytic solution is defined as the reciprocal of its resistance.

$$\text{Conductance } (L) = \frac{1}{R} \text{ Ohm}^{-1} \text{ or mho or } \Omega^{-1} \text{ or Siemens (S)} \quad \dots(1.3)$$

The conventional unit of conductance is ohm^{-1} or mhos or Ω^{-1} . In SI system the same unit is called Siemens and is represented by symbol S.

The reciprocal of specific resistance is defined as **conductivity** or **electrolyte conductivity** or **specific conductance**. Of these three terms only conductivity and electrolytic conductivity are recognised by IUPAC and therefore specific conductance and specific resistance are no longer in use. This quantity, designated by κ (kappa), may be defined as the conductance of unit volume of the solution. In other words electrolytic conductivity is the conductivity of a solution taken in between electrodes of unit area of cross section and separated by a unit distance, Fig. 1.1.

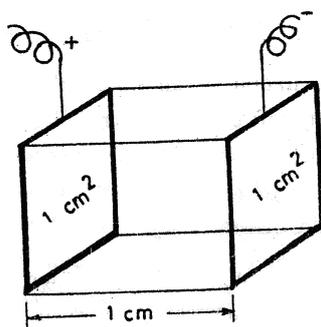


Fig. 1.1 Electrolyte conductivity.

In CGS system the conductivity is expressed in S cm^{-1} or mho cm^{-1}

$$\text{Conductivity} \quad \kappa = \frac{1}{\rho} = \frac{1}{\text{Ohm cm}} = \text{mho cm}^{-1} = \text{S cm}^{-1} \quad \dots(1.4)$$

In SI system, meter being the fundamental unit of distance, the conductivity is expressed as S m^{-1} . The conversion factor of both CGS & SI systems is,

$$1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1} \quad \text{or} \quad 1 \text{ S m}^{-1} = 0.01 \text{ S cm}^{-1}$$

The electrolyte conductivity is dependent upon the concentration of electrolyte. The conductivity increases with increase in the concentration of electrolyte at a given temperature, Table 1.1. A relation between conductivity and conductance could be obtained starting from our definition represented by eqn. (1.4).

$$\text{Conductivity} \quad \kappa = \frac{1}{\rho}$$

$$\text{But from eq. (1.6)} \quad \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a}$$

$$\text{i.e.,} \quad \kappa = \frac{1}{R} \times \frac{l}{a}$$

Substitute L for $1/R$ (from eqn. 1.3)

$$\kappa = L \frac{l}{a} \quad \dots(1.5)$$

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

Because the concentration of all pure solids is taken as unity, the electrolytic conductivity of electrolytes remains constant at a constant temperature.

1.3.2 Equivalent Conductance

Since conductance and electrolyte conductivity are concentration dependent terms, to allow a comparison between different electrolytes, F. W. Kohlrausch (1876) suggested the use of **equivalent conductivity/ equivalent conductance**, represented by Λ_v (Greek : Capital Lambda).

It is defined as the *conductance of all the ions produced by the dissociation of one gram equivalent of an electrolyte, dissolved in a certain volume, V , of the solvent at a constant temperature.*

Mathematically it is expressed as;

$$\Lambda_v = 1000 \frac{\kappa}{C} \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1} \quad \dots(1.6)$$

where C is the concentration of the solution in gram equivalents per litre. Since V is the volume of solution containing 1 equivalent of electrolyte

$$V = \frac{1000}{C}$$

Therefore eqn. (1.6) becomes

$$\Lambda_v = \kappa V \text{ Ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \quad \dots(1.7)$$

The equivalent conductivity of a solution can thus be readily obtained from a knowledge of concentration (or volume of solution containing one equivalent of electrolyte) and electrolyte conductivity. Eq. (1.7) also suggests that equivalent conductivity of a solution of unit volume containing one gram equivalent of a substance is equal to the equivalent conductivity.

In SI system equivalent conductance is expressed as;

$$\Lambda_v = \frac{1000 \kappa (\text{S m}^{-1})}{C (\text{eq m}^{-3})} = \text{S m}^2 \text{ eq}^{-1}$$

Conversion of SI units into CGS units and vice-versa is done using the conversion factor;

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

1.3.3 Molar Conductance

In recent times it has become a practice to express the concentration in moles per litre rather than equivalents per litre. Keeping in pace with this new practice the term **molar conductivity/molar conductance** was introduced. This quantity is also sometimes referred to as **molecular conductivity**. Molar conductivity is defined as the conductance of all the ions produced by the dissociation of one gram molecular weight of an electrolyte dissolved in a certain volume, V of the solvent at constant temperature. This quantity is generally denoted by the symbols μ and Λ_m . Similar to equivalent conductance, molar conductance is given by the expressions,

$$\mu = 1000 \frac{\kappa}{C}$$

and
$$\mu = \kappa V \quad \dots(1.8)$$

where V is the volume of the liquid containing 1 mole of the electrolyte.

The units of μ in CGS system are $\text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ or $\text{S cm}^2 \text{ mol}^{-1}$ and in SI system it is $\text{S m}^2 \text{ mol}^{-1}$. The conversion factors between these systems is

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

1.3.4 Relation between Molar Conductivity and Equivalent Conductivity

The relationship between molar conductivity and equivalent conductivity can be obtained by comparing eqn. (1.7) and (1.8).

$$\frac{\lambda_v}{\mu} = \frac{\frac{1000 \kappa}{C(\text{in equivalents per litre})}}{\frac{1000 \kappa}{C(\text{in moles per litre})}}, \quad \frac{\lambda_v}{\mu} = \frac{C(\text{in moles})}{C(\text{in equivalents})}$$

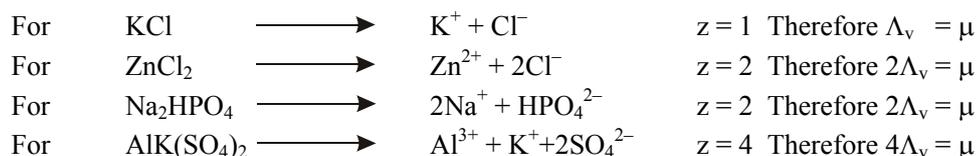
But $C(\text{mol/L}) = \frac{W}{M}$, $C(\text{eq/L}) = \frac{W}{E}$

and $E = \frac{W}{z}$ where z is the total charge carried by cations (or anions) liberated out of dissociation of the electrolyte.

$$C(\text{eq/L}) = \frac{W}{(W/z)} = z \cdot C(\text{mol/L})$$

Therefore $\frac{\Lambda_v}{\mu} = \frac{C(\text{mol/L})}{z \cdot C(\text{mol/L})} = \frac{1}{z}$ (1.9)

This can be well demonstrated by considering the following examples.



Problem 1.

The equivalent conductivity of 0.1 N barium chloride was found to be 105.2 S cm² eq⁻¹ at room temperature. What would be its molar conductivity at the same temperature?

Barium chloride dissociated through following equation,



The total charge carried by individual ions $z = 2$

We know from eqn. (1.13) $\frac{\lambda_v}{\mu} = \frac{1}{z}$

given $\Lambda_v = 105.2 \text{ S cm}^2 \text{ eq}^{-1}$ and $z = 2$ (sum of change on cation/anion)

$$\frac{105.2}{\mu} = \frac{1}{2}$$

or Molar conductivity $\mu = 105.2 \times 2$

$$= 210.45 \text{ cm}^2 \text{ mol}^{-1}$$

1.3.5 Measurement of Conductivity of Electrolytes

Experimental determination of conductivity of electrolytic solutions is important in covering both the basic and applied aspects of electrochemistry. The basic aspects such as nature and quantification of intermediate ionic attractions, ion-ion and ion-solvent pairings, etc., can be done through conductometric measurements. On the applied front the study of corrosion and passivity occupies the top priority. In addition, these measurements are widely used for testing the purity of water obtained from an ion-exchanger to determine quantities such as solubility of sparingly soluble salts, dissociation constants of weak electrolytes, ionic product of water, to compare the strengths of acids and bases and to carry out conductometric titrations of pure and mixture of electrolytes.

Basically determination of conductance, L , involves estimation of resistance, R , of the electrolytic solution. This is usually done by means of **Wheatstone bridge circuit** which involves a comparison of unknown resistance with a standard resistance. The Wheatstone bridge circuit is shown in Fig. 1.2.

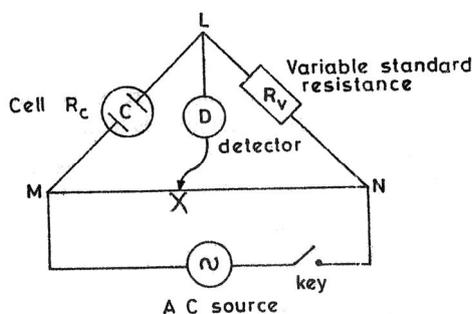


Fig. 1.2 Wheatstone bridge circuit.

The electrolyte of known concentration is taken in a container called **conductivity cell**. It consists of two platinum plates of area of cross section a cm² and separated by a distance 1 cm. These plates are generally coated with platinum black to decrease the polarization effects. This forms one arm of the circuit. The other arm of the circuit is fitted with a variable standard resistance. These two arms are attached to both ends of a meter bridge. A source of alternating current is also attached to both extremes of the meter bridge. The preference of alternating current over direct current is for the following reasons.

- (i) Direct current changes the concentration of electrolyte due to electrolysis,
- (ii) Gases liberated at the electrodes undergo polarization and thereby affect the conductance, and
- (iii) By employing alternating current the direction of current is reversed few thousand times and pulses produced in opposite direction mutually cancel the polarization effects.

The current balance detector, D, fixed between R_c and R_v is generally a head piece or magic eye for less accurate measurements and a cathode ray oscillator for precision measurements.

Now the sliding contact, often called jockey, is moved over the long and uniform meter bridge wire MN, the point of least current through the detector, X, indicated by least buzzing noise of a head phone or smallest signal of an oscilloscope is noted. Under these conditions Wheatstone bridge principle suggests that the ratio of the resistances in the meter bridge arms, i.e., MX to NX is equal to the ratio of LM to LN.

$$\frac{MX}{NX} = \frac{LM}{LN}$$

But the resistance in LM is that of conductivity cell, i.e., R_c , and the resistance in arm LN corresponds the variable resistance, R_v .

Therefore,

$$\frac{MX}{NX} = \frac{R_c}{R_v}$$

Since R_v is known and MX and NX are determined through experiment, the resistance of the cell R_c can be calculated. Inverse of R_c gives the conductance of the experimental solution.

To calculate the electrolyte conductivity of the solution we take help of the eqn. (1.5).

$$\kappa = L \frac{l}{a} \quad \dots(1.10)$$

A knowledge of l and a allow us to calculate the electrolytic conductivity of the solution. But in the normally available cells the electrodes are far from parallel to obtain an exact value for l and far from perfect geometrical shape to obtain an exact value for a . So, instead of attempting to find the values of l and a of the conductivity cell, it is a matter of great simplification to use the literature electrolytic conductivity values of standard electrolytes like KCl Table 1.2. With these values one can determine its conductivity and use these two values to find the ratio l/a . This ratio is a characteristic of a conductivity cell and is known as cell constant, X . The eqn. (1.10) may thus be written as

or $\kappa = L \times X \quad \dots(1.11)$

Electrolyte conductivity = Conductance \times Cell constant.

1.3.6 Determination of Cell Constant

In finding the cell constant, first and foremost step is to remove organic and oily impurities sticking to the walls of the cell and electrodes by treating with dilute chromic acid. It is then thoroughly rinsed with conductivity water. The electrodes of the cell are then dipped in a standard KCl solution, say N/10 KCl, thermostated to required temperature and its conductance is measured. The electrolytic conductivity of N/10 KCl, as determined accurately by Kohlrausch and verified by other scientists at 25 °C is equal to 0.012856 S cm⁻¹. If our experimental temperature is also 25 °C, then cell constant is obtained from the following expression.

$$\text{Cell constant} = \frac{0.012856}{\text{Observed conductance}}$$

The cell constant so obtained can be used in finding the electrolytic conductivity of experimental electrolyte solution.

Various conductivity cells are designed to meet the requirements of different conductance measurements. For solutions of high conductance measurements the electrodes are widely spaced, Fig. 1.3(a), while for low conducting liquids they are closely spaced Fig. 1.3(b).

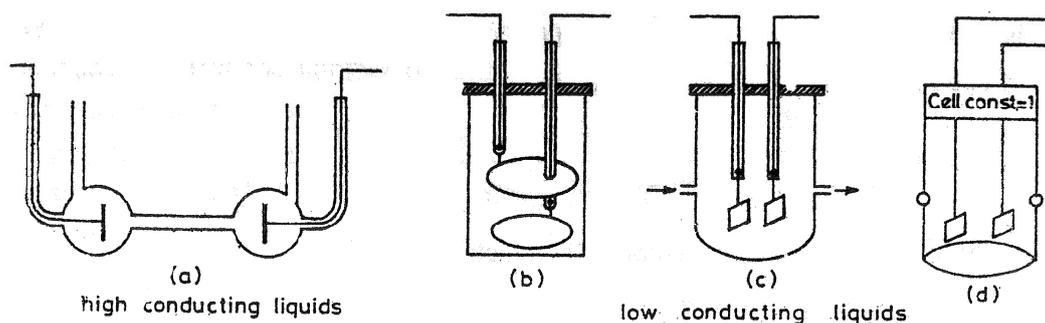


Fig. 1.3 Types of conductance cells.

Fig. 1.3(c) gives the arrangement of a conductivity cell used for on line conductance measurements and Fig. 1.3(d) is a commercial dipping type cell.

For liquids having large conductance values normal distilled water is satisfactory. For low conducting substances, the electrolyte is dissolved in a special grade water called conductivity water. It is prepared in all quartz still. First the water is refluxed, for sufficiently long time, with alkaline permanganate to oxidize the volatile organic impurities. Then it is distilled and collected into an air tight quartz container. Purity of the water can be established by comparing the conductivity with the literature value.

$$\begin{aligned} \text{Conductivity of water after single distillation in glass at } 25^\circ\text{C} \\ = 2.0 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Conductivity of triple distilled water at } 25^\circ\text{C} \\ = 0.8 \times 10^{-6} \text{ to } 1 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Conductivity of conductivity grade water at } 25^\circ\text{C} \\ = 0.056 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Conductivity of purest water available at } 25^\circ\text{C} \\ = 0.038 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

If the measured conductivity is low, the real conductivity of an electrolytic solution is obtained by subtracting conductivity contribution (due to dissociation) of water used for making the solution.

Problem 2.

The resistance of an 0.1 N solution of an electrolyte is 40 ohm. If the distance between the electrodes is 1.2 cm and area of cross section is 2.4 cm^2 , calculate the equivalent conductivity.

Given $l = 1.2 \text{ cm}$, $a = 2.4 \text{ cm}^2$, $C = 0.1 \text{ N}$, $R = 40 \text{ ohm}$

$$\text{Cell constant} = \frac{l}{a} = \frac{1.2}{2.4} = 0.5 \text{ cm}^{-1}$$

$$\text{Observed conductivity} = \frac{1}{40} = 0.025 \text{ S}$$

$$\begin{aligned} \text{Electrolyte conductivity } \kappa &= L \times X \\ &= 0.5 \times 0.025 \\ &= 0.0125 \text{ S cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Equivalent conductivity } \Lambda &= \frac{1000\kappa}{C} = \frac{1000 \times 0.0125}{0.1} \\ &= 125 \text{ S cm}^2 \text{ eq}^{-1}. \end{aligned}$$

1.3.7 Effect of Dilution on Conductance

We already learnt that conductance depends on three factors, viz.,

- (i) on the number of ions,
- (ii) on the charge of the ions, and
- (iii) on the mobility (mass) of ions.

Addition of an electrolyte, till saturation limit, increases the population of free ions and it is reasonable to expect a simultaneous increase of conductance. But the number of ions of an electrolyte are decided by the ionic character of a bond. Further, with the increase in concentration of a solute, the ions get closer amounting to an increase in the electrostatic forces of attraction and viscosity of the medium. These factors tend to reduce the conductance of the solution. A cumulative effect of all the above factors is:

- (i) The conductance increases with increase in the concentration of the electrolyte to a certain maximum level, and
- (ii) Any further increase will only result in a fall in the conductance value.

This trend is well demonstrated in case of highly soluble electrolytic solutions of KOH and acetic acid, Fig. 1.4. However, in majority of the cases, saturation limit precedes the segment representing a fall in the conductance. Therefore we often notice only an increase in conductance with the increase in concentration followed by a simple plateau representing the arrival of saturation limit. Because electrolytic conductivity is defined as the conductance of a unit cube of solution, it adopts the trends followed by conductance.

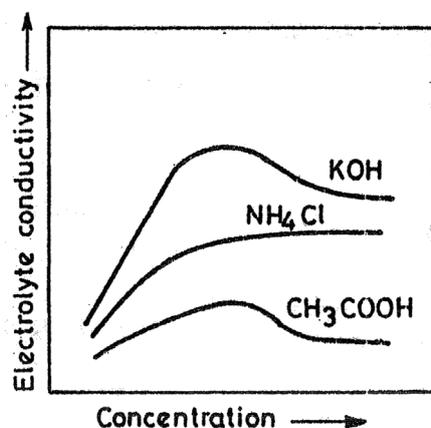


Fig. 1.4 Variation of conductivities of electrolytes with concentration.

