

Section-A

1. Electrochemistry

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Electrolytes are electrovalent substances that form ions in solution which conduct an electric current. Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes.

Nonelectrolytes, on the other hand, are covalent substances which furnish neutral molecules in solution. Their water-solutions do not conduct an electric current. Sugar, alcohol and glycerol are typical nonelectrolytes.

An electrolyte invariably undergoes chemical decomposition as a result of the passage of electric current through its solution.

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed Electrolysis (*lyo* = breaking).

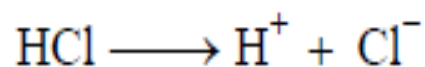
The process of electrolysis is carried in an apparatus called the **Electrolytic cell**. The cell contains water-solution of an electrolyte in which two metallic rods (electrodes) are dipped. These rods are connected to the two terminals of a battery (source of electricity). The electrode connected to the positive terminal

of the battery attracts the negative ions (anions) and is called **anode**. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called **cathode**.

MECHANISM OF ELECTROLYSIS

How the electrolysis actually takes place, is illustrated in Fig 24.1. The cations migrate to the cathode and form a neutral atom by accepting electrons from it. The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes chemical reaction takes place.

Example. Let us consider the electrolysis of hydrochloric acid as an example. In solution, HCl is ionised,

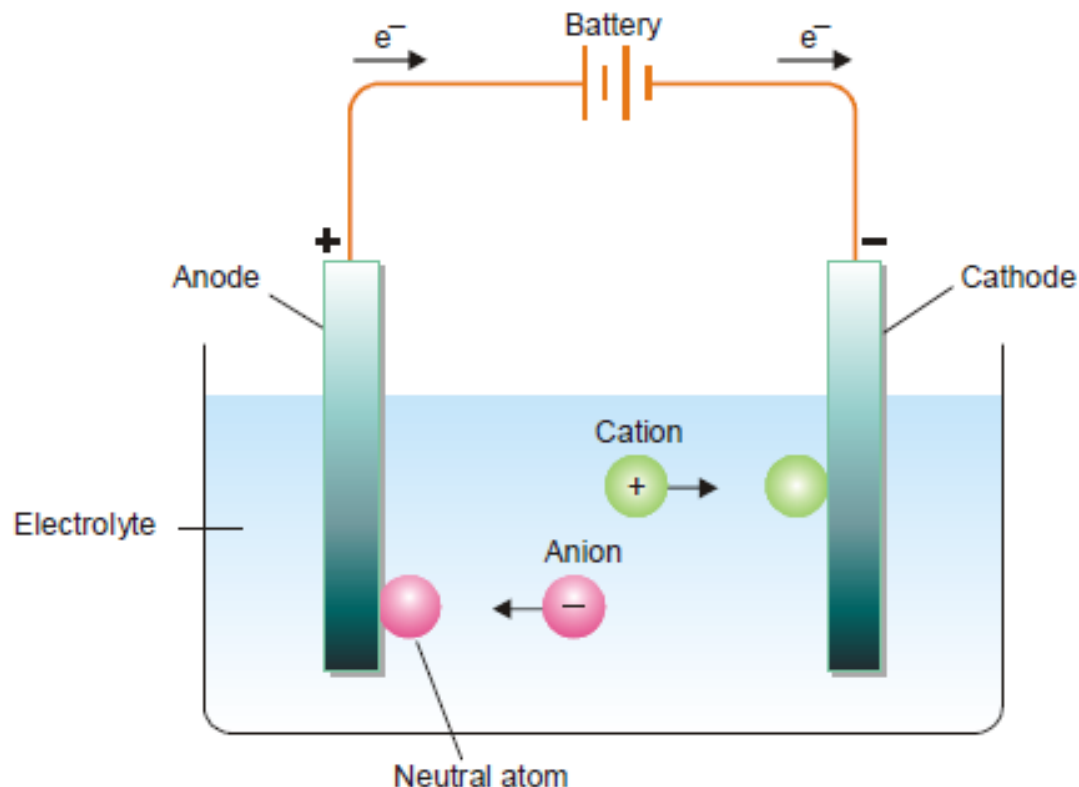


In the electrolytic cell Cl^- ions will move toward the anode and H^+ ions will move toward the cathode. At the electrodes, the following reactions will take place.

At cathode :



As you see, each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Pairs of hydrogen atoms then unite to form molecules of hydrogen gas, H_2 .



■ **Figure 24.1**
The mechanism of electrolysis.

At Anode :



After the chloride ion loses its electron to the anode, pair of chlorine atoms unite to form chlorine gas, Cl_2 .

The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction is :



ELECTRICAL UNITS

There are a few electrical units which we should understand before taking up the study of quantitative aspects of electrolysis. These are :

Coulomb

A coulomb is a **unit quantity of electricity**. It is the amount of electricity which will deposit 0.001118 gram of silver from a 15 per cent solution of silver nitrate in a coulometer.

Ampere

An ampere is a **unit rate of flow of electricity**. It is that current which will deposit 0.001118 gram of silver in one second. In other words, an ampere is a current of one coulomb per second.

Ohm

An ohm is a **unit of electrical resistance**. It is the resistance offered at 0°C to a current by a column of mercury 106.3 cm long of about 1 sq mm cross-sectional area and weighing 14.4521 grams.

Volt

A volt is a **unit of electromotive force**. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

FARADAY'S LAWS OF ELECTROLYSIS

Michael Faraday studied the quantitative aspect of electrolysis. He discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. In 1834, he formulated two laws which are known as **Faraday's Laws of Electrolysis**. These are :

First Law

The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution.

Second Law

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

Definition of Electrochemical equivalent in light of First Law

If m is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity, then

$$m \propto Q \quad (\text{First Law})$$

We know that

$$Q = I \times t$$

where I is the strength of current in amperes and t is the time in second for which the current has been passed.

Therefore,

$$m \propto I \times t$$

or

$$m = Z \times I \times t$$

where Z is the constant known as the Electrochemical equivalent of the substance (electrolyte).

If $I = 1$ ampere and $t = 1$ second, then

$$m = Z$$

Thus, **the electrochemical equivalent is the amount of a substance deposited by 1 ampere current passing for 1 second (i.e., one coulomb).**

The Electrical unit Faraday

It has been found experimentally that the quantity of electricity required to liberate one gram-equivalent of a substance is 96,500 coulombs. This quantity of electricity is known as **Faraday** and is denoted by the symbol F .

