

## 15

# ELECTROCHEMISTRY

**E**lectrochemistry deals with the conversion of electrical energy into chemical energy and vice versa. When electric current is passed through an aqueous solution of certain substances or through molten salts, it causes a chemical reaction to occur. On the other hand, in dry cells, button cells or lead acid batteries chemical reactions occur which produce electrical energy. In this lesson you will study some aspects of these processes.



## Objective

After reading this lesson you will be able to:

- understand oxidation and reduction in terms of electron transfer concept;
- calculate oxidation number (ON) of an atom in a molecule or ion;
- balance the chemical equation for redox reaction;
- explain electrolytic conduction, conductance and molar conductivity;
- describe the effect of dilution on conductivity and molar conductivity of an electrolyte;
- differentiate between electrolytic and Galvanic cell;
- state standard electrode potential and use it for calculation of standard electrode potential of a cell;
- explain standard Hydrogen electrode;
- describe electrochemical series and its application;
- state effect of concentration on electrode potential (Nernst equation);
- solve numericals based on Nernst equation and
- find relationship between emf and Gibbs energy change.

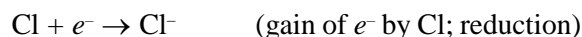
## Chemical Dynamics



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## 15.1 Oxidation and Reduction as Electron Transfer Process

Oxidation and reduction reactions constitute a very important class of chemical reaction. The electronic concept looks at oxidation and reduction in terms of electron transfer : process in which an atom or ion loses one or more electron to the other is called oxidation and the process in which an atom or ion gains one or more electron is termed as reduction. In the formation of NaCl from Na and Cl



Sodium undergoes oxidation and chlorine undergoes reduction. Here, sodium helps chlorine to undergo reduction and therefore it is called a reducing agent or reductant.

A reductant is a species in a chemical reaction which loses its electron to another reactant. Chlorine, on the other hand accepts electron, therefore it is an oxidising agent or oxidant. An oxidant is a species which accepts electrons in a chemical reaction.

It may be noted that oxidation and reduction processes do not take place independently but occur simultaneously and are thus called **oxidation-reduction** reaction or **redox** reactions. A redox reaction is a sum of oxidation and reduction half reactions in a chemical reaction.

## 15.2 Oxidation Number

It is easy to identify species undergoing oxidation or reduction in simple molecules. However, in polyatomic molecules, it is difficult to do the same. In the example of NaCl taken earlier it was easy to identify as sodium undergoing oxidation and chlorine undergoing reduction but in the reaction involving ferrous sulphate with potassium permanganate ( $\text{KMnO}_4$ ) it is difficult. Therefore, a new term called **Oxidation number** has been introduced, **Oxidation number** is the apparent charge which an atom appears to have when each pair of electrons is counted with more electronegative atom. Oxidation number is always assigned to an atom. It is a number written with +ve or -ve sign. The number indicates the number of electrons that has been shifted from an atom towards a more electro-negative atom, in a heteronuclear covalent bond. The +ve sign for the atom shifting its electron away from itself and -ve is given to more electro -ve atom. The concept of Oxidation Number is based on the assumption that in a polyatomic covalent bonding, shared pair of electrons belongs to more electro-ve atom. Oxidation state (OS) is also used for Oxidation Number.

## 15.2.1 Rules for Assigning Oxidation Number

There are certain rules that are followed for computing the oxidation number of an atom in a molecule or ion.

1. Oxidation number is taken as zero if atoms are present in elemental form. For example,  $\text{O}_2$ , Na,  $\text{P}_4$  are elemental forms. They have oxidation number zero.
2. The oxidation number of a monatomic ion is the same as the charge present on it. For example,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cl}^-$ ,  $\text{S}^{2-}$  will have oxidation no +1, +2, +3, -1, -2 respectively.
3. The oxidation number of oxygen is -2 in almost all the compounds except (a) in



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peroxides e.g.  $\text{Na}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$  where oxidation number is  $-1$  and (b) super oxides ( $\text{KO}_2$ ) where it is  $-\frac{1}{2}$ .