On the other hand equivalent conductivity and molar conductivity are inversely proportional to the concentration and therefore, increase with increase in dilution (decrease in concentration), Fig. 1.5.

Equivalent conductivity

$$\Lambda_v = 1000 \frac{\kappa}{C} = \kappa V$$

Molar conductivity

$$\mu = 1000 \frac{\kappa}{C} = \kappa V$$

The trends of decrease in electrolytic conductivity and increase in equivalent and molar conductivity values with dilution is shown in Table 1.1.

Table 1.1 Electrolytic and molar conductivities of aqueous solutions of KCl at different concentrations (25 °C).

Concentration $C \text{ mol L}^{-1}$	Volume containing 1 mole, $V \text{ mL}$	Electrolytic conductivity $\kappa \text{ S cm}^{-1}$	Molar* conductivity : $\text{S cm}^2 \text{ mol}^{-1}$
1.0	1,000	0.11173	111.73
0.1	10,000	0.012856	128.56
0.05	20,000	0.00667	133.4
0.02	50,000	0.002766	138.3
0.01	1,00,000	0.001413	141.3
0.005	2,00,000	0.0007175	143.5
0.001	10,00,000	0.0001469	146.9
0.0005	20,00,000	0.0000739	147.8

* KCl being uni-univalent electrolyte its equivalent and molar conductances are same.

Comparative information on the variation of equivalent conductivities with concentration of various electrolytes is given in Table 1.3. A close observation of data given in Table 1.2 & 1.3 and the curves (in Fig. 1.5) obtained basing on the data, prompt us to draw the following conclusions.

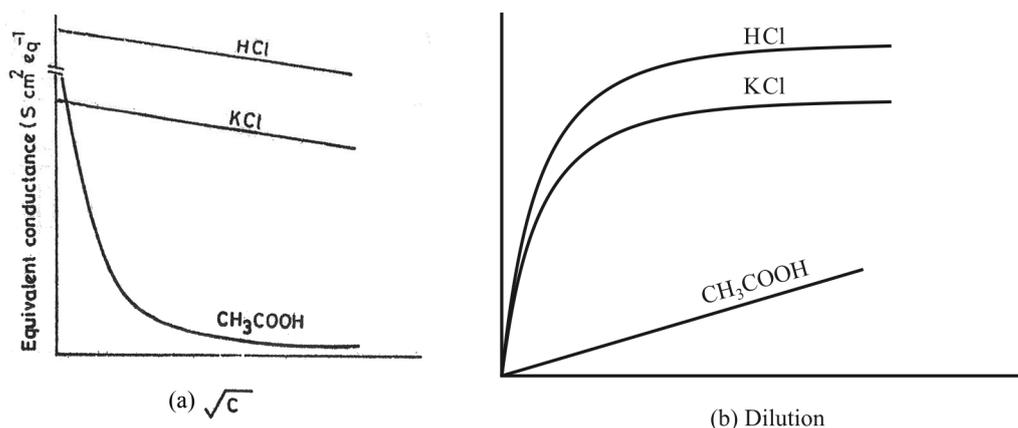


Fig. 1.5 (a) Variation of equivalent conductivity of HCl, KCl and CH₃COOH with square root of concentration and (b) Dilution.

- (i) The electrolytic conductivity increases with increase in concentration of electrolyte.
- (ii) After reaching a particular concentration level, the conductance of some electrolytes may marginally drop and ultimately reach a constant value.
- (iii) In case of less soluble or sparingly soluble salts the conductance may reach the constancy without showing any fall in its value.
- (iv) Equivalent conductivity invariably falls with the increase in the concentration or increase with increase in dilution.
- (v) A gradual, linear change in Λ or κ with square root of concentration is found in case of strong electrolytes like KCl and HCl, known for their complete dissociation in aqueous media.
- (vi) Electrolytes like acetic acid, known for their low ionization, show insignificant change in conductance at higher concentrations but abruptly rise at higher dilutions (lower concentrations).
- (vii) The maximum value of equivalent conductivity is obtained by the extrapolation to zero concentration or infinite dilution of an electrolyte is a characteristic value and is called equivalent conductivity at infinite dilution, Λ_{∞} .

Table 1.2 Variation of equivalent conductivity ($S\text{ cm}^2\text{ eq}^{-1}$) with concentration of various electrolytes at 25 °C.

Concentration $C\text{ mol L}^{-1}$	Strong electrolytes					Weak Electrolyte CH_3COOH
	HCl	KCl	NaOH	AgNO_3	$\frac{1}{2}\text{BaCl}_2$	
0.10	391.3	128.6	221	109.1	105.2	5.2
0.05	399.1	133.4	227	115.2	111.5	7.4
0.02	407.2	138.3	233	121.4	119.1	11.6
0.01	412.0	141.3	237	124.8	123.9	16.2
0.005	415.8	143.5	240	127.2	128.0	22.8
0.001	421.4	146.9	245	130.5	134.3	48.6
0.0005	429.16	149.86	248.11	133.36	139.98	390.71

1.3.8 Classification of Electrolytes

On the basis of curves obtained in case of variation of equivalent conductivity with square root of concentration the electrolytes are grouped into two categories.

A. Strong Electrolytes

Strong electrolytes are the substances whose equivalent conductivity do not change appreciably with the changes in concentration. The equivalent conductances at any dilution are of the same order as the equivalent conductance at infinite dilution. The solutions of mineral acids, bases and many of their simple salts fall in this category of compounds. These ionize completely at low dilutions (KCl, HCl).

B. Weak Electrolytes

Weak electrolytes are the substances which possess low and constant equivalent conductivity values at high concentrations, and these values increase very rapidly in extremely dilute solutions. The carboxylic acids, amines fall in this category of compounds. These do not completely ionize even at high large dilutions.

1.3.9 Kohlrausch Equation

The linear variation of equivalent conductivity with \sqrt{C} of different strong electrolytes, led to the formulation of an empirical relation called **Kohlrausch equation**,

$$\Lambda_v = \Lambda_\infty - b \sqrt{C} \quad \dots(1.12)$$

where b is a constant.

Kohlrausch equation suggests that for strong electrolytes the intercept of Λ_v vs \sqrt{C} plots is equal to Λ_∞ . Weak electrolytes do not obey Kohlrausch relation and therefore this method of calculation of Λ_v is not suitable for weak electrolytes. This is achieved through indirect calculation based on **Kohlrausch's law of independent migration of ions** discussed later.

Problem 3.

The resistance of 0.2 N solution of an electrolyte was found to be 250 ohms at 25 °C. Calculate the equivalent conductivity if the cell constant is 0.75 cm⁻¹.

Observed conductance

$$L = \frac{1}{R} = \frac{1}{250}$$

but Electrolytic conductivity

$$\begin{aligned}\kappa &= X \times L \\ &= 0.75 \times (1/250) \\ &= 0.003 \text{ mho cm}^{-1}\end{aligned}$$

Equivalent conductivity of 0.2 N electrolyte

$$\begin{aligned}\Lambda_v &= \frac{1000\kappa}{C} = \frac{1000 \times 0.003}{0.2} \\ \Lambda_v &= 15 \text{ mho cm}^2 \text{ eq}^{-1}\end{aligned}$$

Problem 4.

The equivalent conductivity of HCl of concentrations 0.1, 0.01 and 0.001 N solutions are 391.3, 412.0 and 421.4 S cm² equiv⁻¹ respectively. Calculate Kohlrausch constant and Λ_4 . (HCl.)

According to Kohlrausch law $\Lambda_v = \Lambda_\infty - b\sqrt{C}$

Substituting the given data, we have;

$$391.3 = \Lambda_\infty - b\sqrt{0.1} \quad \text{I}$$

$$412.0 = \Lambda_\infty - b\sqrt{0.01} \quad \text{II}$$

$$421.4 = \Lambda_\infty - b\sqrt{0.001} \quad \text{III}$$

II-I gives,

$$(412 - 391.3) = 0 - b [\sqrt{0.01} - \sqrt{0.1}]$$

$$20.7 = -b (0.1 - 0.316)$$

$$b = \frac{20.7}{0.216} = 95.8$$

Substituting the value of b in equation II

$$412 = \Lambda_\infty - (95.80) \sqrt{0.01}$$

$$\Lambda_\infty = 412 + 95.8 (0.1)$$

$$\Lambda_\infty = 421.6$$

Similar result can be obtained by taking any other pair of equations given above.

1.4 Ionic Mobilities-Kohlrausch Law

In a state of infinite dilution all strong electrolytes ionize or dissociate cent percent, and the ions can be expected to be wide apart not to have any electrostatic or any other type of attraction or repulsion.

Under these conditions, we achieve an ideal situation where all the charge is expected to be carried by the ions independent of each other. During our discussion on the variation of equivalent conductivity with square root of concentration we noticed that equivalent conductivity increases with dilution to reach a limiting value characteristic of the electrolyte and named it as equivalent conductivity at infinite dilution, Λ_{∞} . In 1875 Kohlrausch made a series of measurements, involving strong electrolytes with common cations and common anions and calculated their differences. He obtained a constant difference in Λ_{∞} values of an ion pair, irrespective of the nature of the common counter ion employed, as exemplified by following results obtained at 25 °C.

Difference between Λ_{∞} values of some pairs of electrolytes having K^+ and Na^+ cations and common anions :

KCl	149.85	KBr	151.64	KOH	272.10	KNO ₃	144.96
NaCl	126.45	NaBr	128.24	NaOH	248.70	NaNO ₃	121.56
Diff	23.40		23.40		23.40		23.40

Difference between Λ_{∞} values of some pairs of electrolytes having OH and Cl ions and common cations :

NaOH	248.70	NH ₄ OH	272.15	LiOH	237.28	½Ba(OH) ₂	262.23
NaCl	126.45	NH ₄ Cl	149.9	LiCl	115.03	½BaCl ₂	139.98
Diff	122.25		122.25		122.25		122.25

Basing on similar observations, Kohlrausch advanced a hypothesis called **Law of independent migration of ions**. This law states that *at infinite dilution each ion makes a definite contribution towards the equivalent conductivity of an electrolyte, irrespective of nature of the co-ion with which it is associated in the solution*. Therefore equivalent conductivity at infinite dilution is made up of two independent terms, called **ion conductivities**, characteristic of each ionic constituent of an electrolyte in solution. We can express the same conclusion mathematically as

$$\Lambda_{\infty} = \lambda_{+} + \lambda_{-} \quad \dots(1.13)$$

where λ_{+} and λ_{-} are the ion conductances of cation and anion respectively. The ion conductance of any ion is a fixed characteristic value in a given solvent. (In the absence of any specific mention, these values are always for aqueous solutions), and are dependent on temperature. The ion conductivity values of some common ions at 25 °C is presented in Table 1.3.

Table 1.3 Ion conductivities at infinite dilution at 25 °C in S cm² equiv.

Cation	λ_+	Anion	λ_-
H ⁺	349.81	OH ⁻	197.6
Li ⁺	38.68	Cl ⁻	76.35
Na ⁺	50.10	Br ⁻	78.14
K ⁺	73.50	I ⁻	76.84
Ag ⁺	61.92	NO ₃ ⁻	71.46
NH ₄ ⁺	73.55	ClO ₄ ⁻	67.36
½Mg ²⁺	53.05	IO ₄ ⁻	54.38
½Ca ²⁺	59.50	HCO ₃ ⁻	44.50
½Sr ²⁺	59.46	½SO ₄ ²⁻	80.02
½B _a ²⁺	63.63	Acetate ⁻	40.90
½Cu ²⁺	54.00	Benzoate ⁻	32.30
½Zn ²⁺	53.00	½Oxalate ²⁻	24.00

1.4.1 Ionic Conductivities / Mobilities

Equivalent conductivity of any electrolyte at any dilution is directly proportional to the charge carried by the ions and their velocities. The conductivity is thus given by the products of charge and velocity of individual ions. At infinite dilution the ionization is complete and solution containing one equivalent of various electrolytes contain equivalent number of ions. Hence at infinite dilution total charge carried by all ions is same in every case. Because the total charge is constant at infinite dilution, the Λ_∞ must depend exclusively on ionic velocities.

Defining the **ionic velocity or mobility** as the speed with which a charged particle at infinite dilution moves under a potential gradient of one volt per cm, we have,

$$\lambda_+ \propto u_+ \quad \lambda_- \propto u_-$$

or

$$\lambda_+ = ku_+ \quad \lambda_- = ku_-$$

where k is a proportionality constant and u_+ and u_- represent the ionic velocities at infinite dilution. Since 1 equivalent of an ion under unit potential gradient carries a charge of 1 Faraday per sec., the proportionality constant $k = 96500$ coulombs.

Therefore,

$$u_+ = \frac{\lambda_+}{k} \quad \& \quad u_- = \frac{\lambda_-}{k} \quad \dots\dots(1.14)$$

$\text{Ionic mobility} = \frac{\text{Ionic conductivity}}{96500} \quad \dots\dots(1.15)$

Ionic conductivity is expressed in S cm², while ionic mobility is expressed in cm s⁻¹. Calculated ionic mobilities of few common ions at 25 °C are given in Table 1.4.

Table 1.4 Calculated ionic mobilities of few common ions at 25 °C

Cations	u_+ (cm s ⁻¹)	Anions	u_- (cm s ⁻¹)
H ⁺	36.2×10^{-4}	OH ⁻	20.5×10^{-4}
K ⁺	7.61×10^{-4}	SO ₄ ²⁻	8.27×10^{-4}
Ba ⁺⁺	6.60×10^{-4}	Cl ⁻	7.91×10^{-4}
Na ⁺	5.19×10^{-4}	NO ₃ ⁻	7.40×10^{-4}

Exceptionally high mobilities of H⁺ and OH⁻ ions is attributed great affinity of these ions for water molecules, which can initiate a chain of transfers from one to other as shown below;

Mechanism of H⁺ ion transfer :



Mechanism of OH⁻ ion transfer:



This additional mobility/conductivity is referred to as **Grotthus conductivity**.

1.4.2 Applications of Kohlrausch's law

The introduction of concept of ionic conductivity opened the vistas towards numerous applications. A few of them are discussed below.

I. Estimation of equivalent conductivity at infinite dilution of weak electrolytes

Method 1: The extrapolation technique used for the determination of λ_4 of strong electrolytes is not useful for weak electrolytes. This is due to the steepness of the curve (Fig. 1.7) at the approach of zero concentration or infinite dilution. Λ_4 of weak electrolytes is calculated using Kohlrausch's law. Using acetic acid as an example, we have at infinite dilution

$$\lambda_{\infty(\text{CH}_3\text{COOH})} = \lambda_{\infty(\text{CH}_3\text{COO}^-)} + \lambda_{\infty(\text{H}^+)}$$

Adding Λ_{∞} of the salt of a strong acid and strong base, e.g., NaCl

$$\lambda_{\infty(\text{CH}_3\text{COOH})} = \lambda_{\infty(\text{CH}_3\text{COO}^-)} + \lambda_{\infty(\text{H}^+)} + \lambda_{\infty(\text{Na}^+)} + \lambda_{\infty(\text{Cl}^-)}$$

on rearranging the ions on R.H.S, we may write

$$\lambda_{\infty(\text{CH}_3\text{COOH})} = \lambda_{\infty(\text{NaCl})} + \lambda_{\infty(\text{CH}_3\text{COONa})} + \lambda_{\infty(\text{HCl})}$$

or

$$\lambda_{\infty(\text{CH}_3\text{COOH})} = \lambda_{\infty(\text{CH}_3\text{COONa})} + \lambda_{\infty(\text{HCl})} - \lambda_{\infty(\text{NaCl})}$$

Because all the electrolytes on the right hand side are strong electrolytes, Λ_{∞} values of these electrolytes can be obtained by the extrapolation of a Λ_v versus \sqrt{C} plots and there by Λ_4 value of acetic acid.

II. Calculation of degree of dissociation and dissociation constant of a weak electrolyte

The ratio of equivalent conductivity at any dilution (Λ_v) to that at infinite dilution (Λ_4) is called **conductance ratio**.

$$\alpha = \frac{\Lambda_v}{\Lambda_{\infty}} \quad \dots\dots(1.16)$$

In dilute solutions of strong electrolyte, the conductance ratio is almost independent of the nature of the salt and is a constant value close to unity at any given concentration. For weak electrolytes this ratio is quite small and is a characteristic quantity called **degree of dissociation**. This in fact represents the fraction of molecules dissociated out of unit concentration of the electrolyte.

	$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$
Initial conc.	1 0 0
Equilibrium conc.	$1 - \alpha$ α α
When C moles are taken initially	$(1 - \alpha)C$ αC αC
Dissociation constant	

$$K_D = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{\alpha C \times \alpha C}{(1 - \alpha)C}$$

K_D of uni-uni valent electrolyte

$$K_D = \frac{\alpha^2 C}{(1 - \alpha)}, \quad \text{where} \quad \alpha = \frac{\Lambda_v}{\Lambda_{\infty}}$$

where C is the concentration of the weak electrolyte and Λ_v is the corresponding equivalent conductivity.