It is obvious that the quantity of electricity needed to deposit 1 mole of the substance is given by the expression.

$$\text{Quantity of electricity} = n \times F$$

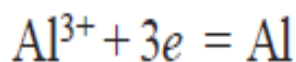
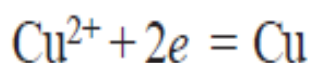
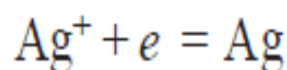
where n is the valency of its ion. Thus the quantity of electricity required to discharge :

$$\text{one mole of Ag}^+ = 1 \times F = 1F$$

$$\text{one mole of Cu}^{2+} = 2 \times F = 2F$$

$$\text{one mole of Al}^{3+} = 3 \times F = 3F$$

We can represent the reactions on the cathode as :



It is clear that the moles of electrons required to discharge one mole of ions Ag^+ , Cu^{2+} and Al^{3+} is one, two and three respectively. Therefore it means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say that.

$$\mathbf{1 \text{ Faraday} = 96,500 \text{ coulombs} = 1 \text{ Mole electrons}}$$

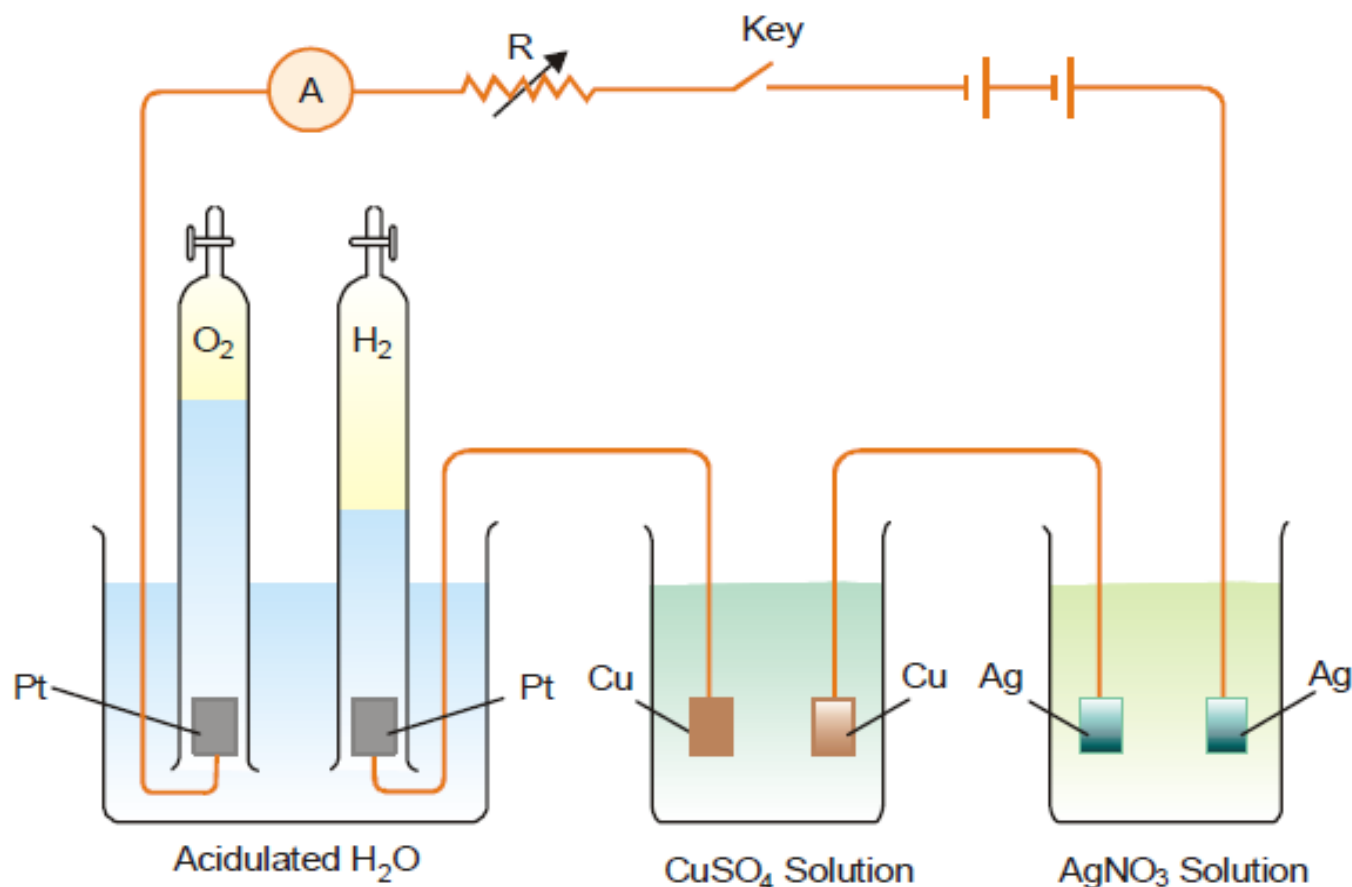
Importance of the First law of Electrolysis

With the help of the first law of electrolysis we are able to calculate :

- (1) the value of electrochemical equivalents of different substances; and
- (2) the masses of different substances produced by passing a known quantity of electricity through their solutions.

Verification of the Second law of Electrolysis

According to this law when the same quantity of electricity is passed through different electrolyte solutions, the masses of the substances deposited on the electrodes are proportional to their chemical equivalents.



Importance of the Second law of Electrolysis

The second law of electrolysis helps to calculate :

- (1) the equivalent weights of metals
- (2) the unit of electric charge
- (3) the Avogadro's number

SOLVED PROBLEM 1. 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

SOLUTION

Here $t = 50$ minutes $= 50 \times 60$ seconds; $I = 0.2$ ampere. Quantity of electricity used is

$$Q = I \times t = 0.2 \times 50 \times 60 = 600 \text{ coulombs}$$

Amount of copper deposited by 600 coulombs $= 0.1978$ g

$$\text{Amount of copper deposited by 1 coulomb} = \frac{0.1978}{600} \text{ g} = 0.0003296 \text{ g}$$

\therefore Electrochemical equivalent of copper $= 0.0003296$

CONDUCTANCE OF ELECTROLYTES

We have seen that electrolyte solutions conduct electric currents through them by movement of the ions to the electrodes. The power of electrolytes to conduct electric currents is termed **conductivity** or **conductance**. Like metallic conductors, electrolytes obey Ohm's law. According to this law, the current I flowing through a metallic conductor is given by the relation.

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

where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω). The resistance R of a conductor is directly proportional to its length, l , and inversely proportional to the area of its cross-section, A . That is,

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

or

$$R = \rho \times \frac{l}{A} \quad \dots(1)$$

where ρ "rho" is a constant of proportionality and is called **resistivity** or **specific resistance**. Its value depends upon the material of the conductor. From (1) we can write