- The oxidation number of H is  $+1$  when combined with non-metal and is  $-1$  when combined with metal e.g. in  $\text{HCl}$  the O.N. of H is  $+1$  but in  $\text{CaH}_2$  it is  $-1$ .
- The Oxidation Number of alkali metal is  $+1$  in its compounds.
- In a compound made up of different elements the more electro negative element will have negative oxidation number and less electro negative atoms will have positive oxidation number e.g. in  $\text{NCl}_3$ , N has  $+3$  oxidation number and Cl has  $-1$  oxidation number.
- The sum of the oxidation numbers of all the atoms in a neutral compound is zero.
- In a polyatomic ion, the sum of the oxidation numbers of all the atoms is equal to the charge on the ion. e.g. in  $\text{CO}_3^{2-}$ , the sum of oxidation Number of carbon and oxygen is  $-2$ .

Let us illustrate the above rules taking few examples. The oxidation number of S, N and Cl atoms in : (a)  $\text{H}_2\text{SO}_4$  (b)  $\text{NO}_3^-$  (c)  $\text{ClO}_4^-$  respectively will be calculated as

(a) 1. Let the oxidation number of sulphur be  $x$ .

- Since the oxidation number of O is  $-2$ . Therefore the sum of four O atoms is equal to  $-8$ .
- The oxidation number of each H is  $+1$  as bonded to a non-metal so two H atoms have total oxidation number of  $+2$ .
- $\text{H}_2\text{SO}_4$  is a neutral molecule. Therefore the sum of all the oxidation numbers is equal to zero. Thus

$$+2 + x - 8 = 0$$

$$x = +6$$

Therefore oxidation number of sulphur in  $\text{H}_2\text{SO}_4$  is  $+6$ .

(b)  $\text{NO}_3^-$  first assign  $-2$  oxidation number to each O atom. Here the sum of the oxidation number of all the atoms will equal to charge present on the ion.

$$\therefore x - 6 = -1$$

$$x = +5$$

oxidation number of N is  $+5$ .

(c) In  $\text{ClO}_4^-$   $x - 8 = -1$

$$x = +7$$

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## 15.3 Balancing Redox Reaction

The redox reaction can be balanced by any of the following methods :

- Oxidation number method.
- Ion electron method.

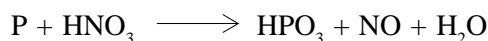
## 15.3.1 Balancing by Oxidation Number method.

The steps involved in balancing redox reactions by this method are as follows:

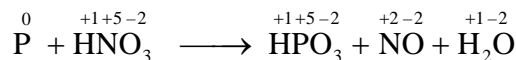
- Write the skeletal equation of reaction i.e. chemical equation without the stoichiometric coefficient.
- Write the oxidation number of each atom above its symbol in the equation.
- Identify the atoms undergoing change in oxidation number.
- Calculate the increase or decrease in oxidation number per atom for the atom undergoing a change in oxidation number. If more than one atom is involved, multiply the increase or decrease in number with the number of atoms undergoing the change to determine the total change in oxidation number.
- Equate the increase and decrease in oxidation number on the reactant side by multiplying the formulae of the oxidising and reducing agents suitably.
- Balance the equation with respect to all the atoms except hydrogen and oxygen.
- Finally balance H and O also.
- If the reaction is taking place in acidic medium balance the O atoms by adding required number of  $\text{H}_2\text{O}$  molecule on the side where O atoms are less in number. Balance the H atoms by adding  $\text{H}^+$  to the side deficient in H atoms.
- In the basic medium by add required number of negative charges by adding required number of  $\text{OH}^-$  ions to the side deficient in the magnitude of charges, then add  $\text{H}_2\text{O}$  molecules to balance  $\text{OH}^-$  ions.

For example : When Phosphorus is treated with nitric acid, nitric oxide is formed.

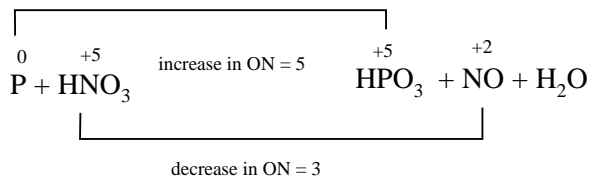
- The skeletal equation is



- Write the oxidation number of each atom on the given skeletal equation



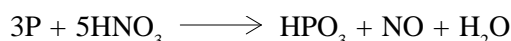
- P and N are undergoing change in Oxidation Number.