III. Calculation of Ionic Product of Water

Water is a weak electrolyte, which dissociates partially to give H^+ and OH^- ions.

	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$
For 1 mole at equilibrium	$1 - \alpha$ α α
For C moles	$C(1 - \alpha)$ $C\alpha$ $C\alpha$

$$\text{Ionic product of water } K_w = [\text{H}^+][\text{OH}^-] = (C\alpha) \cdot (C\alpha) = C^2 \alpha^2$$

$$\text{Weight of 1000 mL of water} = 1000 \times 0.997 = 997 \text{ g}$$

18 g (1 mole) of water dissolved in 1000 mL of water gives 1 M solution.

So 997 g of water present in 1000 mL of water has a concentration

$$\text{qual to} = \frac{997}{18} = 55.4 \text{ M} = 55.4 \text{ N}$$

Equivalent conductivity of water

$$\begin{aligned}\Lambda_v &= \frac{1000\kappa}{C} = \frac{1000 \times 5.54 \times 10^{-8}}{55.4} \\ &= 1 \times 10^{-6} \text{ S cm}^2 \text{ equiv}^{-1}\end{aligned}$$

Limiting equivalent conductivity $\Lambda_\infty = 349.8 + 197.6 = 547.4$

Degree of dissociation

$$\alpha = \frac{\lambda_v}{\lambda_\infty} = \frac{1 \times 10^{-6}}{547.4} = 1.827 \times 10^{-9}$$

$$\begin{aligned}[\text{OH}^-] &= [\text{H}^+] = \alpha C \\ &= 1.827 \times 10^{-9} \times 55.4 = 1.01 \times 10^{-7}\end{aligned}$$

Therefore, Ionic product of water

$$= [\text{H}^+][\text{OH}^-] = (1.01 \times 10^{-7})^2 = 1.02 \times 10^{-14}$$

IV. Determination of Solubility Products

Another application of conductance measurements is the determination of solubility products of sparingly soluble salts. Salts like AgCl, PbSO₄, AgI, BaSO₄, PbI₂, etc., are *soluble to a negligible extent* and whatever that gets into solution dissociate completely. If S is the solubility, in gram equiv. per litre, of a given salt and κ is the specific conductance of the saturated solution, then Λ_v of the solution is given by;

$$\Lambda_v = \frac{1000\kappa}{S}$$

These solutions are usually so dilute that their equivalent conductivity, Λ_v , is almost equal to Λ_∞ . Therefore,

$$\Lambda_\infty = \frac{1000\kappa}{S}$$

$$S = \frac{1000\kappa}{\Lambda_\infty} \quad \dots(1.17)$$

Since the solutions are extremely dilute, the conductance contribution due to pure water is appreciable part of the total conductance and needs to be subtracted from the total value to get the contribution of dissolved salt.

Therefore,

$$S = \frac{1000(\kappa - \kappa_w)}{\lambda_{\infty}} \quad \dots(1.18)$$

where κ_w is the specific conductance of pure water. In case of uni-univalent electrolyte like AgCl.

The solubility product $K_{sp} = (a_{Ag^+}) (a_{Cl^-})$

The solution is dilute enough to regard the activity coefficient are unity. Therefore, $a_{Ag^+} = a_{Cl^-} = S$

Therefore $K_{sp} = S^2$

In case of AgCl

$$\begin{aligned} \Lambda_{4(AgCl)} &= \lambda_{Ag^+} + \lambda_{Cl^-} \\ &= 61.90 + 76.35 \\ &= 138.25 \text{ S cm}^2 \end{aligned}$$

$$k \text{ of AgCl solution} = 3.41 \times 10^{-6} \text{ S cm}^{-1}$$

$$k \text{ of pure water} = 1.60 \times 10^{-6} \text{ S cm}^{-1}$$

$$\begin{aligned} k \text{ of dissolved AgCl} &= (3.41 - 1.60) \times 10^{-6} \text{ S cm}^{-1} \\ &= 1.81 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

Substituting the above results in equation (1.17)

$$\text{Solubility of AgCl} = \frac{1000 \times 1.81 \times 10^{-6}}{138.25}$$

$$S = 1.31 \times 10^{-5} \text{ eq L}^{-1}$$

$$\begin{aligned} \text{Solubility product} &= K_{sp} = S^2 = (1.31 \times 10^{-5})^2 \\ &= 1.72 \times 10^{-10} \text{ eq}^2 \text{ L}^{-2} \end{aligned}$$

Problem 5.

The equivalent conductivities of sodium benzoate and HCl at 25 °C are 82.4 and 426.16 S cm² equiv⁻¹ respectively. If the transport numbers of benzoate and H⁺ ions are 0.392 and 0.821 in the above mentioned compounds, find the equivalent conductivity of benzoic acid at 25 °C.

$$\begin{aligned} \text{Given,} \quad \Lambda_4 (\text{Sodium benzoate}) &= 82.4 \text{ S cm}^2 \text{ equiv}^{-1} \\ \Lambda_{\infty} (\text{HCl}) &= 426.16 \text{ S cm}^2 \text{ equiv}^{-1} \\ t_+ (\text{in HCl}) &= 0.821 \quad \& \quad t_- (\text{in Sodium benzoate}) = 0.392 \\ \lambda_+ &= t_+ \Lambda_{\infty} \quad \& \quad \lambda_- = t_- \Lambda_{\infty} \\ \lambda_{H^+} &= 0.821 \times 426.16 = 349.9 \text{ S cm}^2 \text{ equiv}^{-1} \\ \lambda_{\text{benzoate}} &= 0.392 \times 82.4 = 32.3 \text{ S cm}^2 \text{ equiv}^{-1} \\ \lambda_{\infty} (\text{Benzoic acid}) &= \lambda_{\text{benzoate}} + \lambda_{H^+} \\ \lambda_{\infty} \text{ Benzoic acid} &= 32.3 + 349.9 = 382.2 \text{ S cm}^2 \text{ equiv}^{-1} \end{aligned}$$

Problem 6.

The equivalent conductance values of 0.0005M (at 25 °C) NaCl, NH₄Cl, NaOH and NH₄OH are 124.50, 149.1, 245.6 and 9.38 mho cm² equiv⁻¹ respectively. Calculate the dissociation constant of NH₄OH.

$$\begin{aligned}\lambda_{\infty(\text{NH}_4\text{OH})} &= \lambda_{\infty(\text{NH}_4\text{Cl})} + \lambda_{\infty(\text{NaOH})} - \lambda_{\infty(\text{NaCl})} \\ &= 149.1 + 245.6 - 124.50 \\ &= 270.2 \text{ S cm}^2 \text{ equiv}^{-1}\end{aligned}$$

Degree of dissociation

$$\alpha = \frac{\lambda_v}{\lambda_{\infty}} = \frac{9.38}{270.2} = 0.0347$$

Dissociation constant $K = \alpha^2 C$

$$\begin{aligned}&= (0.0347)^2 \times (1/100) \\ &= 1.2 \times 10^{-5}\end{aligned}$$

Problem 7.

Calculate the conductance of pure water at 25 °C, when measured employing a cell with a cell constant 1.0. The ion conductivities of H⁺ and OH⁻ are 349.8 and 197.6 S cm² equiv⁻¹ respectively. Density of water at 25 °C is 0.997 g cm⁻³.

$$\Lambda_4 = \lambda_{\text{H}^+} + \lambda_{\text{OH}^-} = 349.8 + 197.6 = 547.4$$

Ionic product of water $K_w = 1 \times 10^{-14}$



Initial	1	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

$$[\text{H}^+] = [\text{OH}^-] = C\alpha = 1 \times 10^{-7}$$

Therefore,

$$\text{Degree of dissociation } = \alpha = \frac{1 \times 10^{-7}}{C}$$

Concentration of water C

$$= \frac{997}{18} = 55.4 \text{ M}$$

Degree of dissociation

$$\alpha = \frac{1 \times 10^{-7}}{55.4} = 1.8 \times 10^{-9}$$

But
$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

Therefore,

$$\Lambda_v = \alpha \Lambda_\infty = 547.4 \times 1.8 \times 10^{-9} = 9.85 \times 10^{-7}$$

$$\Lambda_v = \frac{1000\kappa}{C}$$

$$\kappa = \frac{9.85 \times 10^{-7} \times 55.4}{1000} = 5.46 \times 10^{-8} \text{ S Cm}^{-1}$$

$$\text{Conductance} = \frac{\text{Conductivity}}{\text{Cell constant}}$$

$$\text{Conductance} = \frac{5.46 \times 10^{-8}}{1} = 5.46 \times 10^{-8} \text{ mho}$$

Problem 8.

The conductivity of a saturated solution at 298 K of a sparingly soluble salt MX is $2.5 \times 10^{-6} \text{ S cm}^{-1}$, while that of pure water is $1.61 \times 10^{-6} \text{ S cm}^{-1}$. If the equivalent conductivity of MX at infinite dilution is $156 \text{ S cm}^2 \text{ equiv}^{-1}$, calculate the solubility product of the salt.

$$\text{Conductivity of a saturated solution} = 2.5 \times 10^{-6} \text{ S cm}^{-1}$$

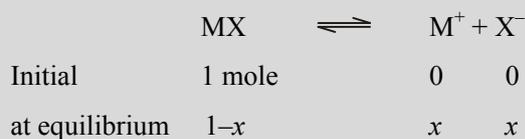
$$\text{Conductivity of pure water} = 1.61 \times 10^{-6} \text{ S cm}^{-1}$$

$$\begin{aligned} \text{Conductivity contribution of only salt (k)} &= (2.5 - 1.61) \times 10^{-6} \\ &= 0.89 \times 10^{-6} \text{ S cm}^{-1} \end{aligned}$$

$$\Lambda_\infty \text{ of the salt} = 156 \text{ S cm}^2 \text{ equiv}^{-1}$$

$$\text{Solubility } S = \frac{1000\kappa}{\lambda_\infty} = \frac{1000 \times 0.89 \times 10^{-6}}{156} = 5.7 \times 10^{-6} \text{ mol L}^{-1}$$

MX being a uni-uni valent salt



$$\begin{aligned} \text{Solubility product (K}_{sp}\text{)} &= [\text{M}^+] [\text{X}^-] = x^2 \\ &= (5.7 \times 10^{-6})^2 = 32.5 \times 10^{-12} \text{ mol}^2 \text{ L}^{-2} \end{aligned}$$

$$\text{Solubility product of MX} = 32.5 \times 10^{-12} \text{ mol}^2 \text{ L}^{-2}.$$

1.5 Conductometric Titrations

This is another interesting application which exploits the variation of conductance of a solution during a titration. This technique can be used advantageously with,

- colored solutions where selection of proper indicator is difficult;
- acids and bases and their mixtures;
- ions and their mixtures that are readily precipitated by the addition of titrant.

A grave disadvantage of conductivity based titrations is their non-applicability with solutions contaminated with high concentrations of electrolyte impurities. Presence of excess of electrolyte (ions) and hence high electrolytic conductivity masks the minor changes in conductivity, taking place as a result of addition of titration. Few examples of acid-base and precipitation titrations are discussed below.

1.5.1 Titration of a strong acid (HCl) with a strong base (NaOH)

Strong acids dissociate completely to give hydrogen ions. The ionic conductance data, Table 1.6 suggest that protons (H^+) are almost two times more conducting than hydroxy ions (OH^-), which themselves are more conducting than all the other ions. When NaOH is added to a solution of HCl we have the reaction.



During the course of neutralization initially high conducting H^+ ions present in the acid are replaced by sodium ions having a much lower conductance. Therefore, addition of alkali is accompanied by a fall (curve AB) in the conductance till all the H^+ ions are totally neutralized. Further addition of alkali may be interpreted as only an addition of hydroxyl ions which are no longer used up in the acid-base reaction. Hence, after neutralization conductance of the reaction solution increases linearly (curve BC) with the volume of the alkali added. The titration graph will have the form shown in Fig. 1.6. Interpolation of both the linear segments AB and BC to meet at B gives the end point of the titration.

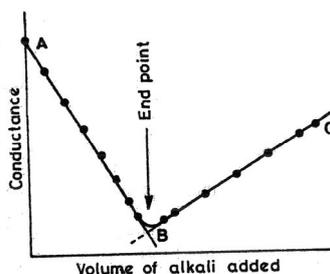


Fig. 1.6 Conductometric titration of a strong acid Vs strong base.

Precise measurements leave a small rounding near equivalent point B and is attributed to water dissociation.

1.5.2 Titration of Weak Acid (CH₃COOH) by Strong Base (NaOH)

A weak acid, like acetic acid, is characterized through its insignificant dissociation. Therefore, at the beginning of titration the acid solution has a low conductance. Addition of alkali to this moderately weak acid solution, initially result in a small fall of conductance owing to the replacement of free H⁺ ions by acetate ions. If the acid is very weak, e.g., boric acid and phenol, the initial decrease of conductance upon neutralization is not observed due to insignificant dissociation. After the addition of a few drops of the alkali, the conductance increases in a regular fashion. This is due to suppression of ionization equilibrium of acetic acid by the acetate ions formed (buffering action) and increase in ionic population (sodium acetate is a strong electrolyte) in the solution.



Beyond neutralization point, addition of alkali result in a steep raise in conductance, the strong base being a better conductor than the salt. This trend in indicated by the segment B, C, D in Fig. 10.7.

1.5.3 Conductometric titration of a mixture of a strong (HCl) and a weak acid (CH₃COOH) with a strong base (NaOH)

One of the valuable features of conductometric titrations is the titration of a mixture of a strong acid and a weak acid in one titration without employing any indicator. In the presence of a strong acid, the dissociation of a weak acid is completely suppressed due to common ion effect. Therefore, addition of a base to such a mixture will first result in the neutralization of the strong acid. The weak acid starts reacting only after neutralization of the strong acid. In the titration graph, Fig. 1.7, the line segment AB represents the neutralization of strong acid and the line segment BC represents the neutralization of weak acid.

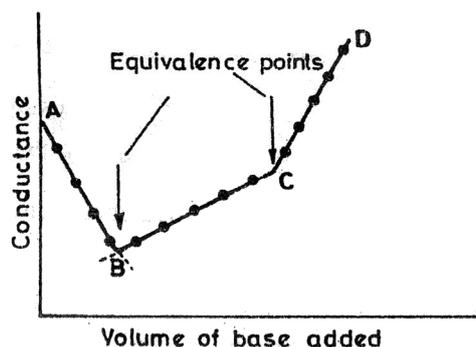


Fig. 1.7 Conductometric titration of a mixture of strong and weak acid *V*s strong base.

Problem 9.

At 18 °C the conductivities at infinite dilution of NH_4Cl , NaOH and NaCl are 129.8, 217.4 and 108.9 mhos respectively. If the equivalent conductivity of N/100 solution of NH_4OH is 9.33 mhos, calculate the degree of dissociation of NH_4OH

$$\lambda_{\infty(\text{NH}_4\text{Cl})} = \lambda_{\infty\text{NH}_4^+} + \lambda_{\infty\text{Cl}^-} = 129.8 \text{ S cm}^2 \quad \text{I}$$

$$\Lambda_{\infty(\text{NaOH})} = \lambda_{\infty\text{Na}^+} + \lambda_{\infty\text{OH}^-} = 217.4 \text{ S cm}^2 \quad \text{II}$$

$$\Lambda_{\infty(\text{NaCl})} = \lambda_{\infty\text{Na}^+} + \lambda_{\infty\text{Cl}^-} = 108.9 \text{ S cm}^2 \quad \text{III}$$

$$\text{I} + \text{II} - \text{III}$$

$$\lambda_{\infty(\text{NH}_4\text{OH})} = (129.8 + 217.4) - 108.9 = 238.3$$

Degree of dissociation

$$\alpha = \frac{\lambda_v}{\lambda_{\infty}} = \frac{9.33}{238.3} = 0.039$$

Dissociation constant

$$K = \frac{\alpha^2 C}{1 - \alpha} = 1.58 \times 10^{-5}$$

Problem 10.

At 25 °C the equivalent conductivity of 0.1M benzoic acid is $8.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$. The ionic conductivities at infinite dilution, of the hydrogen ion and benzoate ions are 349.8 and $32.3 \text{ ohm}^{-1} \text{ cm}^2$ respectively. Calculate the degree of dissociation of 0.1 M benzoic acid.

$$\Lambda_v = 8.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

$$\Lambda_{\infty} = \lambda_{\infty\text{H}^+} + \lambda_{\infty\text{benzoate}} = 349.8 + 32.3 = 382.1$$

$$\alpha = \frac{\Lambda_v}{\Lambda_{\infty}} = \frac{8.9}{382.1} = 0.023$$

Degree of dissociation of benzoic acid = 0.023

Problem 11.