$$\rho = R \times \frac{A}{l}$$

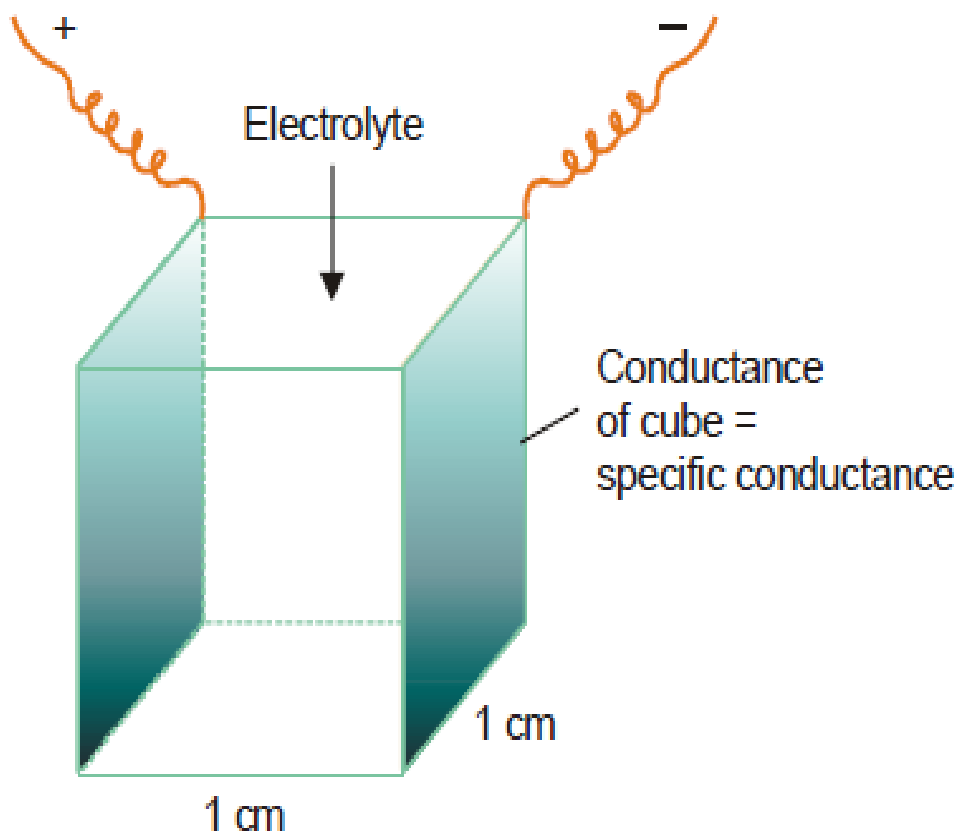
If $l = 1$ cm and $A = 1$ sq cm, then

$$\rho = R$$

Thus it follows that the **Specific resistance** of a conductor is the resistance in ohms which one centimetre cube of it offers to the passage of electricity.

Specific Conductance

It is evident that a substance which offers very little resistance to the flow of current allows more current to pass through it. Thus the power of a substance to conduct electricity or conductivity is the converse of resistance. The reciprocal of specific resistance is termed **Specific conductance** or **Specific conductivity**.



■ **Figure 24.3**
Diagrammatic illustration of definition of specific conductance.

It is defined as : **the conductance of one centimetre cube (cc) of a solution of an electrolyte.**

The specific conductance is denoted by the symbol κ (kappa). Thus,

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

Units of Specific conductance

Specific conductance is generally expressed in reciprocal ohms (r.o) or **mhos** or **ohm⁻¹**. Its unit can be derived as follows :

$$\begin{aligned}\kappa &= \frac{1}{A} \times \frac{l}{R} = \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \\ &= \text{ohm}^{-1}\text{cm}^{-1}\end{aligned}$$

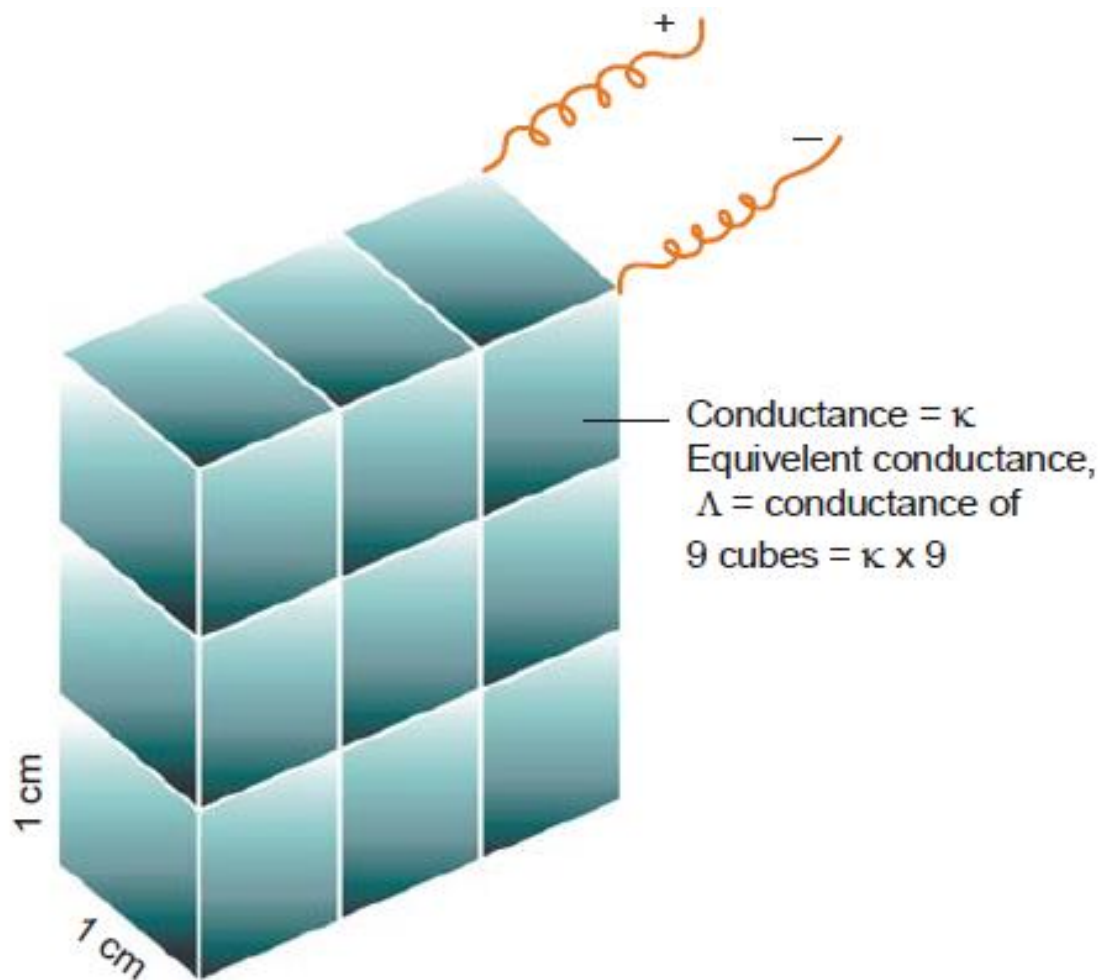
The internationally recommended unit for ohm⁻¹ (or mho) is **Siemens, S**. When S is used, the conductance is expressed as **S cm⁻¹**. It may be noted that Siemens is not a plural, the unit is named after Sir William Siemens—a noted electrical engineer.

The specific conductance increases with : (i) ionic concentration, and (ii) speeds of the ions concerned.

In measuring the specific conductance of the aqueous solution of an electrolyte, the volume of water in which a certain amount of the electrolyte is dissolved is always measured in cubic centimeters (cc) and this is known as **dilution**. If the volume of a solution is V_{cc} , the specific conductance of the solution is written as κ .

Equivalent Conductance

It is defined as **the conductance of an electrolyte obtained by dissolving one gram-equivalent of it in V cc of water.**



■ **Figure 24.4**

Solution of 1 g-eqvt. dissolved in 9 cc water between electrode plates 1 cm apart has $L = \kappa \times 9$.

The equivalent conductance is denoted by Λ . It is equal to the product of the specific conductance, κ and the volume V in cc containing one gram-equivalent of the electrolyte at the dilution V .