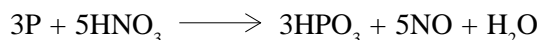


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4. Equating the increase and decrease in Oxidation Number of P and N on the reactant side



5. Balance the P and N atoms on both sides of the equation



6. O and H are already balanced in the equation.

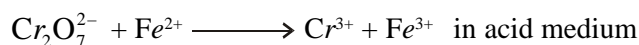
### 15.3.2 Balancing by Ion Electron Method

This method is based on the principle that electrons lost during oxidation half reaction is equal to the electrons gained in the reduction half reaction. The steps involved are

1. Write the skeleton equation.
2. Write the oxidation number of all the atoms above their symbols in the skeletal equation.
3. Find the atoms undergoing change in Oxidation Number. Thus find out the species getting oxidised and reduced respectively.
4. Split the whole (net) equation into two half reactions i.e. oxidation half reaction and reduction half reaction.
5. Balance the atoms, undergoing change in oxidation number in each half reaction.
6. Calculate the total change in oxidation number in each half reaction which is equal to total number of electron transfer.
7. Add total number of electron transfer as calculated above on the reactant side in reduction half and on the right hand side on the oxidation half reaction.
8. Balance the charges by adding  $\text{H}^+$  (for reactions in acidic medium) or  $\text{OH}^-$  (reactions basic medium) either on left or right of equation.
9. Finally balance H and O by adding  $\text{H}_2\text{O}$  on the required side of the reaction.
10. Add the two half reactions such that total number of electrons cancel out on both sides. To do so half reactions may be required to multiplied by some numbers to make the number of electrons equal on both sides.

### 15.3.3 Example of Balancing

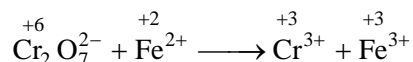
**Example 15.1 :** Balance the following skeletal reaction by ion electron method



Referring to the rules given :

#### Step I and II

Write the oxidation number of the atoms above their symbol in the skeletal equation



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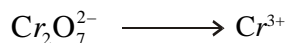


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**Step III :** Oxidation number of  $\text{Fe}^{2+}$  is increasing; therefore it is undergoing oxidation and oxidation number of Cr is decreasing so it is undergoing reduction.

**Step IV :** Split the reactions in two half reactions

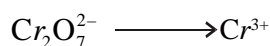
(a) Reduction half reaction



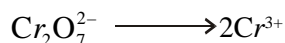
(b) Oxidation half reaction



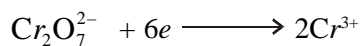
Balance the first reduction half reaction



**Step V :** Balance the atoms undergoing change in Oxidation Number.



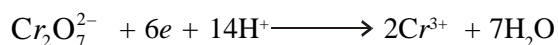
**Step VI & VII :** Write the total number of electron transfer taking place. Here each atom undergoes change in ON by 3 therefore two Cr atoms undergoes change in Oxidation Number by 6.



**Step VIII :** Balance the charge by adding  $\text{H}^+$  on the left side



**Step IX :** Balance the H and O by adding  $\text{H}_2\text{O}$  on either side

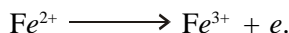


### Balancing the oxidation half reaction

According to the steps as followed for reduction half reaction

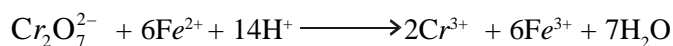
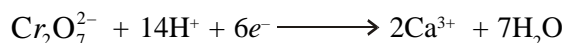


(i) Atoms are balanced on both side so we go to next step, that is number of electron transfer taking place



(iii) Balance the charge and it is balanced.

**Step X :** Add the two half reactions





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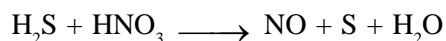
**Intext Questions 15.1**

1. Determine the Oxidation number of element in the bold letter in the following :

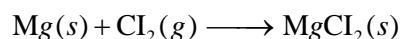
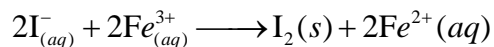


2. How does oxidation number change in oxidation and reduction?

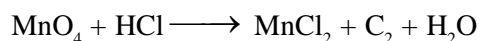
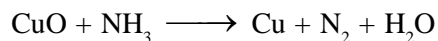
3. Mention the oxidising agent and reducing agent in the following.