The equivalent conductivity of NH_4Cl at infinite dilution is $149.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ and the ionic conductances of OH^- and Cl^- are 198 and $79.3 \text{ ohm}^{-1} \text{ cm}^2$ respectively. Calculate Λ_{∞} of NH_4OH .

$$\Lambda_{\infty(\text{NH}_4\text{Cl})} = \lambda_{\text{NH}_4^+} + \lambda_{\text{Cl}^-} = 149.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \quad \text{I}$$

$$\begin{aligned}\lambda_{\infty\text{OH}^-} &= 198 && \text{II} \\ \lambda_{\infty\text{Cl}^-} &= 79.3 && \text{III} \\ \text{I} + \text{II} - \text{III} &= 268.4 \\ \Lambda_{\infty} \text{ of } \text{NH}_4\text{OH} &\text{ is } 268.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}.\end{aligned}$$

Problem 12.

Calculate the cell constant of a cell where the area of the electrode is 2.5 sq cm and distance between them is 10 cm

$$\text{Cell constant} = X = \frac{l}{a} \times \frac{10}{2.5} = 4 \text{ cm}^{-1}$$

Problem 13.

Specific conductance of a 0.02 M KCl solution at 25 °C is 0.002768 mhos m^{-1} . If the resistance of a cell containing this solution is 400 ohms, what is the cell constant?

$$\begin{aligned}\text{Cell constant} &= \text{Specific conductance} \times \text{Resistance} \\ &= 0.002768 \times 400 = 1.1 \text{ cm}^{-1}\end{aligned}$$

Problem 14.

When a certain conductance cell was filled with 0.02 M KCl, it had a resistance of 82.4 ohms at 25°C. When it is filled with 0.005 N K_2SO_4 , it had a resistance of 326 ohms. Find the equivalent conductivity of the given K_2SO_4 solution. The specific conductivity of 0.02 M KCl is 0.002768 $\text{ohm}^{-1} \text{ cm}^{-1}$ at 25°C.

$$\begin{aligned}X &= \kappa R \\ X &= 0.002768 \times 82.4 = 0.2281 \text{ cm}^{-1} \\ \lambda_{\text{K}_2\text{SO}_4} &= \frac{0.2281}{326} = 0.0006996 \text{ mho cm}^2 \text{ eq}^{-1} \\ \lambda_{\text{K}_2\text{SO}_4} &= \frac{1000\kappa}{C} = \frac{1000 \times 0.0006996}{0.005} \\ &= 139.9 \text{ mho cm}^2 \text{ eq}^{-1}\end{aligned}$$

Problem 15.

The equivalent conductivity of 0.05 N solution of propionic acid at 25 °C is 6.32 $\text{equiv}^{-1} \text{ ohm}^{-1} \text{ cm}^2$ and the value increases to 385.6 $\text{cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1}$ at infinite dilution. Calculate the degree of dissociation of the acid at that temperature.

Degree of dissociation of propionic acid

$$\alpha = \frac{\Lambda_v}{\Lambda_{\infty}} = \frac{6.32}{385.6} = 0.0164$$

Problem 16.

In a conductivity cell 0.01 N KCl solution gave a resistance of 225 ohms, while a 0.01 N solution of HCl gave a resistance of 77.1 ohms. Specific conductance of 0.01N KCl is $0.00141 \text{ ohm}^{-1} \text{ cm}^{-1}$. Calculate the cell constant and equivalent conductance of HCl.

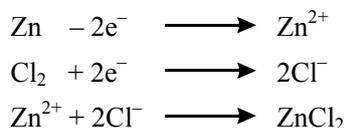
$$\begin{aligned} \text{Cell constant} &= \text{sp. conductance} \times \text{resistance} \\ &= 0.00141 \times 225 = 0.31725 \text{ cm}^{-1} \\ \kappa_{\text{HCl}} &= \frac{0.31725}{77.1} = 0.0041 \text{ mho cm}^{-1} \\ \Lambda_{(\text{HCl})} &= \frac{1000\kappa}{C} = \frac{1000 \times 0.0041}{0.01} \\ &= 410 \text{ mho cm}^2 \text{ eq}^{-1} \end{aligned}$$

1.6 Introduction to EMF

Chemical changes are always accompanied by energy changes, where the difference appears generally in the form of heat (either evolution or absorption). Thus, when a zinc rod is placed in chlorine water, electron exchange takes place between Zn atoms and Cl_2 molecules at the point of inter-phase and Zn dissolves accompanied by evolution of heat.



This is an oxidation - reduction reaction for which partial ionic equations are



Since electrical energy is another form of energy, we could devise a reaction system in such away that all electron movement takes place through an external electrical conductor and there by tap electrical energy. Conversely, a chemical reaction could be initiated by passing electricity through a reaction system. *The chemical and electrical changes are carried in a physical entity called cell. A cell may be defined as a single arrangement consisting of two electrodes and capable of producing electricity due to chemical reaction and vice versa.* A battery is a combination of two or more cells arranged either in series or parallel.

There are two types of cells in which the above electrochemical processes are carried out.

- (i) **A galvanic or voltaic cell** uses the energy released from a spontaneous chemical reaction to generate electricity.
- (ii) **An electrolytic cell** uses the electrical energy to cause a non-spontaneous chemical reaction to occur in spontaneous manner, and the process is commonly called **electrolysis**.

Modern society depends on the galvanic cells for running cars, radios, calculators, medical instruments, computers, on the field analytical devices, emergency flash lights and so on. The

electrolytic cells are used in the chemical and metallurgical industries for the extraction, synthesis and purification of various chemicals. In this chapter our interest lies mainly with the galvanic cells.

1.7 Galvanic Cells, Electrochemical Cells

Under normal circumstances a redox reaction occurs when the oxidizing agent comes in contact with the reducing agent as in the reaction between Zn and Cl_2 described above. The electrons are transferred directly from the reducing agent to the oxidizing agent. In order to tap the energy of the reaction in the form of electrical energy, the reactants must be physically separated so as to prevent direct transfer of electrons. Electrons are then allowed to go from Zn to Cl_2 through an external circuit, made out of a wire or metallic conductor. In the current example both Zn rod and Cl_2 taken in two separate compartments which are separated either through a porous partition or a salt bridge. The porous partition or salt bridge prevents direct mixing of the reactants and at the same time are permeable to ions, Fig. 1.8.

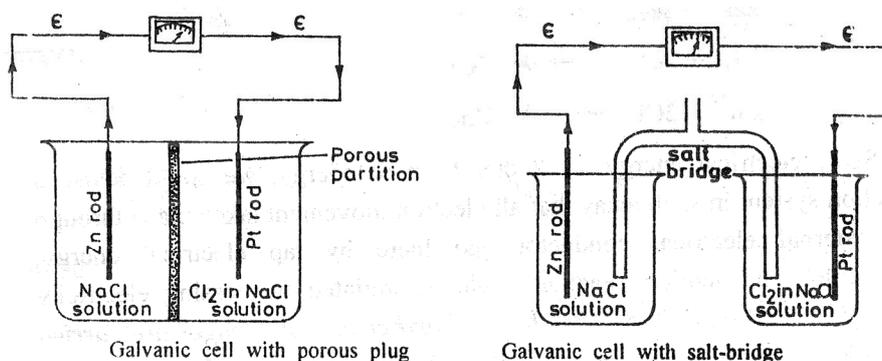


Fig. 1.8 A Galvanic cell.

Since the Cl_2 itself is a non-conductor unlike Zn rod, to conduct electricity in the Cl_2 compartment an inert metal wire like Pt is placed. The Zn rod and Pt wire are called electrodes. By definition the electrode at which oxidation occurs is called the anode (Zn electrode); the electrode at which reduction occurs is known as cathode (electrode is also called chlorine gas electrode).

For this system the individual oxidation and reduction reactions at the electrodes are called **half-cell reactions**.

Half-cell reaction of Zn electrode (anode) :



Half-cell reaction of Pt electrode (cathode) :



Total cell reaction :

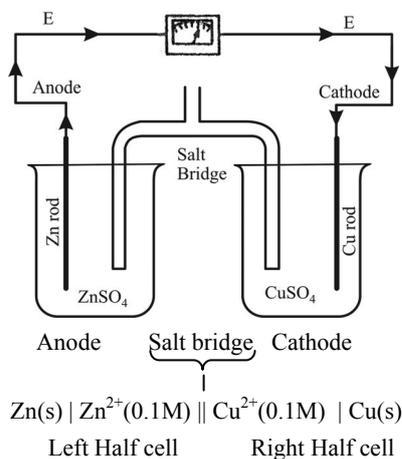


In order to maintain electrical neutrality of both the compartments the Cl^- and Zn^{2+} move across the porous partition. For the movement of each Zn^{2+} ion from anodic compartment to cathodic compartment there is a concurrent migration of two Cl^- ions from cathodic compartment to anodic compartment. In the present example addition of NaCl is only to facilitate easy movement of ions before sufficient concentration of ions is built up with the course of time. A cell operates only so long as the chemical reaction, on which the cell is based, proceed. The electricity ceases as soon as one of the reactant is exhausted or the reaction reaches equilibrium.

Electric current flows from negative to positive electrode through external circuit, but long standing convention defines that current flows from positive to negative electrode (taking the medium into consideration). The passage of electrons from one electrode to the other suggests the presence of a potential difference between them. *The difference of potential, which causes the current to flow from an electrode at higher potential to the one of lower potential is called the electromotive force (emf) of the cell.*

1.7.1 Representation of a Cell

Sketching an electrochemical cell as in Fig. 1.8 is a tedious process. A symbolic representation is often used to describe a cell. This representation is called a **cell diagram**. Following rules are adopted in these representations. For example, a Daniell cell is represented as;



- (i) The anode, where oxidation occurs is represented at the left and at cathode, where reduction takes place, is represented on the right of the cell diagram.

This order can be easily remembered by recollecting the Hindi phrase "LAO SaR CaR" or simply remembering the south asian country LAOS. Here the letters LAOS, stands for Left Anode Oxidation Salt bridge.

In the Daniell cell $\text{Zn} \mid \text{Zn}^{2+}$ half cell is an oxidizing electrode and is written on the left.

- (ii) A single vertical line represents the boundary between different phases that constitute an electrode.
- (iii) A double vertical line indicates that the liquid junction potential has been decreased to minimum by suitable means like using a salt bridge.
- (iv) The concentration of the dissolved substances are indicated in the parenthesis.
- (v) In case of gases at equilibrium it is necessary to represent the pressure of the gas.



- (vi) When two oxidation states of the same species are present in a homogenous medium, they are usually separated by a comma.



1.7.2 Weston Standard Cell

A standard cell is one whose potential is highly reproducible, accurate up to a fraction of a millivolt and has a very small temperature coefficient. **Weston standard cell** is best suited for this purpose. It is a H shaped tube. The negative electrode (Cathode) consists of 12.5% cadmium amalgam, sprinkled with $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ crystals over its top. The anodic limb (positive electrode) consists of mercury covered with solid mercurous sulphate. Now the H shaped tube is filled with a saturated cadmium sulphide solution, Fig. 1.9. The cell is represented as

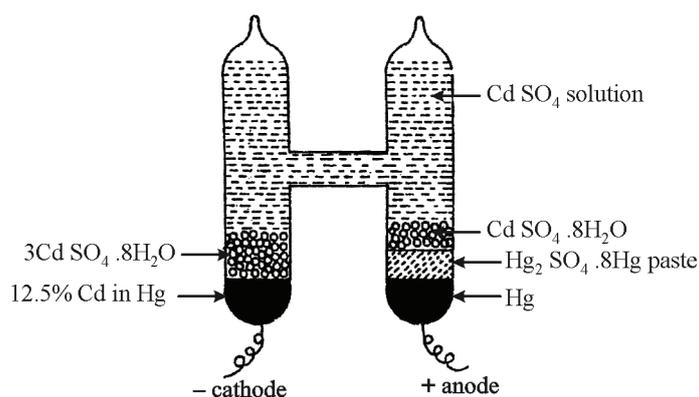


Fig. 1.9 The Weston standard cell.

The *emf* of this cell lies within the range 1.0188 to 1.0198 V, depending on the exact activity of amalgam. The cell has a very small temperature coefficient as to be negligible.

1.7.3 Potentiometer

Approximate estimates of *emf* of a cell may be obtained by connecting an ordinary voltmeter across the electrodes. This method is inaccurate because the *current drawn by the voltmeter* disturbs the electrochemical equilibrium of the cell, thereby bringing some changes in the *emf*. At the most, a voltmeter is satisfactory only in measuring large *emf* values. For obtaining *emf* values without disturbing the electrochemical equilibrium **Poggendorff compensation principle** is widely used. In this technique the *emf* of a cell under examination is balanced by an equal and opposite *emf* from another source, Fig. 1.10.

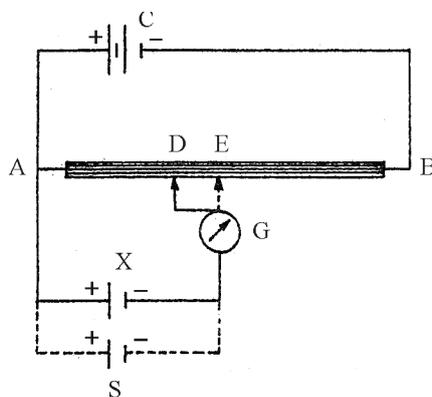


Fig. 1.10 Measurement of *emf*.

A storage cell *C* is connected across a uniform resistance wire *AB*. Now a cell *X*, whose *emf* is under study, is connected through a galvanometer *G* such that it opposes the *emf* of the storage cell. Now the position of the tap key *D* is adjusted until no current passes through the galvanometer. Under these circumstances

$$\frac{\text{emf of } X}{\text{emf of } C} = \frac{AD}{DB} \quad \dots(1.19)$$

Measurement of *AD* and *BD* enables us to calculate the *emf* of the unknown cell provided *emf* of the storage cell is known. But the *emf* of a storage cell is sensitive to minor changes in acid concentration, condition of the lead plates, temperature etc. To counter this problem the cell *X* is replaced by a standard cell *S*, whose *emf* is accurately known to a fraction of a millivolt and has negligible temperature coefficient. So if *E* is the balancing point when

standard cell is used, then

$$\frac{\text{emf of } X}{\text{emf of } C} = \frac{AD}{AE} \quad \dots(1.20)$$

$$\text{Therefore; } \text{emf of } X = \frac{AD}{AE} \times \text{emf of } S \quad \dots(1.21)$$

Thus we get the *emf* of an unknown cell *X*.

1.7.4 Single Electrode Potential

The foregone conclusions suggest the presence of two half cell reactions and the *emf* of a cell gives only the difference in the driving forces of the electrodes. In the Daniell cell we can find more rational answer for the question of why copper does not displace zinc ion from the solution by understanding more about this driving force. When the cell reaction takes place, what we actually observe as **emf** or **cell potential** or **cell voltage** is a kind of tug-of-war between these driving forces. The species with greater tendency to reduce acquires an electron supplied by the less reducing species that gets oxidized. In the zinc-copper cell, therefore, copper ion must have a larger reducing nature or **reduction potential** than zinc. Thus;

$$E_{\text{cell}} = \text{Reduction potential of reduced species} - \text{Reduction potential of oxidized species}$$

$$\text{or } E_{\text{cell}} = \text{Reduction potential of reduced species} + \text{Oxidation potential of oxidized species}$$

$$\text{or in short } E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad \dots(1.22)$$

(Remember that when no specific mention is made the electrode potential is always the reduction potential)

$$\text{or } E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \quad \dots(1.23)$$

In the Daniell cell, therefore;

$$E_{\text{cell}}^0 = E_{\text{Cu}^{2+}|\text{Cu}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0 \quad \dots(1.24)$$

where $E_{\text{Cu}^{2+}|\text{Cu}}^0$ is the standard reduction potential for copper ion and $E_{\text{Zn}^{2+}|\text{Zn}}^0$ is the standard reduction potential for zinc ion.

Since $E_{\text{Cu}^{2+}|\text{Cu}}^0$ is larger than $E_{\text{Zn}^{2+}|\text{Zn}}^0$, E_{cell}^0 should be positive for a spontaneous reaction. Here the prefix standard implies experimental conditions where the **half-cell potential** or **single electrode potential** are measured at 25°C, maintaining unit concentration of reversible ions. The **standard cell potential**, E_{cell}^0 , represents the magnitude of difference between reduction potentials of two half cells of a redox reaction or sum of the standard oxidation potential and standard reduction potential of respective electrodes. *The emf is an intensive property like temperature and therefore 'independent' of the volume of the solution and size of the electrodes.*

Knowing the standard electrode potential of one of the electrode, it is possible to determine electrode potentials of all the other electrodes by suitably coupling and measuring the cell voltage. Unfortunately, even to start with, it is impossible to determine the absolute values of a single electrode potential. So arbitrarily the emf of a standard hydrogen electrode is chosen as zero and relative to this standard electrode, electrode potentials of various electrodes were determined primary standard hydrogen electrode. A standard hydrogen electrode consists of a platinum foil encased in a glass sleeve through which hydrogen gas is passed at a pressure of 1atm and is placed in one molar acid solution, Fig. 1.11. Platinum foil is coated with a layer of platinum black. In addition to providing a conducting surface, the platinum electrode adsorbs molecular hydrogen and helps in maintaining the following equilibrium.