In general, if an electrolyte solution contains N gram-equivalents in 1000 cc of the solution, the volume of the solution containing 1 gram-equivalent will be $1000/N$. Thus,

$$\Lambda = \frac{\kappa \times 1000}{N}$$

Unit of Equivalent conductance

The unit of equivalent conductance may be deduced as follows :

$$\begin{aligned}\Lambda &= \kappa \times V \\ &= \frac{1}{R} \times \frac{l}{A} \times V \\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{eqvt}} \\ &= \text{ohm}^{-1} \text{cm}^2 \text{eqvt}^{-1}\end{aligned}$$

ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

CELL TERMINOLOGY

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (–) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is shown as (+) in cell diagrams.

Electrolyte is the salt solutions in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

ARRHENIUS THEORY OF IONISATION

Savante Arrhenius studied the conduction of current through water solutions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions. In 1884, Arrhenius put forward his theory of ionisation. **Arrhenius theory of ionisation** may be stated as :

(1) When dissolved in water, **neutral electrolyte molecules are split up into two types of charged particles**. These particles were called ions and the process was termed **ionisation**. The positively charged particles were called **cations** and those having negative charge were called **anions**.

In its modern form, the theory assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic force. When placed in water, these neutral molecules *dissociate* to form separate anions and cations. Thus,



For that reason, this theory may be referred to as the theory of electrolytic dissociations.

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



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

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

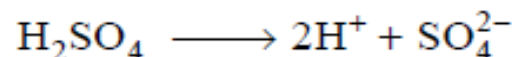
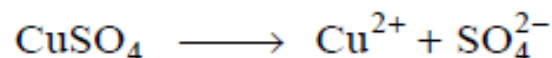
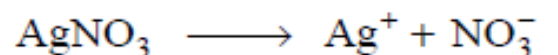
where K is called the **Dissociation constant**.

(3) The **charged ions are free to move through the solution to the oppositely charged electrode**. This movement of the ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

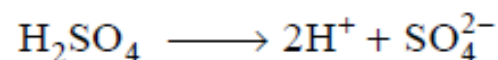
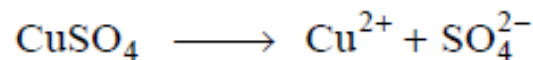
(4) The **electrical conductivity of an electrolyte solution depends on the number of ions present in solution**. Thus the degree of dissociation of an electrolyte determines whether it is a strong electrolyte or a weak electrolyte.

MIGRATION OF IONS

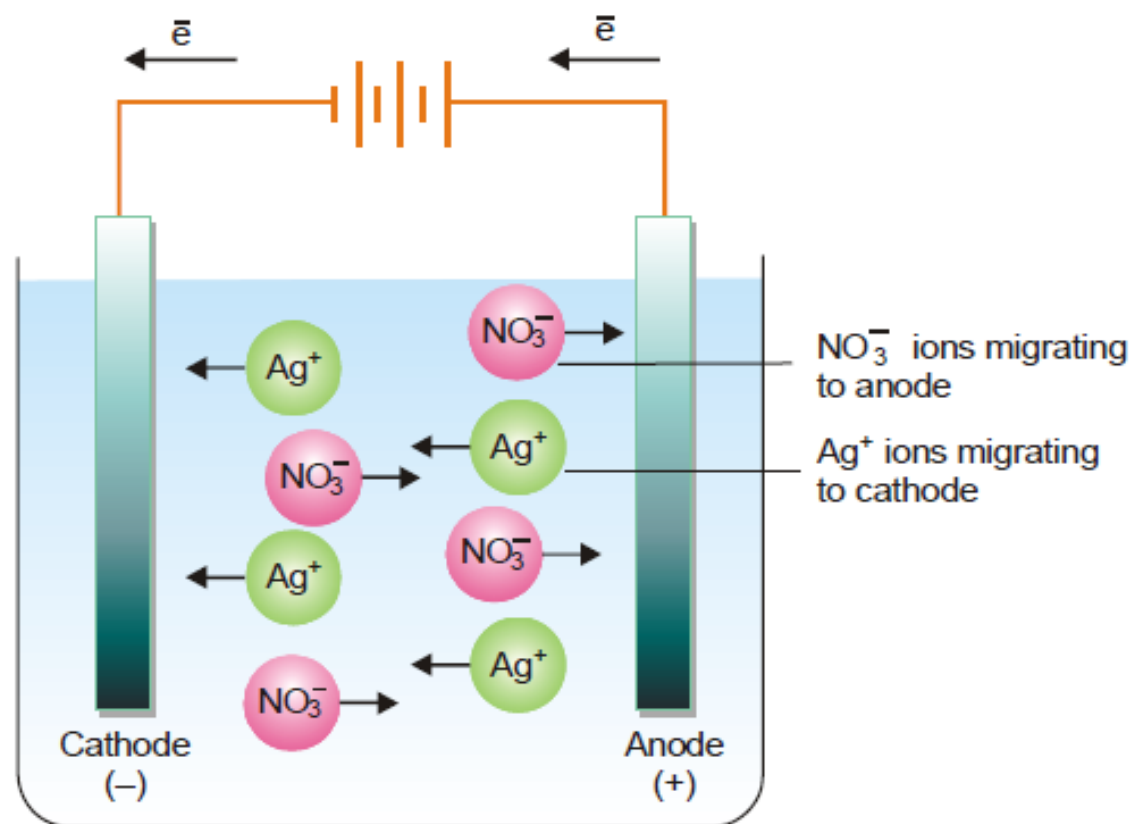
We know that electrolytes dissociate in solution to form positive ions (cations) and negative ions (anions).



As the current is passed between the electrodes of the electrolytic cell, the ions migrate to the opposite electrodes. Thus in the electrolytic solution of $AgNO_3$, the cations (Ag^+) will move to the cathode and anions (NO_3^-) will move to the anode. Usually different ions move with different rates. The migration of ions through the electrolytic solution can be demonstrated by the following experiments.



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■ **Figure 25.1**

Migration of ions through electrolytic solution to opposite electrodes.

WHAT IS TRANSPORT NUMBER ?

During electrolysis the current is carried by the anions and the cations. **The fraction of the total current carried by the cation or the anion is termed its Transport number or Hittorf's number.** If v_+ represents the speed of migration of the cation and v_- that of the anion,

$$\text{the transport number of cation} = \frac{v_+}{v_+ + v_-}$$

$$\text{the transport number of anion} = \frac{v_-}{v_+ + v_-}$$

The transport number of the cation is represented by t and that of the anion by t_- .

Thus
$$t_+ = \frac{v_+}{v_+ + v_-} \quad \text{and} \quad t_- = \frac{v_-}{v_+ + v_-}$$

or
$$\frac{t_+}{t_-} = \frac{v_+}{v_-} \quad \text{and} \quad t_+ + t_- = 1$$

If the speed ratio v_+/v_- be denoted by r , we have,

$$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$$

and
$$t_- = \frac{1}{1 + r}$$

KOHLRAUSCH'S LAW

From a study of the equivalent conductances of different electrolytes at infinite dilution (λ_{∞}), Kohlrausch discovered that each ion contributes to the conductance of the solution. In 1875, he enunciated a generalisation which is called the **Kohlrausch's Law**. It states that : **the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.**

The law may be expressed mathematically as :

$$\lambda_{\infty} = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cation.