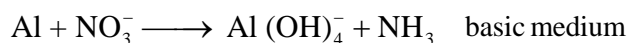
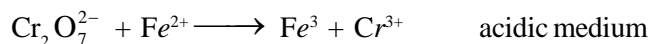
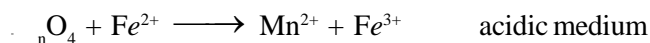
4. Write the half reaction for the following



5. Balance the equation by oxidation number method



6. Balance the following by ion eelectro half reaction method

**15.4 Electrolytic Conduction**

When electricity is passed through an aqueous solution, it may or may not conduct current. The chemical substances whose aqueous solutions conduct electricity are called electrolytes

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and those which do not conduct current are called as non-electrolytes. This phenomenon of conduction of current through a solution is called electrolytic conduction.

Electrolytic conduction takes place due to the movement of cations and anions in a solution. The electrical conductance of a solution, depends upon (a) nature of solute (b) valency of its ion, (c) the concentration in solution and (d) the temperature. In this section we will learn about various ways of expressing the conductance of electrolytes and the factors affecting them.

### 15.4.1 Conductance and Conductivity

Like solid conductors, electrolytic solutions also obey Ohm's Law. When a current of  $I$  amperes flows through a solution which offers a resistance of  $R$  ohms and a potential difference of  $V$  volts is applied, then according to ohm's law

$$V = I \cdot R$$

If the solution is taken in a conductivity cell which has two parallel electrodes  $l$  cm apart and each having an area of cross section  $A$  cm<sup>2</sup>, the resistance  $R$  of the electrolyte is found to be directly proportional to  $l$  and inversely proportional to  $A$  i.e.

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

$$\text{or} \quad R = \rho \cdot \frac{l}{A} \quad \dots(i)$$

Where  $\rho$  "rho" is a constant of proportionality and is called *specific resistance* or *resistivity*. It is characteristic of the nature of electrolyte, its concentration and temperature.

In case of solutions, it is preferred to discuss their *conductance* and *conductivity* rather than their resistance and specific resistance. **The conductance is reciprocal of resistance and the conductivity is reciprocal of specific resistance.**

Conductance is denoted by  $L$  and is measured in the unit of ohm<sup>-1</sup> which has now been named as *siemens*,  $S$ . The conductivity is denoted by  $k$  "kappa". Thus by definition

$$L = \frac{1}{R} \quad \text{and} \quad k = \frac{1}{\rho} \quad \dots(ii)$$

The units of  $k$  can be worked out from relation (i) as under :

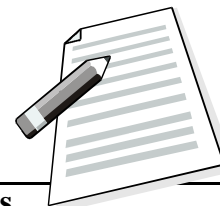
The inverse of (i) is,

$$\frac{1}{R} = \frac{1}{\rho} \cdot \frac{A}{l}$$

$$\text{or} \quad L = k \frac{A}{l}$$

$$\begin{aligned} \text{and} \quad k &= L \frac{l}{A} \\ &= S \frac{\text{cm}}{\text{cm}^2} \\ &= S \text{ cm}^{-1} \end{aligned}$$





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The conductivity (K) is expressed in  $\text{S cm}^{-1}$  or  $100 \text{ S m}^{-1}$ .

### 15.4.2 Measurement of Conductance

The conductance of an electrolyte is measured with the help of a conductivity cell. Conductivity cell is a device which has two parallel platinum electrodes coated with platinum black.

The SI unit of length is metre, hence SI unit of conductivity (K) is  $\text{Sm}^{-1}$ , but the commonly used unit is  $\text{Scm}^{-1}$ . In the

expression for conductivity,  $\frac{l}{A}$  is a constant. Here  $l$  represents the distance between the two parallel electrodes and  $A$  represents the area of cross section of the electrodes. Thus

for a given conductivity cell,  $\frac{l}{A}$  is a constant called cell constant.