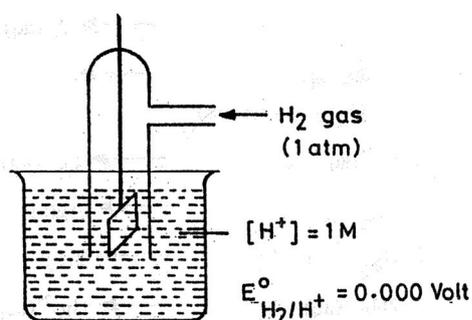
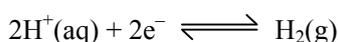


Fig. 1.11 Hydrogen gas electrode.

When hydrogen electrode is paired with another electrode (half-cell) in a galvanic cell, it can undergo either oxidation or reduction depending on the magnitude of potential of coupled electrode relative to hydrogen electrode. The cell *emf* so determined, directly gives the single electrode potential of the coupled electrode. Some of the half cell reactions and corresponding standard reduction potentials are listed in Table 1.5.

The standard reduction potential table serves many useful purposes.

1. From these tables, at a glance, we can make out the good reducing agents and good oxidizing agents. Thus fluorine tops the list of oxidizing agents as it has highest standard reduction potential. From a higher positive reduction potential we can understand that H⁺ is a much powerful oxidizing than Zn²⁺. Similarly lithium metal may be considered as best reducing agent.
2. A knowledge of reduction potentials also helps in deciding whether a given redox reaction will proceed spontaneously in the forward direction or not. Suppose if we consider the Zn-Cu cell reaction.



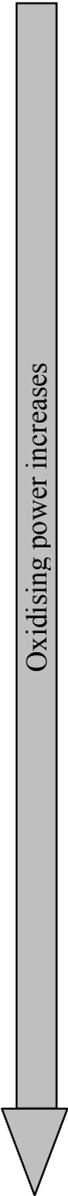
Table 1.5 Standard Reduction Potentials at 25 °C*

Electrode	Electrode Reaction	E^0 (V)
Li ⁺ Li	Li ⁺ (aq) + e ⁻ → Li(s)	- 3.045
K ⁺ K	K ⁺ (aq) + e ⁻ → K(s)	- 2.925
Ba ²⁺ Ba	Ba ²⁺ (aq) + 2e ⁻ → Ba(s)	- 2.90
Sr ²⁺ Sr	Sr ²⁺ (aq) + 2e ⁻ → Sr(s)	- 2.89
Ca ²⁺ Ca	Ca ²⁺ (aq) + 2e ⁻ → Ca(s)	- 2.87
Na ⁺ Na	Na ⁺ (aq) + e ⁻ → Na(s)	- 2.714
Mg ²⁺ Mg	Mg ²⁺ (aq) + 2e ⁻ → Mg(s)	- 2.37
Be ²⁺ Be	Be ²⁺ (aq) + 2e ⁻ → Be(s)	- 1.85
Al ³⁺ Al	Al ³⁺ (aq) + 3e ⁻ → Al(s)	- 1.66
Mn ²⁺ Mn	Mn ²⁺ (aq) + 2e ⁻ → Mn(s)	- 1.18
OH ⁻ H ₂ (g) Pt	H ₂ O + e ⁻ → H ₂ (s) + OH ⁻ (aq)	- 0.828
Zn ²⁺ Zn	Zn ²⁺ (aq) + 2e ⁻ → Zn(s)	- 0.763
Cr ³⁺ Cr	Cr ³⁺ (aq) + 3e ⁻ → Cr(s)	- 0.74
Fe ²⁺ Fe	Fe ²⁺ (aq) + 2e ⁻ → Fe(s)	- 0.440
Co ²⁺ Co	Co ²⁺ (aq) + 2e ⁻ → Co(s)	- 0.408
SO ₄ ²⁻ PbSO ₄ (s) Pb	PbSO ₄ + 2e ⁻ → Pb(s) + SO ₄ ²⁻ (aq)	- 0.31
Co ²⁺ Co	Co ²⁺ (aq) + 2e ⁻ → Co(s)	- 0.28
Ni ²⁺ Ni	Ni ²⁺ (aq) + 2e ⁻ → Ni(s)	- 0.25
Sn ²⁺ Sn	Sn ²⁺ (aq) + 2e ⁻ → Sn(s)	- 0.14
Pb ²⁺ Pb	Pb ²⁺ (aq) + 2e ⁻ → Pb(s)	- 0.126
H ⁺ H ₂ (g) Pt	2H ⁺ (aq) + 2e ⁻ → H ₂ (s)	0.000
Sn ²⁺ , Sn ⁴⁺ Pt	Sn ⁴⁺ (aq) + 2e ⁻ → Sn ²⁺ (s)	+ 0.13

Oxidising power increases

Table 1.5 Contd...

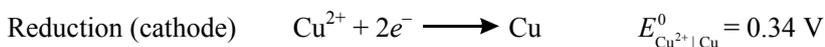
Electrode	Electrode Reaction	E^0 (V)
$\text{Cu}^{2+} \text{Cu}$	$\text{Cu}^{2+}(\text{aq}) + 1\text{e}^- \longrightarrow \text{Cu}^+(\text{s})$	+ 0.15
$\text{Cl}^- \text{AgCl}(\text{s}) \text{Ag}$	$\text{AgCl}(\text{s}) + 2\text{e}^- \longrightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+ 0.2223
$\text{Cl}^- \text{Hg}_2\text{Cl}_2(\text{s}) \text{Hg}$ §	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{s}) + 2\text{Cl}^-(\text{aq})$	+ 0.268
$\text{Cu}^{2+} \text{Cu}$	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+ 0.337
$\text{OH}^- \text{O}_2(\text{g}) \text{Pt}$	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$	+ 0.401
$\text{Cu}^+ \text{Cu}$	$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}(\text{s})$	+ 0.521
$\text{I}^-, \text{I}_2 \text{Pt}$	$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+ 0.5355
$\text{MnO}_4^-, \text{OH}^- \text{MnO}_2 \text{Pt}$	$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+ 0.59
$\text{Fe}^{2+}, \text{Fe}^{3+} \text{Pt}$	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+ 0.771
$\text{Ag}^+ \text{Ag}$	$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+ 0.7991
$\text{Hg}_2^{2+} \text{Hg} \text{Pt}$	$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+ 0.85
$\text{Hg}_2^{2+} \text{Hg}_2^{2+} \text{Pt}$	$2\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}(\text{aq})$	+ 0.920
$\text{Br}^-, \text{Br}_2 \text{Pt}$	$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+ 1.0652
$\text{H}^+ \text{O}_2 \text{Pt}$	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+ 1.229
$\text{Cr}_2\text{O}_7^{2-}, \text{H}^+, \text{Cr}^{3+} \text{Pt}$	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+ 1.33
$\text{Cl}^- \text{Cl}_2 \text{Pt}$	$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow \text{Cl}^-(\text{aq})$	+ 1.3595
$\text{Au}^{3+} \text{Au}$	$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+ 1.50
$\text{MnO}_4^-, \text{Mn}^{2+} \text{H}^+ \text{Pt}$	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+ 1.51
$\text{Ce}^{3+}, \text{Ce}^{4+} \text{Pt}$	$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \longrightarrow \text{Ce}^{3+}(\text{aq})$	+ 1.61
$\text{H}^+ \text{H}_2\text{O}_2 \text{Pt}$	$\text{Ce}^{3+}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+ 1.77
$\text{Co}^{2+}, \text{Co}^{3+} \text{Pt}$	$\text{H}_2\text{O}_2(\text{aq}) + \text{e}^- \longrightarrow \text{Co}^{2+}(\text{aq})$	+ 1.82
$\text{H}^+ \text{O}_3, \text{O}_2 \text{Pt}$	$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+ 2.07
$\text{F}^- \text{F}_2 \text{Pt}$	$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$	+ 2.87

 Oxidising power increases
 

* All the ions are at unit activity and gases at 1 atm pressure.

§ EMF of the calomel electrode containing saturated KCl is 0.2415 V and with 1 N and 0.1 N KCl solutions are 0.280 and 0.334 V respectively.

We have the two half cell reactions



$$E_{\text{cell}}^0 = E_{\text{Zn}|\text{Zn}^{2+}}^0 - E_{\text{Cu}^{2+}|\text{Cu}}^0$$

or
$$E_{\text{cell}}^0 = E_{\text{oxidation}}^0 + E_{\text{reduction}}^0$$

$$E^0 = 0.76 + 0.34$$

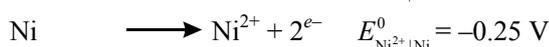
$$= 1.10 \text{ V}$$

The positive E_{cell}^0 value suggest that the redox reaction is spontaneous in the forward direction.

Let us now test the spontaneity of the reaction



The two half cell reactions are



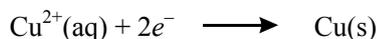
$$E_{\text{cell}}^0 = E_{\text{Fe}^{2+}|\text{Fe}}^0 - E_{\text{Ni}^{2+}|\text{Ni}}^0$$

$$= -0.44 - (-0.25)$$

$$= -0.19 \text{ V}$$

Because E_{cell}^0 computed is negative, we draw the conclusion that this reaction is not spontaneous under standard conditions.

3. *The standard electrode potential data is highly helpful in deciding the course of electrolysis reactions.* From the data given we see that the reduction potential for copper is 0.34V, for H₂O -0.83V and for aluminium -1.66V. During electrolysis of a Cu²⁺ solution, copper ions are more readily reduced (potential being more positive) than water and will plate on the electrode according to the half reaction.



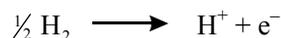
In case of aluminium, due to more positive reduction potential (or less negative potential) of H₂O than aluminium, H₂O is preferentially reduced and no deposition of aluminium is seen.



1.8 Types of Electrodes

1.8.1 Gas Electrode-Hydrogen Electrode (Primary Standard)

The electrode reaction of this electrode is written as;



Applying Nernst equation

$$E_{1/2\text{H}_2|\text{H}^+} = E_{1/2\text{H}_2|\text{H}^+}^0 - \frac{0.0592}{1} \log \frac{a_{\text{H}^+}}{p_{\text{H}_2}^{1/2}}$$

at 1 atm pressure

$$E_{1/2\text{H}_2|\text{H}^+} = E_{1/2\text{H}_2|\text{H}^+}^0 - 0.0592 \log a_{\text{H}^+}$$

$$E_{1/2\text{H}_2|\text{H}^+} = E_{1/2\text{H}_2|\text{H}^+}^0 + 0.0592 \text{ pH} \quad \dots\dots(1.25)$$

Advantages of Hydrogen Gas Electrode: It gives satisfactory results in the entire pH range of 0-14. The potential and pH are free from salt errors.

Limitations: The hydrogen gas used must be sufficiently pure. The electrode can not be used in the presence of gas impurities like air and oxygen and electrolyte impurities like oxidizing and reducing agents. It is very susceptible to poisoning by cyanides, arsenic, antimony compounds and alkaloids. It is cumbersome to handle in a normal laboratory.

1.8.2 Reference Electrodes (Secondary Standard)

Although all the electrode potentials are measured relative to hydrogen electrode, whose potential is arbitrarily taken as zero, it is not always convenient to use this gas electrode in day to day potentiometric measurements. The main difficulties with this **primary reference electrode** is;

- (a) Inconvenience in handling gases
- (b) Maintenance of accurate pressures throughout the measurements
- (c) Availability of sufficiently pure hydrogen gas.
- (d) Necessity to platinize the platinum electrode with a solution of chloro platinic acid quite often.

For these reasons some **secondary reference electrodes** like silver chloride electrode and calomel electrode whose standard potentials are very accurately determined against a hydrogen electrode are widely used.

(a) Standard Calomel Electrode - SCE

Calomel electrode is particularly very simple to construct, free from surface sensitivity and accurate to use even in a very normal laboratory.

A compact form of calomel electrode, as supplied by many commercial manufacturers is shown in Fig. 1.12.

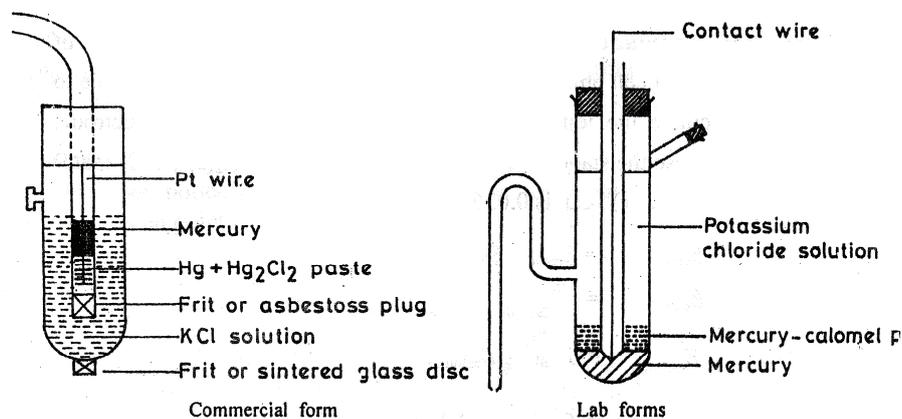
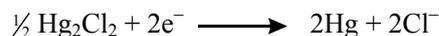


Fig. 1.12 The calomel electrode.

The calomel electrode consists of an inner glass tube and an outer jacket. In the inner glass tube a platinum wire is dipped into mercury which rests on a paste of mercurous chloride, Hg₂Cl₂ (commercially known as calomel) and mercury. This paste is in contact with KCl present in the outer jacket, through the glass frit plug fixed at the bottom of inner glass tube. The calomel electrode comes in contact with the experimental solution through a frit arranged to the outer jacket. The potential of this electrode depends on the concentration of KCl taken in the outer jacket. Some of the most popularly used concentrations of KCl and corresponding single electrode (reduction) potentials on the hydrogen scale at 25 °C are given below;

0.1M KCl Hg ₂ Cl ₂ (s) Hg, Pt	0.3338V
1.0M KCl Hg ₂ Cl ₂ (s) Hg, Pt	0.2800V
Saturated KCl Hg ₂ Cl ₂ (s) Hg, Pt	0.2415V

The corresponding electrode reaction is;

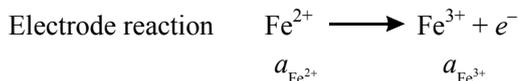


and corresponding Nernst's expression is;

$$E_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-} = E_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-}^0 - \frac{2.303}{F} \log a_{\text{Cl}^-}^2$$

(b) Redox electrode - Quinhydrone Electrode

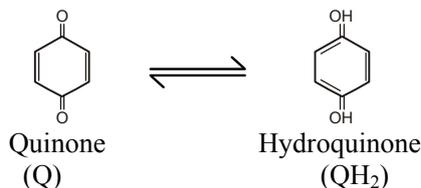
Platinum rod dipped in a mixture of two different oxidation states of a metal or two redox states of any compound is called a **redox electrode**. Platinum wire immersed in a mixture of ferrous and ferric ion mixture is a typical example of this class.



The electrode potential at any $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ ratio is given by the expression,

$$E_{\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}} = E_{\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}}^0 - \frac{0.0592}{1} \log \frac{a_{\text{Fe}^{3+}}}{a_{\text{Fe}^{2+}}}$$

Quinhydrone electrode : This is a redox electrode reversible to protons and often replaces the hydrogen electrode. Quinhydrone is a 1:1 molar mixture of quinone and hydroquinone. The electrode consists of a shiny platinum electrode dipped in an acid / base test solution, which is saturated with quinhydrone. The electrode reaction is given by



The electrode potential at 25°C is given by,

$$E_{\text{Pt}|\text{Q}, \text{H}^+, \text{QH}_2} = E_{\text{Pt}|\text{Q}, \text{H}^+, \text{QH}_2}^0 - \frac{0.0592}{2} \log \frac{a_{\text{QH}_2}}{a_{\text{Q}} a_{\text{H}^+}^2}$$

Since quinone and hydroquinone are taken in equimolar amounts, i.e., $a_{\text{Q}} = a_{\text{QH}_2}$

We have

$$E = E^0 - \frac{0.0592}{2} \log \frac{1}{a_{\text{H}^+}^2}$$

$$E = E^0 + 2 \times \frac{0.0592}{2} \log a_{\text{H}^+}$$

$$E = E^0 + 0.0592 \log a_{\text{H}^+}$$

$$E_{\text{Q}, \text{QH}_2} = E_{\text{Q}, \text{QH}_2}^0 - 0.0592 \text{ pH}$$

Quinhydrone electrode can thus be used to measure pH of a solution. Due to instability of quinone in strong alkaline medium, this hydrogen ion indicator electrode is suitable only up to a pH of 8.

1.8.3 Advantages

The quinhydrone electrode is simple to set up and needs no removal of air. The reversibility equilibrium is achieved faster than hydrogen gas electrode thereby allowing a quicker

measurement. pH values of solutions containing reducible substances like Cu^{2+} , Cd^{2+} , unsaturated acids, NO_3^- etc., and catalytic poisons can be measured using quinhydrone electrode, where hydrogen electrode can not be used.