For example, the equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45. The equivalent conductance of Na^+ and Cl^- ion is 50.11 ohm^{-1} and 76.34 ohm^{-1} respectively. Thus,

$$\lambda_{\infty}(\text{NaCl}) = \lambda_{\text{Cl}^-} + \lambda_{\text{Na}^+}$$

or
$$126.45 = 50.11 + 76.34$$

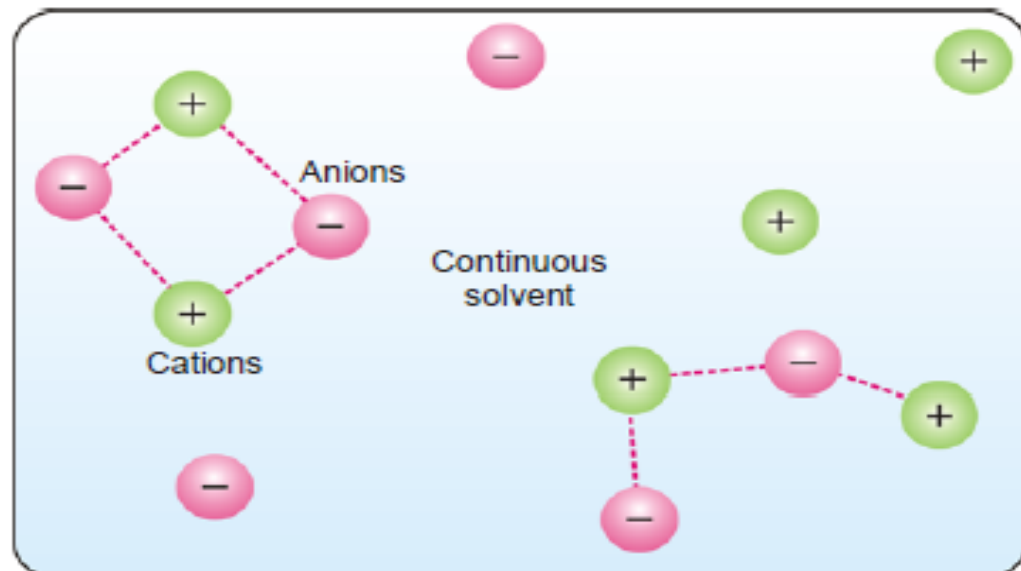
This is in conformity with the Kohlrausch's Law.

Debye-Huckel Theory

In 1923 Debye and Huckel and in 1926 Onsagar put forward the **modern theory of strong electrolytes** in which account is taken of the electrostatic forces between the ions. Without going into its mathematical details, a brief outline of the main ideas of the theory is given below :

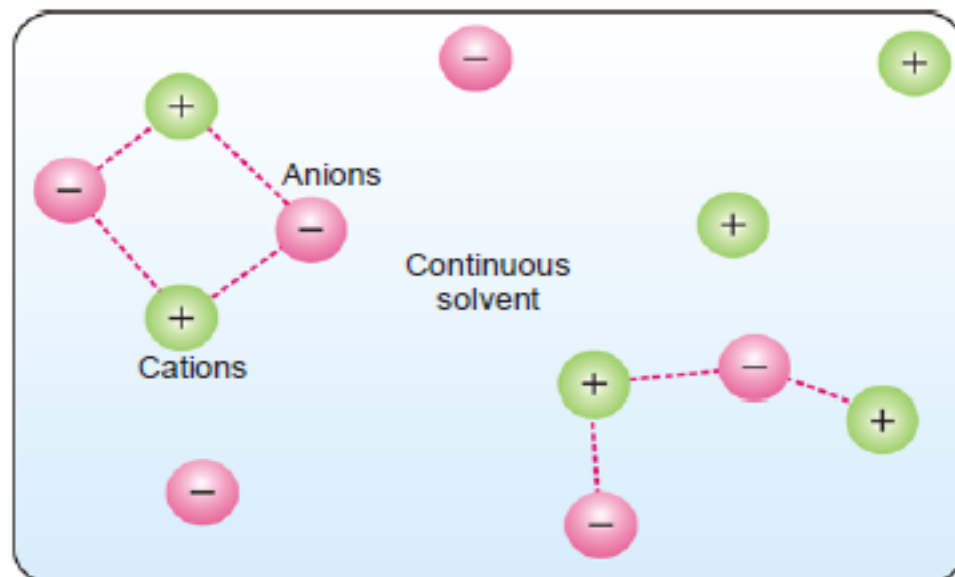
(1) **The strong electrolyte is completely ionised at all dilutions.** The present position as it has emerged from the study of Raman spectra, X-ray analysis of crystals, Distribution coefficients and vapour pressures is that there is a very small amount of unionised substance also present and therefore instead of saying 'completely ionised' we should say 'almost completely ionised'.

(2) **Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and vice-versa** (Fig. 26.1). Though the solution is on the whole neutral, there is in the vicinity of any given ion a predominance of ions of opposite charge which we call as **counter ions**. The ions are all the time on the move in all directions but on the average, more *counter ions* than like *ions* pass by any given ion. This spherical haze of opposite charge is called **ionic atmosphere**.



■ **Figure 26.1**

The ions of a particular charge are surrounded by more ions of the opposite charge and solvent molecules. Because of the large number of ions in concentrated



■ **Figure 26.1**

The ions of a particular charge are surrounded by more ions of the opposite charge and solvent molecules. Because of the large number of ions in concentrated solution, the ion activity is reduced due to hindered movement of the ions.

(3) Decrease in equivalent conductance with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and *vice-versa*.

(4) The ratio $\lambda_v / \lambda_\infty$ does not correctly give the degree of dissociation α for strong electrolytes but only the conductance or conductance coefficient f_c .

(5) In spite of almost complete ionisation, λ_v is much less than λ_∞ .