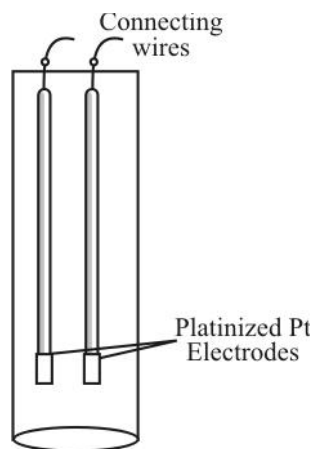


Fig. 15.1 : Conductivity Cell

$$K (\text{conductivity}) = \text{conductance} \times \text{cell constant}$$

The conductivities of some substances are given in the table.

Table 15.1 : The values of conductivity of some selected substances at 298 K

Substance	k/S $\text{cm}^{-1}$	Substance	k/S $\text{cm}^{-1}$
Pure water	$6.0 \times 10^{-8}$	Silver metal	$6.1 \times 10^5$
0.1 M HCl	$3.5 \times 10^{-2}$	Mercury metal	$1.0 \times 10^4$
0.1M NaCl	$9.2 \times 10^{-3}$	Glass	$1.0 \times 10^{-14}$
0.1M $\text{CH}_3\text{COOH}$	$4.7 \times 10^{-4}$		
0.1M $\text{NH}_4\text{OH}$	$3.4 \times 10^{-4}$		

We find from the table that the conductivities of metals are very high and that of pure water and glass very low.

### 15.4.3 Molar Conductivity

The electrolytic conductivity of a solution depends on the concentration of the electrolyte in the solution. Therefore, the conductivity of an electrolyte is normally expressed as molar conductivity.

**Molar conductivity is the conducting power of all the ions furnished by one mole of an electrolyte in a solution of specified concentration.**

It is denoted by  $\lambda_m$  and is related to K by the relation.

$$\lambda_m = \frac{1000 K}{M} \quad \text{.....(vi)}$$

Where M is the molarity of the solution. Its units are  $\text{S cm}^2 \text{ mol}^{-1}$ .



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### 15.5 Factors Affecting Conductivity

As mentioned the conductivity of an electrolyte depends upon the following aspects of the electrolyte.

- (a) **Nature of Electrolyte :** Conductivity of an electrolyte depends upon the nature of electrolyte on the following points :
  - (i) **Weak or strong electrolyte :** A weak electrolyte furnishes fewer ions therefore it has lower conductivity than a strong electrolyte of same concentration.
  - (ii) **Valency of the ions :** The ions with higher valency carry more charge and therefore they conduct more charge than the ion of lower valency. Thus higher the valency of the ion greater is the conducting power.
  - (iii) **Speed of the ion :** The ion which can move faster will carry the charge also faster and therefore has more conducting power.
- (b) **Temperature :** Conductivity of an electrolyte generally increases by 2–3 percent for each degree rise in temperature. With increase in temperature the viscosity of the solvent decreases and thus ion can move faster. In case of weak electrolyte, when the temperature is increased its degree of dissociation increases, thus conductivity increases.
- (c) **Concentration :**
  - (i) **Variation of conductivity ( $k$ ) with concentration.** When the solution is diluted its conductivity also decreases. It is because  $k$  is the conducting power of all the ions present per  $\text{cm}^3$  of the solution. When the solution is diluted the number of ions per  $\text{cm}^3$  also decreases, hence  $k$  decreases.

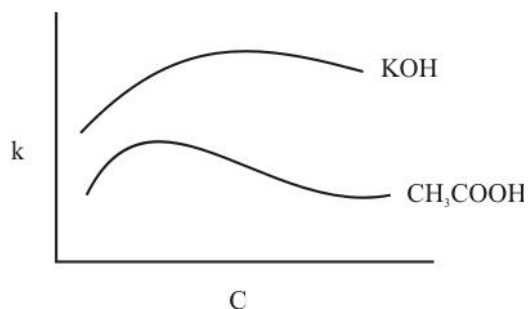


Fig. 15.2 : Variation of conductivity with concentration

- (ii) **Variation of Molar and Equivalent conductivity with concentration :** As the solution is diluted its molar conductivity increases.  $\lambda_m$  is given as

$$\lambda_m = \frac{1000k}{M}$$

where  $k$  is conductivity and  $M$  is molar concentration.