Limitations : The electrode can not be used at pH values greater than 8. Even this electrode fails in the presence of strong oxidizing and reducing agents.

Metal / Metal insoluble Salt electrode – Calomel Electrode: This electrode has Hg in contact with its insoluble salt Hg_2Cl_2 and chloride ions. Construction, Electrode reaction and Nernst equation of calomel electrode is discussed below.

1.8.4 Ion Selective Electrodes – Glass electrode

Credit for the first glass sensing pH electrode is given to Cremer, who first described it in his paper published in 1906. Later several groups contributed for development of different ion selective electrodes. An **Ion-selective electrode (ISE)** (also known as a specific ion electrode, or SIE) is a sensor which converts the activity of a specific ion dissolved in a solution into an electrical potential which can be measured by some potentiometric device like a voltmeter or pH meter. As we know, the emf is theoretically dependent on the logarithm of the ionic activity (concentration), in accordance with the Nernst equation. Basically a concentration cell is developed with respect to the ion under observation. The sensing part of the electrode is usually made as an ion-specific membrane which is coupled with a reference electrode. So we need to have different ISEs for different ions.

The Electrochemical Circuit for an Ion Selective Electrode measurement

An ISE (with its own internal reference electrode - more details later) is immersed in an aqueous solution containing the ions to be measured, together with a separate, external reference electrode. The electrochemical circuit is completed by connecting the electrodes to a sensitive milli-volt meter using special low-noise cables and connectors. A potential difference is developed across the ISE membrane when the target ions diffuse through from the high concentration side to the lower concentration side (Fig. 1.13).

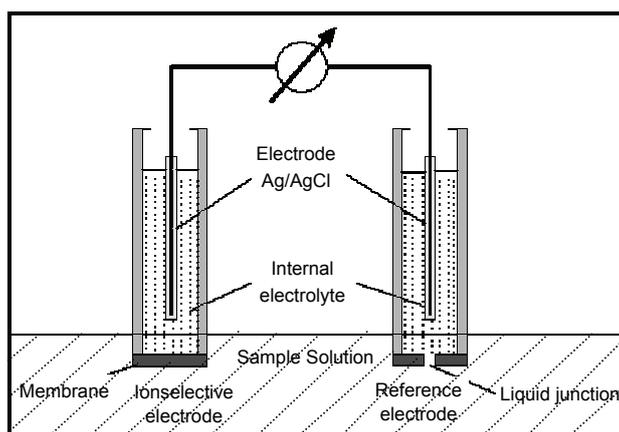


Fig. 1.13 Ion Selective Electrode (ISE) Measurement set-up.

Working of ISE

Ion Selective Electrodes (including the most common pH electrode) work on the basic principle of the galvanic cell. By measuring the electric potential generated across a membrane by "selected" ions, and comparing it to a reference electrode, a net charge is determined. The strength of this charge is directly proportional to the concentration of the selected ion. The basic formula is given for the galvanic cell:

$$E_{\text{cell}} = E_{\text{ise}} - E_{\text{ref}}$$

where the potential for the cell is equivalent to the potential of the ISE *minus* the potential of the reference electrode.

General principle of ISE analysis

At equilibrium, the membrane potential is mainly dependent on the concentration of the target ion outside the membrane and is described by the Nernst equation. Briefly, the measured voltage is proportional to the logarithm of the concentration, and the sensitivity of the electrode is expressed as the electrode Slope - in millivolts per decade of concentration. Thus the electrodes can be calibrated by measuring the voltage in solutions containing, for example, 10ppm and 100ppm of the target ion, and the Slope will be the slope of the (straight) calibration line drawn on a graph of *mV* versus Log (*concentration*).

Unknown concentrations samples can then be determined by measuring the voltage and plotting the result on the calibration graph or by automatically converting by a device.

Types of ion-selective membranes

There are four main types of ion-selective membranes used in ion-selective electrodes.

Glass membranes

Glass membranes are made from an ion-exchange type of glass (silicate of chalcogenide). This type of ISE has good selectivity, but only for several single-charged cations; mainly H^+ , Na^+ , and Ag^+ . Chalcogenide glass also has selectivity for double-charged metal ions, such as Pb^{2+} , and Cd^{2+} . The glass membrane has excellent chemical durability and can work in very aggressive media. A very common example of this type of electrode is the pH glass electrode.

Crystalline membranes (*Insoluble Inorganic Salts*)

Crystalline membranes are made from mono- or polycrystallites of a single substances of inorganic salts of low solubility. They have good selectivity, because only ions which can introduce themselves into the crystal structure can interfere with the electrode response. Selectivity of crystalline membranes can be for both cation and anion of the membrane-forming substance. An example is the fluoride selective electrode based on LaF_3 crystals.

Ion-exchange resin membranes

Ion-exchange resins are based on special organic polymer membranes which contain a specific ion-exchange substance (resin). They selectively bind certain small ions from the aqueous phase and exchange them across the membrane creating the potential. Usage of specific resins allows preparation of selective electrodes for tens of different ions, both single-atom or multi-atom. They are also the most widespread electrodes with anionic selectivity. However, such electrodes have low chemical and physical durability as well as "survival time". An example is the potassium selective electrode, based on valinomycin as an ion-exchange agent.

Gas Permeable membranes

This type of membrane is used to measure dissolved gasses such as Ammonia, Carbon Dioxide, Nitrogen Oxide and Dissolved Oxygen. Gas molecules diffuse across the membrane and react with a buffer solution, changing the pH of the buffer. This pH change is measured using an internal glass electrode. This is probably the second most popular probe type after the glass membrane pH probe.

Ion-selective electrodes are used in biochemical and biophysical research, where measurements of ionic concentration in an aqueous solution are required.

Interferences

The most serious problem limiting use of ion-selective electrodes is interference from other, undesired, ions.

- No ion-selective electrodes are completely ion-specific; all are sensitive to other ions having similar physical properties, to an extent which depends on the degree of similarity.
- In some cases the electrode may actually be much more sensitive to the interfering ion than to the desired ion. This requires the interfering ion be present only in relatively very low concentrations, or entirely absent.
- The nitrate electrode is plagued by ionic interferences from chloride, fluoride, and sulfate.

Glass Electrode

Most often used pH electrodes are called glass electrodes and belong to the family of ISEs. They are sensitive only to H^+ ions. Typical glass electrode is made of glass tube ended with small glass bulb sensitive to protons. Inside of the electrode is usually filled with buffered solution of chlorides in which silver wire covered with silver chloride is immersed. pH of internal solution varies - for example it can be 1.0 (0.1M HCl) or 7.0 (Fig. 1.14).

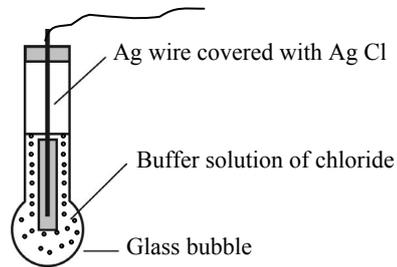


Fig. 1.14 Glass electrode.

Active part of the electrode is the glass bubble. While tube has strong and thick walls, bubble is made to be as thin as possible. Surface of the glass is protonated by both internal and external solution till equilibrium is achieved. Both sides of the glass are charged by the adsorbed protons, this charge is responsible for potential difference. This potential in turn is described by the Nernst equation and is directly proportional to the pH difference between solutions on both sides of the glass.

The majority of pH electrodes available now a days are combination electrodes that have both glass H^+ ion sensitive electrode and reference electrode compartments, conveniently placed in one housing.

Range of a pH glass electrode

The pH range at constant concentration can be divided into 3 parts (Fig. 1.15):



Fig. 1.15 E-pH for ion-selective electrode.

- **Useful Working Range:** Dependence of potential on pH has linear behavior and within which such electrode really works as ion-selective electrode for pH and obeys Nernst equation.

$$E = E^o - \frac{2.303RT}{F} \text{pH}$$

- **Alkali error range:** At low concentration of hydrogen-ions (high values of pH) alkali metal ions interfere. In this situation dependence of the potential on pH become non-linear.
- **Acidic error range:** At very high concentration of hydrogen-ions (low values of pH) the anions plays a big role as interfering ions, in addition to destruction of the glass matrix used for making glass bulb.

Almost all commonly used glass electrodes have a working pH range from pH = 1 till pH = 12. So specially designed electrodes should be used only for working in aggressive conditions.

1.9 Nernst Equation Relationship between Cell reaction and EMF

Nernst (1864-1941) studied the theoretical relationship between the electrochemical reaction and the corresponding cell emf. This relationship is generally known as **Nernst equation**.

Let us consider a galvanic cell whose cell reaction is written as



where lower case letter a,b,c,d represent the number of moles of A, B, C, D respectively at equilibrium. The Nernst equation for the cell is written as;

$$E_{\text{cell}} = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where E_{cell} denotes the *emf* of the cell, R the gas constant, T the temperature, n number of faraday of current F passed, K the equilibrium constant and the quantities in the square brackets refer the respective concentration. The quantity $(RT/nF) \ln K$ is known as standard emf of the cell E_{cell}° .

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots(1.26)$$

or

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots(1.27)$$

At room temperature ($T = 298 \text{ K}$), taking $R = 8.314 \text{ J K}^{-1}$, $F = 96457 \text{ cal}$, the above equation simplifies to

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.05916}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ at } 25^{\circ}\text{C} \quad \dots(1.28)$$

From the equation (1.24) we notice that the standard cell *emf* is equal to the cell *emf* when the activities of both reactants and products is equal to unity.

1.9.1 Nernst Equation - Applications

Nernst equation is also applicable to half cell reactions. Few half cell reactions and corresponding Nernst's expressions are discussed below.

Metal/Metal ion electrode – Zn | Zn²⁺ electrode

This is a typical representative example of *Metal/Metal ion electrode*. This electrode can be constructed by bringing a zinc rod in contact with zinc ions. Oxidation of zinc atoms to give zinc ions is expressed by the following equation;



In the reaction two electrons are exchanged between both the zinc species in the overall redox reaction making $n = 2$. Therefore,

$$E_{\text{Zn}|\text{Zn}^{2+}} = E_{\text{Zn}|\text{Zn}^{2+}}^0 - \frac{0.05916}{2} \log \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$

Since the activity of all the pure solids is unity ($a = 1$)

Therefore,

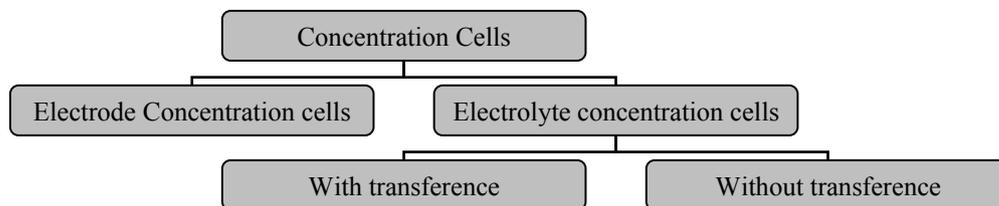
$$E_{\text{Zn}|\text{Zn}^{2+}} = E_{\text{Zn}|\text{Zn}^{2+}}^0 - \frac{0.05916}{2} \log a_{\text{Zn}^{2+}}$$

This expression suggests that the oxidation electrode potential, E , decreases with increase in $[a_{\text{Zn}^{2+}}]$ and equals to standard electrode potential, E^0 , at unit concentration of the electrolyte.

1.9.2 Concentration Cells

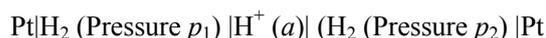
A **Concentration cell** is an electrochemical cell that has two equivalent half-cells of the same material *differing only in concentrations*. One can calculate the potential developed by such a cell using the Nernst Equation similar to an electrochemical cell. In concentration cell the voltage comes from its attempt to reach equilibrium, which will stop when the concentration in both half-cells are equal.

Types of concentration cells: The concentration differences could be affected in the electrode material or in the electrolyte. Further they could be subdivided into cells with transference or without transference.



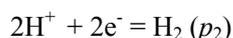
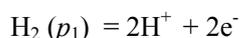
(i) Electrode concentration cells:

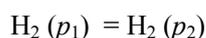
In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressure in the same solution of hydrogen ions constitute a cell of this type.



If $p_1 > p_2$ oxidation occurs at L.H.S. electrode and reduction occurs at R.H.S. electrode.

The Nernst equation can be used to derive an expression for the potential of this electrode concentration cell.

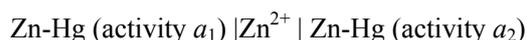




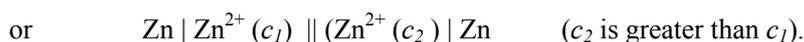
$$E_{\text{cell}} = 0.0591/2 \log(p_1/p_2) \text{ at } 25^\circ\text{C}$$

The standard cell potential is zero because a cell cannot derive a current through a circuit with identical electrodes. Similarly we can construct different gas concentration cells, when coupled with their counter ions.

Two amalgams of the same metal at two different concentrations in the same electrolyte solution also form this class of cells.

**(ii) Electrolyte concentration cells:**

In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of *different concentrations*. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the emf of the cell is maximum and it gradually falls to zero. Such cells are represented in the following manner:



The emf of the cell is given by the following expression:

$$E_{\text{cell}} = 0.0591/n \log c_2/c_1 \text{ at } 25^\circ\text{C}$$

The above examples are typical examples of electrolyte concentration cells with transference. Transference indicates the presence of salt bridge or liquid-liquid contact of electrolytes

Examples of electrolyte concentration cells without transference are difficult to comprehend at this stage and are not considered now.

1.9.3 Applications of Concentration Cells

1. The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.
2. Concentration cell corrosion occurs when two or more areas of a metal surface are in contact with different concentrations of the same solution. There are three general types of concentration cell corrosion.
3. Water in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points. Corrosion will occur at the area of low-oxygen concentration which are anodic. This is the explanation for corrosion of iron piece when in contact of moisture.

1.10 Applications of Electrode Potentials – Potentiometric Titrations

- (i) **Determination of Ionic activities :** From the knowledge of standard cell emf and standard electrode potentials, it is possible to calculate the ionic activities of ions reversible to the electrode. Suppose the standard emf of the cell $\text{Hg(s), Hg}_2\text{Cl}_2\text{(s) | KCl (satd) || Cu}^{2+} (a=x) | \text{Cu}$ is 0.036V.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{Cu}^{2+}|\text{Cu}} - E_{\text{calomel}}$$

$$E_{\text{Cu}^{2+}|\text{Cu}} = E_{\text{cell}} - E_{\text{calomel}}$$

$$= 0.036 + 0.242$$

$$E_{\text{Cu}^{2+}|\text{Cu}} = 0.278 \text{ V}$$

$$\text{But } E_{\text{Cu}^{2+}|\text{Cu}} = E_{\text{Cu}^{2+}|\text{Cu}}^0 - \frac{0.0592}{2} \log \frac{1}{a_{\text{Cu}^{2+}}}$$

$$0.278 = 0.337 + 0.0296 \log a_{\text{Cu}^{2+}}$$

$$\text{or } \log a_{\text{Cu}^{2+}} = \frac{0.278 - 0.337}{0.0296}$$

$$a_{\text{Cu}^{2+}} = 0.01$$

Activity of Cu^{2+} solution = 0.01

- (ii) **Potentiometric titrations** : Potentiometric titrations is a very interesting application of electrode potentials. They involve a study of variation of *emf* with the volume of titrant added. Here we discuss the precipitation titration and acid base titration.
- (a) **Precipitation titrations** : Consider the titration of Ag^+ ions with KCl. On addition of any chloride salt the silver ions fall out of the aqueous solution forming an insoluble precipitate of silver chloride. Hence we study the variation of silver electrode potential with the change in concentration of silver ions.

$$E_{\text{Ag}^+|\text{Ag}^+} = E_{\text{Ag}^+|\text{Ag}^+}^0 - \frac{0.0592}{2} \log a_{\text{Ag}^+}$$

As the $E_{\text{Ag}|\text{Ag}^+}$ varies in a logarithmic scale of the concentration of silver ions, initially even for a hundred fold variation of silver ion concentration the *emf* variation is only 0.118V. With the approach of neutralization point, the E_{Ag^+} gets smaller and smaller, while the *emf*, a log value of Ag^+ , increases rapidly.

Thus we notice a sigmoid curve with the steep portion indicating the neutralization point.

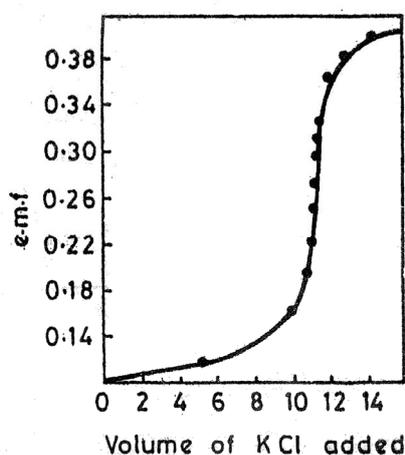
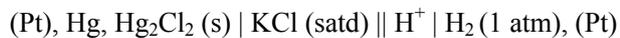


Fig. 1.16 Potentiometric titration of Ag^+ ions with KCl.