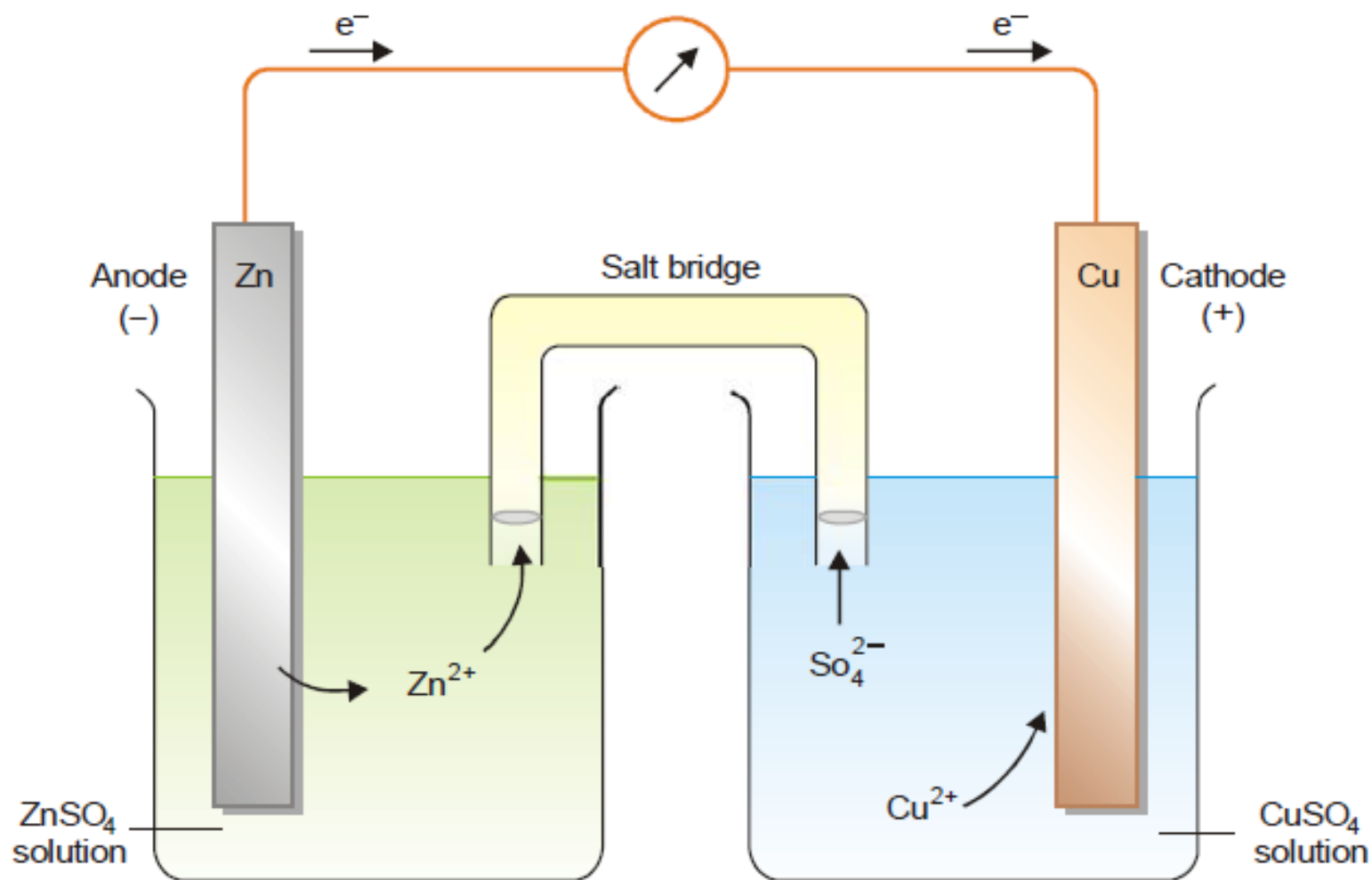
The observed deviations are due to the following reasons :

(1) **Asymmetry or Relaxation Effect.** Imagine a central negative ion. This is surrounded by a number of positively charged ions which form its 'ionic atmosphere.' This atmosphere is symmetrically situated in the absence of any electrical field and the force of attraction exerted by the atmosphere on the central ion is uniform in all directions. When an electric field is applied, the negative ion moves towards the anode and the positive ionic atmosphere towards the cathode. This leaves a large number of positive ions behind it than there are in front of the negative ion with the result that the symmetry

ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell.

ELECTROMOTIVE FORCE : It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm. A volt is a **unit of electromotive force**.



■ **Figure 29.3**

A simple voltaic (galvanic) cell.

CELL TERMINOLOGY

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (-) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is shown as (+) in cell diagrams.

Electrolyte is the salt solutions in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

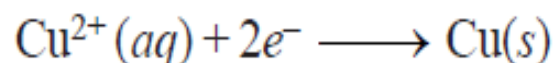
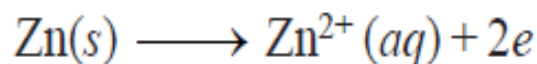
Daniel Cell

It is a typical voltaic cell. It was named after the British chemist John Daniel. It is a simple zinc-copper cell like the one described above.

Cell reaction

The flow of electrons from one electrode to the other in an electrochemical cell is caused by the half-reactions taking place in the anode and cathode compartments. The net chemical change obtained by adding the two half-reactions is called the **cell reaction**. Thus, for a simple voltaic cell described above, we have

(a) Half-reactions :



(b) Cell reaction by adding up the half-reactions :



Cell potential or emf

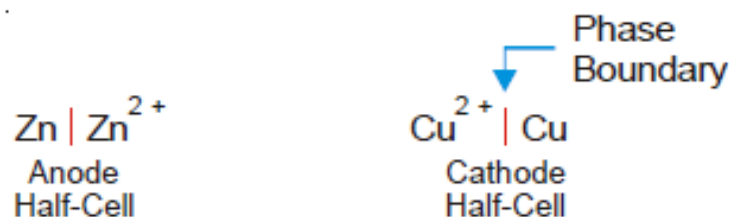
In a Zn-Cu voltaic cell, electrons are released at the anode and it becomes negatively charged. The negative electrode pushes electrons through the external circuit by electrical repulsions. The copper electrode gets positive charge due to the discharge of Cu^{2+} ions on it. Thus electrons from the outer circuit are attracted into this electrode. The flow of current through the circuit is determined by the 'push', of electrons at the anode and 'attraction' of electrons at the cathode. These two forces constitute the 'driving force' or 'electrical pressure' that sends electrons through the circuit. This driving force is called the **electromotive force** (abbreviated **emf**) or **cell potential**. The emf of cell potential is measured in units of volts (V) and is also referred to as **cell voltage**.

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode contact with metal ions in solution.

IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

(1) a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as

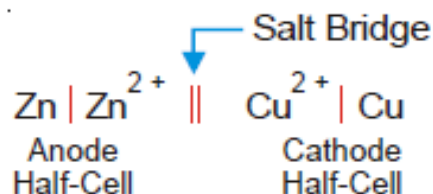


It may be noted that the metal electrode **in anode** half-cell is on the left, while **in cathode** half-cell it is on the right of the metal ion.

(2) A **double vertical line** (||) represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.

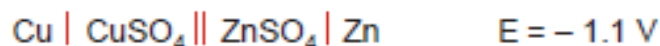
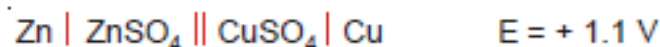
(3) **Anode half-cell is written on the left and cathode half-cell on the right.**

(4) In the **complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between.** The zinc-copper cell can now be written as