The $\text{Ag}|\text{Ag}^+$ electrode which is reversible to silver ion concentration is termed as the **indicator electrode**.

- (b) **Acid-base titrations :** In case of acid - alkali titration a hydrogen electrode may be used as an indicator electrode. The suitable cell may be represented as



The emf of indicator electrode is given as

$$E_{\text{H}_2|2\text{H}^+} = E_{\text{H}_2|\text{H}^+}^0 - 0.0595 \log \text{H}^+$$

Since the standard emf of hydrogen electrode is zero, we have;

$$E_{\text{H}_2|2\text{H}^+} = -0.0595 \log \text{H}^+$$

$$E_{\text{H}_2|2\text{H}^+} = 0.0595 \text{ pH}$$

From the above expression we draw the conclusion that the emf decreases with decrease in the concentration of hydrogen ions or increase in the pH of the solution. On plotting the electrode potential or cell potential against the volume of titrant added, a sigmoid curve is obtained, Fig.1.17. The volume corresponding to zero emf gives the titre value of the acid solution.

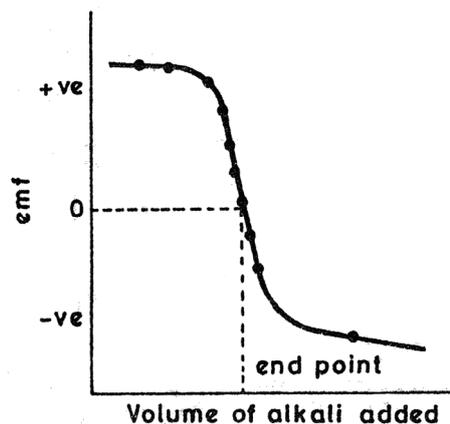
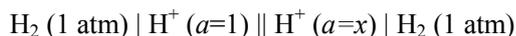


Fig. 1.17 Potentiometric acid-alkali titration curve.

In the laboratory titration generally the quinhydrone electrode is used in place of SHE.

- (iii) **Determination of pH :** The pH of a solution could be determined by employing any electrode reversible to H^+ ions. The hydrogen electrode and quinhydrone electrode discussed above and glass electrode are popularly employed for the estimation of pH of a solution. The hydrogen indicator electrode could be coupled either to a standard hydrogen electrode (SHE) or to a standard calomel electrode (SCE). The cell diagram, when SHE is used as reference electrode, is given by



The emf of the indicator electrode is given by

$$E_{\text{H}_2|\text{H}^+} = -\frac{RT}{F} \ln \frac{a_{\text{H}^+}}{p_{\text{H}_2}}$$

When $p_{\text{H}_2} = 1 \text{ atm}$ and $T = 298 \text{ K}$

Since by definition $\text{pH} = -\log a_{\text{H}^+}$, the above expression in terms of pH is

$$E_{\text{H}_2|2\text{H}^+} = 0.0592 \text{ pH}$$

Because the electrode potential of the reference SHE is zero, for the present cell diagram.

The cell diagram when SCE is used as reference electrode is given by



For this arrangement of room temperature

$$E_{\text{H}_2|2\text{H}^+} = E_{\text{cell}} - E_{\text{SCE}} = 0.05916 \text{ pH}$$

Problem 17.

Verify whether the following cell, as represented below, can function as a voltaic cell (Use reduction potentials given in Table 1.5, where ever necessary).



As per the convention the cell reaction involves oxidation of silver at the left hand electrode (anode) and reduction of copper ions at the right hand electrode (cathode).



Since the above cell diagram gives a negative emf, it is not a spontaneous reaction and the cell as diagrammed cannot function as a voltaic cell.

Problem 18.

Find the *emf* of the cell represented by the cell diagram $\text{Zn} | \text{Zn}^{2+} | \text{H}^+ (1 \text{ M}) | \text{H}_2 (1 \text{ atm}) | (\text{Pt})$.

Given that the oxidation potential of $\text{Zn} | \text{Zn}^{2+}$ is 0.7618V

Emf of the cell

$$E_{\text{cell}} = E_{\text{Zn}|\text{Zn}^{2+}} - E_{\text{H}_2|\text{H}^+}$$

(Oxid) (Oxid)

The hydrogen gas electrode is a standard hydrogen electrode, hence has a zero electrode potential.

Therefore $E_{\text{cell}} = 0.7618 - 0 = 0.7618\text{V}$

Problem 19.

The standard oxidation potential of Cd | Cd²⁺ electrode is 0.403V. Calculate the Cd²⁺ concentration if the electrode potential is 0.5V at 25 °C.

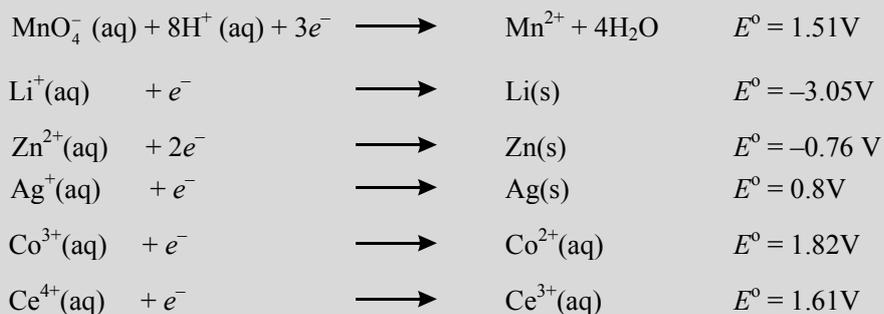
$$\begin{aligned} \text{Cd} &\longrightarrow \text{Cd}^{2+} + 2e \\ E &= E^0 - \frac{RT}{nF} \ln \frac{[\text{Cd}^{2+}]}{[\text{Cd}]} \\ 0.5 &= 0.403 - \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log [\text{Cd}^{2+}] \\ 0.097 &= - \frac{0.05916}{2} \log [\text{Cd}^{2+}] \\ &= - 0.02958 \log [\text{Cd}^{2+}] \\ \log [\text{Cd}^{2+}] &= - \frac{0.097}{0.02958} = -3.279 \\ [\text{Cd}^{2+}] &= 5.26 \times 10^{-4} \end{aligned}$$

Therefore concentration of Cd²⁺ = 5.26 × 10⁻¹ M

Problem 20.

Arrange the following species in order of their increasing oxidizing capability, MnO₄⁻, Li⁺, Zn²⁺, Ag⁺, Co³⁺, Ce⁴⁺.

According to standard emf data.



Higher the standard reduction potential higher is the oxidizing capability. Therefore the order of oxidizing strengths are;



1.11 Battery Chemistry

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery. In everyday usage, 'battery' is also used to refer to a single cell. No single battery design is perfect for every application. There are many parameters like cost, voltage, duty cycle, dimension, stability with time and temperature, shelf life, etc., on which a battery is selected for a particular operation. It is important to prioritize our list of requirements before choosing one and requires compromise. Here *duty cycle* refers to conditions the battery experiences during use like, type of discharge and current drain, e.g., continuous, intermittent, continuous with pulses, etc.

1.11.1 Classification

Batteries are classified into two categories depending on their recharging capabilities.

- (i) **Primary Batteries** - These are non-rechargeable and are meant for a single use and meant to be discarded after use.
- (ii) **Secondary Batteries** - These are rechargeable and are meant for a multi cycle use. After every use the electrochemical reaction could be reversed by external application of voltage. The cycle is reversed till the capacity fades or lost due to leakage or internal short circuit.

1.11.2 Primary Batteries (Non-Rechargeable)

These are non-rechargeable and are less expensive and are often used in ordinary gadgets like torch lights, watches and toys. Commercially many kinds of primary batteries are available but we are going to restrict our discussion to Leclanché cell, Alkaline cell and Lithium cell.

1.11.2.1 Dry Cell (Leclanché Cells or Zinc-Carbon Cell)

Anode : Zinc, **Cathode**: Manganese Dioxide (MnO_2),

Electrolyte : Ammonium chloride or zinc chloride dissolved in water

Applications : Flashlights, toys, moderate drain use equipment

The basic design of the Leclanché cell dates to 1860s, and until World War II, was the only one in wide use. It is still the most commonly used of all primary battery designs because of its low cost, availability, and applicability in various situations.

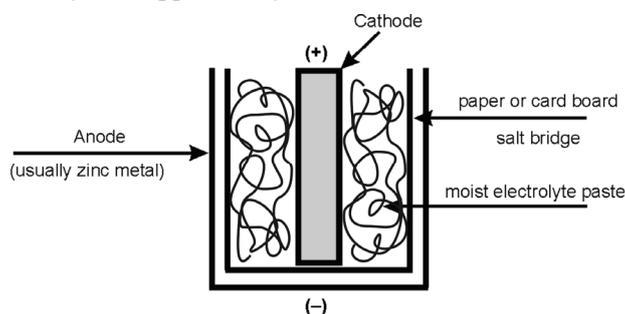


Fig. 1.18 A Cut view of Dry Cell.

In an ordinary Leclanché cell the electrolyte consists (in percent of atomic weight) of 26% NH_4Cl (ammonium chloride), 8.8% ZnCl_2 (zinc chloride), and 65.2% water.

At the cathode, the reduction reaction occurs within the moist paste comprised of ammonium chloride (NH_4Cl) and manganese dioxide (MnO_2):



A thin zinc cylinder serves as the anode and it undergoes oxidation:



The overall cell reaction can be expressed as



The anode Zinc is normally present as the cylindrical container (which is often surrounded by steel to prevent leakage of electrolyte). MnO_2 , is not a good conductor of electricity and hence mixed with graphite to form a paste, with a central graphite rod acting as the current collector. The cell voltage increases by using synthetically produced manganese dioxide instead of that found naturally (called pyrolusite). This does drive the cost up a bit, but it is still inexpensive and environmentally friendly, making it a popular cathode. The aqueous ammonium chloride acting as electrolyte is usually thickened with polymeric material such as starch or methyl cellulose. The resultant cells are reasonably stable against discharging. The self discharging is via evolution hydrogen, a non-electrochemical reaction.



Zinc-chloride cell systems have been found to perform better than the Leclanché under heavier current drain. The electrolyte in a typical zinc chloride cell consists of 15-40% ZnCl_2 and 60-85% water, sometimes with a small amount of NH_4Cl for optimal performance. The overall cell reaction of the zinc chloride as the electrolyte can be expressed:



These cells are the cheapest ones in wide use, but they also have the lowest energy density and perform poorly under high-current applications.

1.11.2.2 Lithium and Other Metal Cells (Non-aqueous cells)

Applications : Pacemakers, defibrillators, watches, meters, cameras, calculators, portable, low-power use

Lithium battery chemistry comprises a number of cell designs that use **lithium as the anode**. Lithium is gaining a lot of popularity as an anode over other metals for a number of reasons as given in Table 1.6.

Table 1.6

Anode	Standard potential (V)	Density g/cm ³	Electrochemical Equivalence (Ah/g)
Li	3.05	0.54	3.86
Na	2.7	0.97	1.16
Mg	2.4	1.74	2.20
Al	1.7	2.7	2.98
Ca	2.87	1.54	1.34
Fe	0.44	7.85	0.96
Zn	0.76	7.1	0.82
Cd	0.40	8.65	0.48
Pb	0.13	11.3	0.26

Note that lithium, the lightest of the metals, also has the highest standard potential (>3V) of all the metals and some of the lithium cell designs have a voltage of nearly 4 V. This means that *lithium has the highest energy density*. The dry cells and alkaline cells discussed earlier have aqueous electrolyte while the lithium cells have non-aqueous medium. Aqueous systems can go upto energy densities of 700 W kg⁻¹ but **Lithium non-aqueous systems** with far higher potential power densities have been reported.

Lithium cells have only recently become commercially viable because *lithium reacts violently with water, as well as nitrogen in air*. This requires sealed cells. High-rate lithium cells can build up pressure if they are short circuited and cause the temperature and pressure to rise. Thus, the cell design needs to include weak points, or safety vents, which rupture at a certain pressure to prevent explosion.

Lithium cells can be grouped into three general categories: (a) liquid cathode, (b) solid cathode, and (c) solid electrolyte.

(a) Liquid cathode lithium Cells :

Anode : Lithium, **Cathode :** SOCl₂, **Electrolyte :** LiAlCl₂

These cells tend to offer *higher discharge rates* because the reactions occur at the cathode surface. In a solid cathode, the reactions take longer because the lithium ions must enter into the cathode for discharge to occur. The direct contact between the liquid cathode and the lithium forms a film over the lithium, called the *solid electrolyte interface (SEI)*. This prevents further chemical reaction when not in use, thus preserving the cell's shelf life. One drawback, though, is that if the film is too thick, it causes an initial voltage delay. Usually, water contamination is the reason for the thicker film.

This cell consists of a high-surface area carbon cathode, a non-woven glass separator. Thionyl chloride acts as the electrolyte solvent and the active cathode material.

The materials react as follows :

Location	Reaction
Anode	$\text{Li} \longrightarrow \text{Li}^+ + \text{e}^-$
Cathode	$4\text{Li}^+ + 4\text{e}^- + 2\text{SOCl}_2 \longrightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$
Overall	$4\text{Li} + 2\text{SOCl}_2 \longrightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$

During discharge the anode gives off lithium ions. On the carbon surface, the thionyl chloride reduces to chloride ions, sulfur dioxide, and sulfur. The lithium and chloride ions then form lithium chloride. Once the lithium chloride has deposited at a site on the carbon surface, that site is rendered inactive. The sulfur and sulfur dioxide dissolve in the electrolyte, but at higher-rate discharges SO_2 will increase the cell pressure leading to explosion. This system has a very high energy density (about 500 Wh/kg) and an operating voltage of 3.3–3.5 V.

In high-rate discharge, the voltage delay is more pronounced and the pressure increases as mentioned before. Low-rate cells are used commercially for small electronics and memory backup. High-rate cells are used mainly for military applications.

(b) Solid Cathode Lithium Cells (LiMnO₂ Cell)

These cells cannot be used in high-drain applications and don't perform well under low temperature conditions. However, they don't have the same voltage delay as liquid cells and don't require pressurization. They are used generally for memory backup, watches, portable electronic devices, etc.

These account for about 80% of all primary lithium cells, one reason being their low cost. The cathode used is a heat-treated MnO_2 and the electrolyte a mixture of propylene carbonate and 1, 2-dimethoxyethane.

The half reactions are :

Anode	$\text{Li} \longrightarrow \text{Li}^+ + \text{e}^-$
Cathode	$\text{Mn}^{\text{IV}}\text{O}_2 + \text{Li}^+ + \text{e}^- \longrightarrow \text{Mn}^{\text{III}}\text{O}_2(\text{Li}^+)$
Overall	$\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 \longrightarrow \text{Mn}^{\text{III}}\text{O}_2(\text{Li}^+)$

$\text{Li}(\text{CF})_n$ Lithium polycarbon monofluoride also falls in this category.

The cathode in this cell is carbon monofluoride. A typical electrolyte is lithium tetrafluorobate (LiBF_4) salt in a solution of propylene carbonate (PC) and dimethoxyethane (DME).

These cells also have a high voltage (about 3.0 V) and a high energy density (around 250 Wh/kg). All this and a 7-year shelf life makes them very suitable for low- to moderate-drain use, e.g., watches, calculators, and memory applications.

(c) Solid Electrolyte Lithium Cells

They perform best in low-current applications and have a *very long* service life. For this reason, they are used in pacemakers

Lithium iodine cells use solid LiI as their electrolyte and also produce LiI as the cell discharges. The cathode is poly-2-vinylpyridine (P2VP) with the following reactions :

Anode	$2\text{Li} \longrightarrow 2\text{Li}^+ + 2\text{e}^-$
Cathode	$2\text{Li}^+ + 2\text{e}^- + \text{P2VP} \cdot n\text{I}_2 \longrightarrow \text{P2VP} \cdot (n-1)\text{I}_2 + 2\text{LiI}$
Overall	$2\text{Li} + \text{P2VP} \cdot n\text{I}_2 \longrightarrow \text{P2VP} \cdot (n-1)\text{I}_2 + 2\text{LiI}$

LiI is formed *in situ* by direct reaction of the electrodes.

1.11.3 Secondary Batteries

These cells are rechargeable and reusable. A combination of all reversible electrochemical cells give secondary batteries. Many kinds of secondary batteries are available in the market but we are restricting our discussion to Lead acid cell, Ni/Cd cells, Ni-metal hydride cells and Lithium ion cells

1.11.3.1 Lead–acid Cells

Anode : Sponge metallic lead,

Cathode: Lead dioxide (PbO_2),

Electrolyte : Dilute mixture of aqueous sulfuric acid

Applications : Automobiles and construction equipment, standby/backup systems

Used mainly for engine batteries, these cells represent over half of all battery sales. Some advantages are their low cost, long life cycle, and ability to withstand mistreatment. They also perform well in high and low temperatures and in high-drain applications.