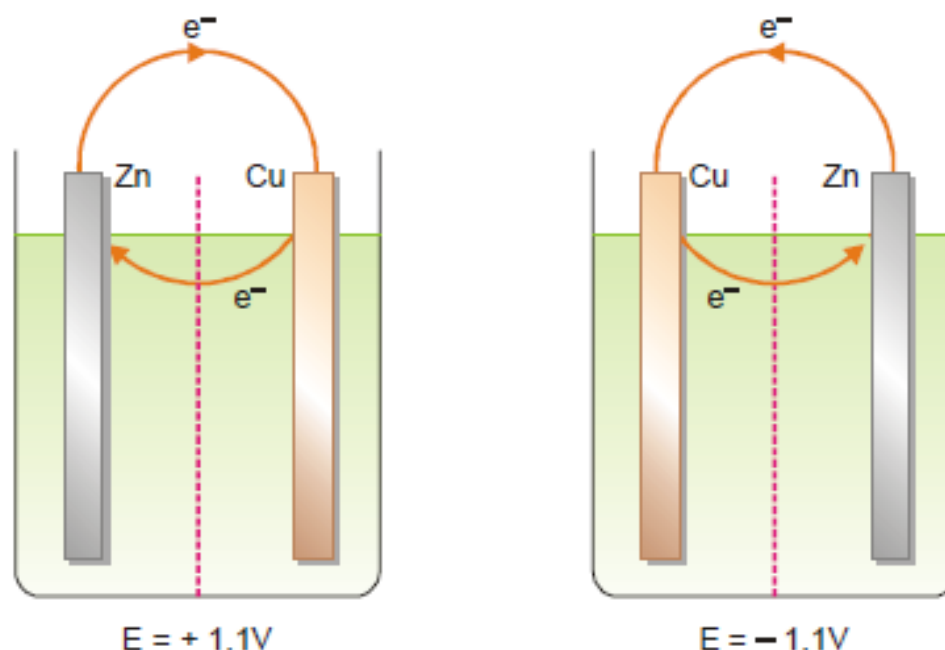


Convention regarding sign of emf value

The magnitude of the emf of a cell reflects the tendency of electrons to flow externally from one electrode to another. The electrons are transported through the cell solution by ions present and pass from the positive electrode (Cu in case of Daniel cell) to the negative electrode. This corresponds to a clockwise flow of electrons through the external circuit. Thus the emf of the cell is given the +ve sign. If the emf acts in the opposite direction through the cell circuit, it is quoted as -ve value. For example, Daniel cell has an emf of 1.1V and the copper electrode is positive. This can be expressed in two ways :



The negative sign indicates that the cell is not feasible in the given direction. The reaction will take place in the reverse direction.



■ **Figure 29.5**
Illustration of emf sign in Daniel cell.

Calculating the emf of a cell

The emf of a cell can be calculated from the half-cell potentials of the two cells (anode and cathode) by using the following formula

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{R}} - E_{\text{L}} \end{aligned} \quad (\text{IUPAC convention 3})$$

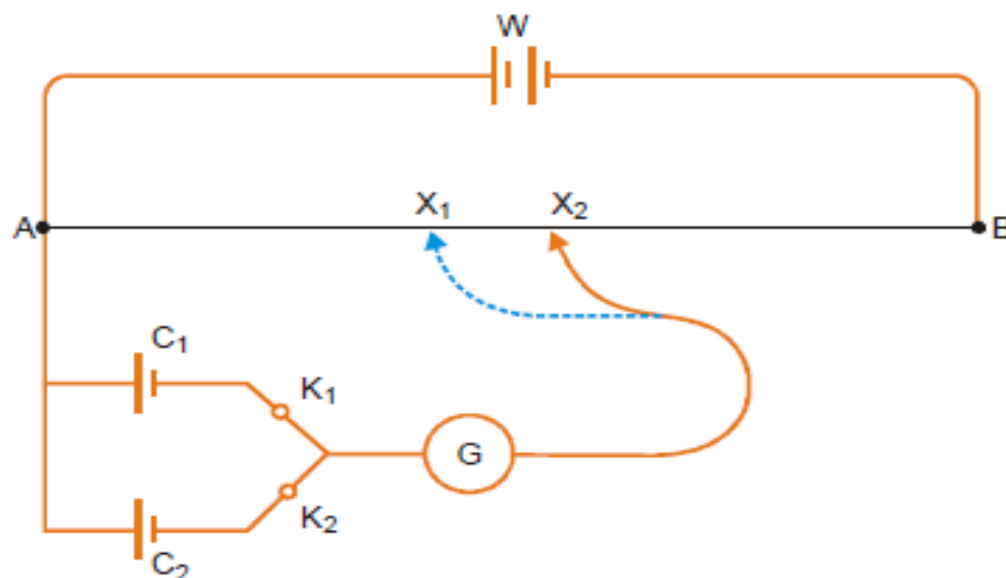
where E_{R} and E_{L} are the reduction potentials of the right-hand and left-hand electrodes respectively. It may be noted that absolute values of these reduction potentials cannot be determined. These are found by connecting the half-cell with a standard hydrogen electrode whose reduction potential has been arbitrarily fixed as zero.

MEASUREMENT OF EMF OF A CELL

The emf of an unknown cell can be measured with the help of a **potentiometer** (Fig. 29.6). It consists of a wire AB which is about one metre long. The two ends of this wire are connected to a working battery W. A standard cell C_1 (*i.e.*, a cell of known emf) is connected to the end A. At the other end, the cell C_1 is connected to a galvanometer through a key K_1 . The galvanometer is then joined to a sliding contact that moves on the wire AB. The cell C_2 whose emf is to be measured is similarly connected to the key K_2 , the galvanometer and then the sliding contact. By using the key K_1 , the cell C_1 is put into the circuit and the contact is moved to and fro along AB. When no current flows through the galvanometer, the point of contact X_1 is recorded. Then by using the key K_2 , the cell C_2 is put into the circuit and the procedure is repeated to find the corresponding point X_2 . The emf of the cell C_2 is calculated by using the following equation :

$$\frac{\text{emf of } C_2}{\text{emf of } C_1} = \frac{\text{distance } AX_2}{\text{distance } AX_1}$$

Cell emf's can also be measured by electronic voltmeters of the analog or digital type.



■ **Figure 29.6**

Measuring the emf of a cell with a potentiometer.

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential**. Thus in a Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+} , a positive charge. The amount of the charge produced on individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (a) concentration of ions in solution; (b) tendency to form ions; and (c) temperature

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E . It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called the **standard emf**. The standard conditions are (a) 1 M solutions of reactants and products; and (b) temperature of 25°C . Thus standard emf may be defined as : **the emf of a cell with 1 M solutions of reactants and products in solution measured at 25°C .**

Standard emf of a cell is represented by the symbol E° . With gases 1 atm pressure is a standard condition instead of concentration.

For a simple Zn-Cu voltaic cell, the standard emf, E° , is 1.10 V. This means that the emf of the cell operated with $[\text{Cu}^{2+}]$ and $[\text{Zn}^{2+}]$ both at 1 M and 25°C is 1.10 V. That is,



USING STANDARD POTENTIALS

In Table 29.1 the standard reduction potentials (E°) are arranged in the order of increasing potentials. The relative position of electrodes (M/M^+) in the table can be used to predict the reducing or oxidising ability of an electrode.

The electrodes that are relatively positive indicate that reduction reaction involving addition of electrons,




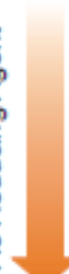
is possible. In case of relatively negative potential involving loss of electrons,



is indicated. It also follows that the system with higher electrode potential will be reduced by the system with lower electrode potential.

Predicting the Oxidising or Reducing Ability

Let us consider a series of elements Cu, H_2 , Ni, Zn and their ions. These four elements could act as reducing agents. On the other hand, their ions Cu^{2+} , H^+ , Ni^{2+} and Zn^{2+} can act as electron acceptors or oxidising agents. If we list the respective half-reactions (or electrodes) in order of descending E° values, we will have placed the oxidising agents in descending order of their ability to attract electrons.

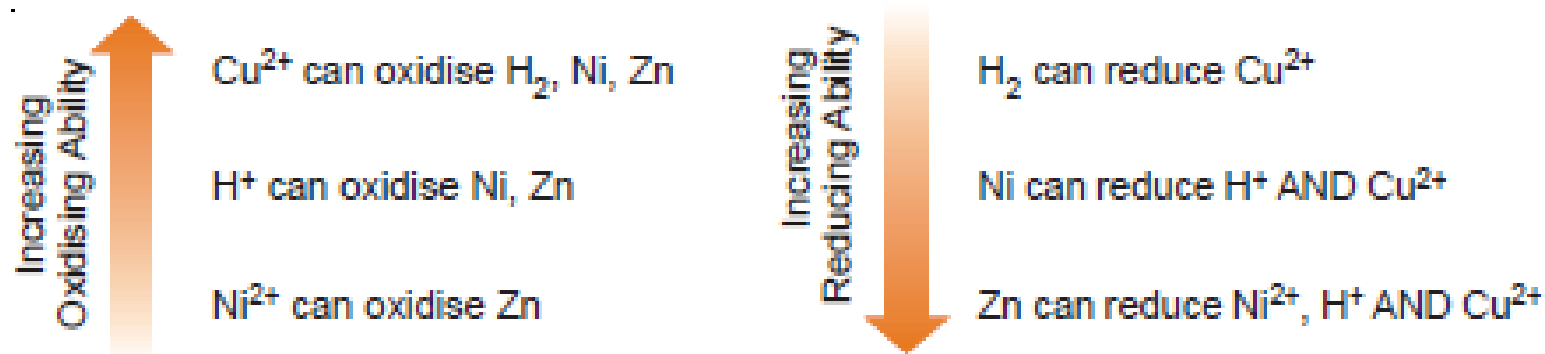
Increasing Strength As Oxidising Agent 	$Cu^{2+} + 2e^- \longrightarrow Cu$	Increasing Strength As Reducing Agent 	$E^\circ = +0.34\text{ V}$
	$2H^+ + 2e^- \longrightarrow H_2$		$E^\circ = 0.00$
	$Ni^{2+} + 2e^- \longrightarrow Ni$		$E^\circ = -0.25$
	$Zn^{2+} + 2e^- \longrightarrow Zn$		$E^\circ = -0.76$

It is noteworthy that the value of E° becomes more negative down the series. This means that Cu^{2+} is the best oxidising agent (most electron-attracting ion) of those in the list. That is, Cu^{2+} shows the greatest tendency to be reduced. Conversely, Zn^{2+} is the worst oxidising agent, being the least electron-attracting ion. Of the elements Cu, H_2 , Ni and Zn, Zn is the best reducing agent (best electron donor), since E° for the half-reaction



has the most positive value. By the reasoning, Cu is the worst reducing agent.

reactions occur spontaneously.



Some important points concerning the Table of Standard Reduction Potentials (Table 29.1

- (1) The more positive the value of E° , the better the oxidising ability (the greater tendency to be reduced) of the ion or compound, on moving upward in the Table.
- (2) The more negative the value of E° the better the reducing ability of the ions, elements or compounds on moving downward in the Table.
- (3) Under standard conditions, any substance in this Table will spontaneously oxidise any other substance lower than it in the Table.

Predicting whether a metal will displace hydrogen from a dilute acid solution

Any metal above hydrogen in the electrochemical series is a weaker reducing agent than hydrogen itself and cannot reduce H^+ to H_2 . Any metal lying below hydrogen is a stronger reducing agent than hydrogen and will convert H^+ to H_2 . This explains why Zn lying below hydrogen reacts with dil H_2SO_4 to liberate H_2 , while Cu lying above hydrogen does not react.



THE NERNST EQUATION

We know experimentally that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889 Walter Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E , from the standard electrode potential, E° , and the temperature of the cell. This relation known as the Nernst equation can be stated as

$$E = E^\circ - \frac{2.303RT}{nF} \log K \quad \dots(1)$$

where

E° = standard electrode potential

R = gas constant

T = Kelvin temperature

n = number of electrons transferred in the half-reaction

F = Faraday of electricity

K = equilibrium constant for the half-cell reaction as in equilibrium law

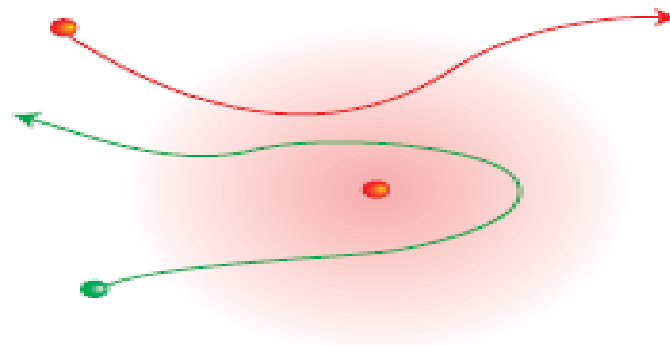


Fig. 9.1 The ionic atmosphere surrounding an ion consists of a slight excess of opposite charge as ions move through the vicinity of the central ion, with counterions lingering longer than ions of the same charge. The ionic atmosphere lowers the energy of the central ion.

The question still remains, however, about how the mean activity coefficients may be estimated. A theory that accounts for their values in very dilute solutions was developed by Peter Debye and Erich Hückel in 1923. They supposed that each ion in solution is surrounded by an ionic atmosphere of counter charge. This ‘atmosphere’ is actually the slight imbalance of charge arising from the competition between thermal motion, which tends to keep all the ions distributed uniformly throughout the solution, and the Coulombic interaction between ions, which tends to attract counterions (ions of opposite charge) into each other’s vicinity and repel ions of like charge (Fig. 9.1). As a result of this competition, there is a slight excess of cations near any anion, giving a positively charged ionic atmosphere around the anion, and a slight excess of anions near any cation, giving a

a limiting law in the sense that it becomes increasingly valid as the concentration of ions approaches zero. The Debye–Hückel limiting law² is

$$\log \gamma_{\pm} = -A|z_+z_-|I^{1/2} \quad (9.4)$$

(Note the common logarithm.) In this expression, A is a constant that for water at 25°C works out as 0.509. The z_j are the charge numbers of the ions (so $z_+ = +1$ for Na^+ and $z_- = -2$ for SO_4^{2-}); the vertical bars

Coulombic interactions between ions in solution are relatively strong, long-range forces compared to the other types of intermolecular force in solution. They are thus an important contributor to the non-ideality of ionic solutions, and in the Debye-Hückel theory of such solutions, they are taken to dominate the non-ideality to such an extent that all other contributions may be neglected.

The theory is based around the simple fact that oppositely charged ions attract one another, whilst like-charged ions repel each other.

As a result, the motion of ions in solution is not entirely random; there is a slight tendency for ions of opposite charge to encounter each other more frequently than ions of the same charge. A time-averaged picture of the solution shows that near any given **ion**, there is an excess of counter-ions.

This time-averaged spherical distribution (in which ions of the same charge as the central ion and counter-ions are both present, though counter-ions predominate) has a net charge equal in magnitude but opposite in sign to the central ion, and is known as its **ionic atmosphere**.

There is a stabilising Coulombic interaction between the central ion and its ionic atmosphere, which has the effect of lowering the **energy** (and thus the chemical potential) of the central ion. This model leads to the Debye-Hückel Limiting Law, which applies only at very low concentrations of **solute** (before other contributions to the non-ideality become important). This law enables calculation of the mean **activity** coefficient from basic properties of the solution:

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

where z_+ and z_- are the charge number of respectively the **cation** and the **anion** concerned. A is an **empirical** parameter, dependant upon the **solvent** and temperature (eg, for a solution in water at 298K, $A = 0.509$). I is the ionic strength of the solution.