The half-cell reactions are :

Half-Reaction	V vs SHE
$\text{Pb} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_4 + 2\text{e}^-$	0.356
$\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.685

There are a few problems with this design. If the cell voltages exceed 2.39 V, the water breaks down into hydrogen and oxygen and may lead to explosion. Another problem arising from this system is that fumes from the acid solution may have a corrosive effect on the area surrounding the battery.

These problems are mostly solved by sealed cells, made commercially available in the 1970s. This sealing in reality is only valve regulated and allowing hydrogen and oxygen recombination using catalytic recombiners. They convert these gases back into water, achieving about 85% efficiency at best. In these batteries the water lost becomes so insignificant that no refill is needed for the life of the battery. For this reason, these cells are often referred to as maintenance-free batteries. Also, this cell design prevents corrosive fumes from escaping.

These cells have a low cycle life, a quick self discharge, and low energy densities (normally between 30 and 40 Wh/kg). However, with a nominal voltage of 2 V and power densities of up to 600 W/kg, the lead-acid cell is an adequate, if not perfect, design for car batteries.

1.11.3.2 Nickel/Cadmium Cells

Anode: Cadmium,

Cathode: Nickel oxyhydroxide NiOOH,

Electrolyte : Aqueous potassium hydroxide (KOH)

Applications : Calculators, digital cameras, pagers, lap tops, tape recorders, flashlights, medical devices (e.g., defibrillators), electric vehicles, space applications

The cathode is nickel-plated, woven mesh, and the anode is a cadmium-plated net. The electrolyte, KOH, acts only as an ion conductor and does not contribute significantly to the cell's reaction. That's why not much electrolyte is needed, so this keeps the weight down (NaOH is sometimes used as an electrolyte, which doesn't conduct as well, but also doesn't tend to leak out of the seal as much). The cell reactions are as follows :

Reaction	V vs SHE
$\text{Cd} + 2\text{OH}^- \longrightarrow \text{Cd}(\text{OH})_2 + 2\text{e}^-$	0.81
$\text{NiOOH} + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O} + \text{OH}^-$	0.45
$\text{Cd} + \text{NiOOH} + 2\text{H}_2\text{O} + \text{OH}^- \longrightarrow \text{Cd}(\text{OH})_2 + \text{Ni}(\text{OH})_2 \cdot \text{H}_2\text{O}$	1.26

Advantages include good performance in high-discharge and low-temperature applications. They also have long shelf and use life. Disadvantages are that they cost more than the lead-acid battery and have lower power densities. Possibly its most well-known limitation is a *memory effect*, where the cell retains the characteristics of the previous cycle. This term refers to a temporary loss of cell capacity, which occurs when a cell is recharged without being fully discharged. This can cause cadmium hydroxide to passivate the electrode, or the battery to wear out. In the former case, a few cycles of discharging and charging the cell will help correct the problem, but may shorten the lifetime of the battery.

1.11.3.3 Lithium Ion Cells

Anode : Carbon compound, graphite,

Cathode : Lithium oxide.

Applications : Laptops, cellular phones, electric vehicles

As discussed earlier Lithium metal batteries have safety disadvantages. These are overcome in *Lithium ion Batteries*.

Cathodes consist of a layered crystal (graphite) into which the lithium is intercalated. Experimental cells have also used lithiated metal oxide such as LiCoO_2 , $\text{NiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$, LiNiO_2 , LiV_2O_5 , $\text{LiV}_6\text{O}_{13}$, LiMn_4O_9 , LiMn_2O_4 , $\text{LiNiO}_{0.2}\text{CoO}_2$.

Electrolytes are usually LiPF_6 , although this has a problem with aluminum corrosion, and so alternatives are being sought. One such is LiBF_4 . The electrolyte in current production batteries is a patented liquid, and uses an organic solvent.

Membranes are necessary to separate the electrons from the ions. Currently the batteries in wide use have microporous polyethylene membranes.

Intercalation keeps the small ions (such as lithium, sodium, and the other alkali metals) into the interstitial spaces in a graphite crystal. This makes the graphite is conductive, dilutes the lithium for safety, is reasonably cheap, and does not allow dendrites or other unwanted crystal structures of Li to form.

1.12 Fuel Cells

A cell in which one or both of the reactants are not permanently contained in the cell, but are continuously supplied from a source external to the cell and the reaction products continuously removed is called a fuel cell. Unlike the metal anodes typically used in batteries, the fuels in a fuel cell are usually gas or liquid, with oxygen as the oxidant.

Around 1900 Nernst and Haber attempted for a direct carbon oxidizing fuel cells but met with a limited success. Later in 1933 Baur, a German scientist, proposed the first fuel cell that can use hydrogen as a fuel and can work at room temperature. This idea was forwarded by Baecon, a British engineer and developed a porous nickel electrode that can withstand high pressures and can give current in kilowatt range at moderate temperatures. This technology found a ready customer in Apollo program of NASA (USA). This fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution. Hydrogen/oxygen fuel cell systems work well in space travel applications because of their *high efficiency, high power-to-weight and volume ratios, and usable reaction product (water)*. In the near future, our vehicles may also be powered by fuel cells.

There are many kinds of H_2/O_2 fuel cells and are categorized on the basis of electrolyte used.

1. Proton Exchange Membrane Fuel Cells (PEMFC)
2. Alkaline Fuel Cells (AFC)

3. Molten Carbonate Fuel Cells
4. Phosphoric acid fuel cells
5. Solid oxide fuels

We are going to have a discussion of the *first two* kinds of fuel cells.

1.12.1 Proton Exchange Membrane Fuel Cells (PEMFC)

The type of fuel cell typically used in automobiles is a *Proton Exchange Membrane (PEM) Fuel Cell*, also called a *Polymer Electrolyte Membrane fuel cell* (Fig. 1.19). A fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution.

At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and electrons.

Half-Reactions	V vs SHE
At Anode $2\text{H}_2 = 4\text{H}^+ + 4\text{e}^-$	0
At Cathode $4\text{H}^+ + \text{O}_2 + 4\text{e}^- = 2\text{H}_2\text{O}$	1.2

The Proton Exchange Membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The electrons must travel along an external circuit to reach the cathode, creating an electrical current.

At the cathode, the negatively charged electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.

Thus we get electricity from environmentally friendly reactants and products.

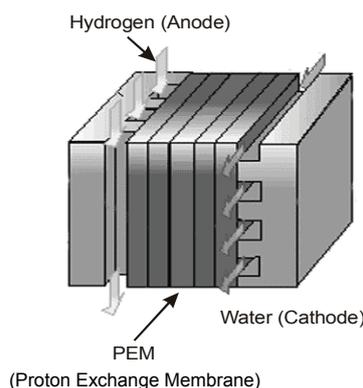


Fig. 1.19 PEM fuel cell.

1.12.2 Alkaline Fuel Cells (AFC)

In these cells, 30-45% aqueous solutions of potassium hydroxide is used as electrolyte (Fig. 27.10). So acidic impurities such as CO_2 should be avoided. Generally this is done by passing the compressed air into lime solution before allowing it to enter the fuel cell. These fuel cells yield highest voltages at comparable current densities in comparison to other classes of fuel cells.

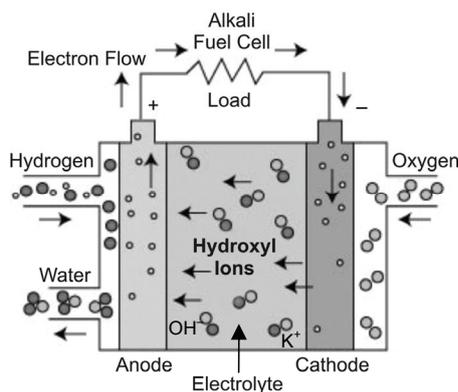


Fig. 1.20 Alkaline fuel cell.

The following half reactions take place in these cells

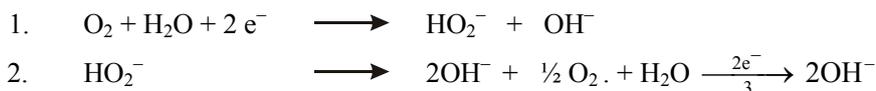
At Anode : Anode involves oxidation of hydrogen in to water by reacting with hydroxide anions from the electrolyte.



At Cathode : Oxygen passed is converted into hydroxide ions by consuming 4 electrons



In fact, this is a two step reaction with intermediate peroxy ion formation.



Over All Reaction :



Baecon fuel cell consists of an anode made of porous nickel and a cathode made of lithiated nickel oxide separated by 30% aqueous KOH serving as electrolyte. This cell operates at 200°C and 5 Mpa (about 50 atm) pressure. Baecon's double porosity fuel cell was used in 1960 NASA Apollo space program by lowering the operational pressure to 0.33 Mpa by activating the electrodes with a catalyst. The space shuttle system in 1974 replaced the heavy bipolar electrode plates with magnesium foils plated with silver. The anode now is a

carbon bonded with polytetrafluoroethylene and consisting Pt-Pd catalyst and cathode consists of 90% gold and 10% platinum plated on to nickel screen. This cell operates at a pressure of 0.42 Mpa and 92^o C and works for 2000 h.

1.12.3 Advantages of Fuel Cells

1. No emission of toxic gases and chemical wastes are in safe limits. The reactants and products are environment friendly and only we have to bother about disposal of cell material
2. High efficiency (75-85%) of energy conversion from chemical energy to electrical energy. So offer an excellent use of our renewable energy resources.
3. No noise pollution like in generators and low thermal pollution.
4. Low maintenance costs, fuel transportation costs, cell parts are modular and exchangeable.
5. The fuels and electrolyte materials are available in plenty and inexhaustible unlike fossil fuels.
6. Unlike solar cells, fuel cells are compact and transportable.
7. Unlike acid cells used in automotives the fuel cells are far less corrosive.
8. Unlike nuclear energy, fuel cell energy is economical and safe.
9. Fuel cells are operatable to 200 ^oC and so find application in high temperature systems.
10. Fuel cells hold promise as good storage devises for future nuclear and solar energy economies.

1.12.4 Limitations of Fuel Cells

1. The main limitation of fuel cells lie in high initial costs associated with electrode material and design costs. The later could be brought down with mass production and suitable R&D in this direction. The low maintenance and longetivity of cells could compensate some of these negative factors.
2. Large weight and volume of H₂ gas-fuel storage system.
3. Lack of infrastructure for distribution and marketing of hydrogen gas. The developing natural gas distribution net-work could pave way for this in the future.
4. High cost of H₂ gas. Technological advances should bring the costs down.
5. Most alkaline fuel cells suffer from carbon dioxide leakages and should be properly filtered and prevented from entering the cell and reacting with the electrolyte.

1.13 Self-Test Questions

1. The resistance of a conductor is directly proportional to
 - (A) Current passed
 - (B) Area of cross section of conductor
 - (C) Length of the conductor
 - (D) Equivalent conductance

2. Sodium chloride is a poor conductor of electricity but transforms into a good conductor in molten state because
- The covalent bonds are broken in molten state
 - The degree of dissociation increases
 - It form liquid crystals
 - The ions get mobility
3. If “ l ” is the distance between the electrodes of a cross sectional area “ a ”, then cell constant is given by the ratio
- l/a
 - a/l
 - $a \times l$
 - $a - l$
4. The resistance of a conductor is 5×10^{-2} ohms. Conductance is the equal to
- 200 mhos
 - 20 mhos
 - 500 mhos
 - 50 mhos
5. The conductivity of 0.1 N KCl is $0.01120 \text{ mho cm}^{-1}$. If the cell constant is equal to 0.5 cm^{-1} , the conductance is equal to
- $2.24 \times 10^{-2} \text{ eq}^{-1}$
 - $5.6 \times 10^{-3} \text{ mhos}$
 - 224 mhos
 - 560 mhos
6. The units of equivalent conductivity is
- $\text{ohm}^{-2} \text{ cm}^{-2} \text{ eq}^{-1}$
 - $\text{ohm}^{-1} \text{ cm}^{-2} \text{ eq}^{-1}$
 - $\text{Ohm}^{-2} \text{ cm}^{-2} \text{ eq}^{-1}$
 - $\text{Ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$
7. According to Kohlrausch law, the mathematical expression is
- $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$
 - $t_+ = \frac{\Lambda_+}{\Lambda_\infty}$
 - $\Lambda_+ + \Lambda_- = \Lambda_\infty$
 - $\Lambda_v = KV$
8. Equivalent conductivity of an electrolytic solution
- Increases with dilution
 - Decreases with dilution
 - Independent of dilution
 - None of the above
9. Cell constant of a conductometric cell
- Increases with dilution
 - Decrease with dilution
 - Depends on the nature of electrolyte
 - Independent of the nature of electrolyte.
10. Equivalent conductivity of any electrolyte is algebraic sum of _____ conductivities.
11. Degree of dissociation = $\frac{\lambda_v}{\lambda_\infty}$
12. Specific conductance = Cell constant x _____

13. If the standard potential of $\text{Ca} | \text{Ca}^{2+}$, $\text{Ni} | \text{Ni}^{2+}$ and $\text{Au} | \text{Au}^{2+}$ couples are 2.87, 0.25 and -1.5V respectively, then
- (A) Ni can reduce Ca^{2+} and Au^{3+} (B) Ca and Ag can reduce Ni^{2+}
 (C) Ni^{2+} can oxidize Au and Cu (D) Au^{3+} can oxidize Ca and Ni
14. In a galvanic cell
- (A) Chemical energy is converted into electrical energy
 (B) Electrical energy is converted into chemical energy
 (C) Chemical energy is converted into heat energy
 (D) Electrical energy is converted into heat energy
15. The cell reaction $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$ is correctly represented by
- (A) $\text{Cu} | \text{Cu}^{2+} || \text{Zn} | \text{Zn}^{2+}$ (B) $\text{Cu} | \text{Cu}^{2+} || \text{Zn}^{2+} | \text{Z}$
 (C) $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ (D) $\text{Zn} | \text{Zn}^{2+} || \text{Cu} | \text{Cu}^{2+}$
16. If the oxidation potential of Zn metal is 0.76V, the E_{cell} for the redox reaction $\text{Zn} + 2\text{H}(\text{aq}, 1\text{M}) \longrightarrow \text{Zn}^{2+} + \text{H}_2(1\text{atm})$ is
- (A) 0.76 (B) -0.76
 (C) +0.38 (D) -0.38

1.14 Short and Essay Type Questions

1. State and explain Kohlrausch' law. Give its applications.
2. Write an account of acid base conductometric titrations.
3. State Kohlrausch law. Explain how it can be used to determine the Λ_4 of acetic acid.
4. What is the principle underlying conductometric titrations? Discuss titration curve obtained for titration of a mixture of HCl and CH_3COOH with NaOH. What are the advantage of conductometric titrations?
5. Define, the terms specific conductance and equivalent conductance. Explain clearly why on dilution the specific conductance decreases but equivalent conductance increases.
6. During conductometric titration of a strong acid against strong base, the conductivity decreases up to the neutralization point and then increases sharply. Explain why this happens

7. Explain the terms cell constant, equivalent conductivity. Give their units. Draw a graph showing the variation of equivalent conductance with concentration for both weak and strong electrolytes.
8. How does Kohlrausch's law of independent migration of ions help in determining the equivalent conductivity of a weak electrolyte like acetic acid at infinite dilution?
9. (a) Define the terms :
 - (i) Resistivity
 - (ii) Conductivity and
 - (iii) Equivalent conductivity.(b) Describe a method for determining the equivalent conductivity of an electrolytic solution.
(c) What is the effect of dilution on conductivity?
10. What is meant by cell constant of a conductivity cell? How is it determined? What are its units?
11. Explain the following terms
 - (a) Single electrode potential
 - (b) Reference electrode
 - (c) Standard hydrogen electrode.
12. What is meant by pH of a solution? How is the pH of a solution determined?
13. How is the *emf* of a cell determined from a knowledge of single electrode potentials? Give a suitable example.
14. Write the cell reaction at 298K of the cell
$$\text{Zn} \mid \text{ZnCl}_2 (a = 0.5) \parallel \text{AgCl} \mid \text{Ag}$$
15. (a) Explain what do you understand by single electrode potential and redox potential?
(b) What is hydrogen electrode? How is it constructed?
16. When a zinc rod is dipped in a solution of aq. copper sulphate, copper is precipitated out.
17. State and Explain the Kohlrausch's law and its applications.
18. What are concentration cells? How can the EMF of a concentration cell be evaluated?
19. Write short notes on single electrode potential and its significance?
20. Define the terms specific, equivalent and molar conductivities. How do they vary with dilution?

21. Calculate the cell constant of a cell having a solution of concentration $N/30$ g, equi/litre of an electrolyte which showed the equivalent conductance of $120 \text{ Mhos cm}^2 \text{ g equiv}^{-1}$.
22. What do you understand by electrochemical series? How is this series useful in the determination of corrosion of metals.
23. The resistance of a $0.1N$ solution of an electrolyte of 40 ohms. If the distance between the electrodes is 1.2 cm and area of cross section is 2.4 cm^2 . Calculate