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This increase in  $\lambda_m$  is a resultant of two factors. On decreasing the concentration both  $k$  and  $M$  decreases. Of the two ( $k$ ) tries to decrease  $\lambda_m$  while the other factor ( $M$ ) tries to increase it. Since the decrease in  $M$  is much more, the net result is that  $\lambda_m$  increases. However, strong and weak electrolyte as show different type of behaviour on dilution (Fig. 15.3)

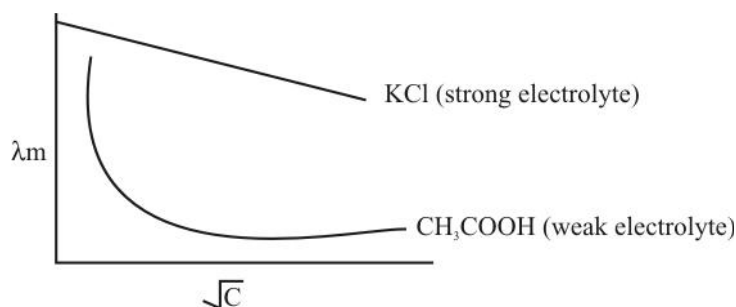


Fig. 15.3 : Variation of molar conductivity with concentration

From the Fig. 15.3 we find that the increase in molar conductivity for a strong electrolyte like KCl is very gradual on dilution and also the value is high at all concentrations. Whereas for a weak electrolyte like  $\text{CH}_3\text{COOH}$ , there is a gradual increase in  $\lambda_m$  on dilution which is followed by a sharper increase on further dilution. These observations can be explained as : since KCl is a strong electrolyte, it is fully dissociated at all concentrations. In concentrated solution, attraction between opposite ions is large and their conducting ability is less. On dilution inter-ionic forces decrease and ions can move faster leading to the increase in molar conductivity.

On the other hand, in weak electrolytes, molar conductivity is low in concentrated solution. This is due to partial dissociation (ionisation) of weak electrolytes. On diluting the solution the degree of ionisation increases, which increases the number of ions. This leads to a sharp increase in molar conductivity in weak electrolytes.

### 15.5.1 Kohlrausch's Law

Kohlrausch determined the molar conductivity at infinite dilution for a large number of strong electrolytes. On the basis of his observations he concluded that at infinite dilution, each ion makes a definite contribution to the total molar conductivity of an electrolyte. This individual contribution is called **molar ionic conductivity**. He generalised his observations as

“At infinite dilution each ion of the electrolyte makes a definite contribution towards conductivity of the electrolyte and it is independent of the presence of other ions of the electrolyte.” This is called Kohlrausch's Law of independent migration of ions.

For a salt like KCl, molar conductivity at infinite dilution can be written as

$$\lambda_m^\infty \text{ KCl} = \lambda_m^\infty \text{ K}^+ + \lambda_m^\infty \text{ Cl}^-$$

In general for a salt of formula  $\text{A}_x\text{B}_y$  the molar conductivity at infinite dilution is written as

$$\lambda_m^\infty (\text{A}_x\text{B}_y) = x \lambda_m^\infty (\text{A}^{y+}) + y \lambda_m^\infty (\text{B}^{x-})$$

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where  $\lambda_m^\infty$  indicates molar conductivity at infinite dilution. This law is used to calculate the molar conductivity at infinite dilution for weak electrolytes whose  $\lambda_m^\infty$  can not be obtained graphically.

**Example 15.2 :**  $\Lambda^0$  for NaCl, HCl and  $\text{CH}_3\text{COONa}$  are 126.0, 426.0 and 91.0  $\text{S cm}^2 \text{mol}^{-1}$  respectively. Calculate  $\Lambda^0$  for  $\text{CH}_3\text{COOH}$ .

**Solution**  $\Lambda^0 \text{CH}_3\text{COOH} = \lambda^0(\text{H}^+) + \lambda^0(\text{CH}_3\text{COO}^-)$

$$= \lambda^0(\text{H}^+) + \lambda^0(\text{Cl}^-) + \lambda^0(\text{Na}^+) + \lambda^0(\text{CH}_3\text{COO}^-) - \lambda^0(\text{Na}^+) - \lambda^0(\text{Cl}^-)$$

$$= 426.0 + 91.0 - 126.0 = 391.0 \text{ S cm}^2 \text{mol}^{-1}.$$

**Intext Question 15.2**

- How does the solution of electrolytes conduct electricity?  
.....
- Define conductivity and molar conductivity.  
.....
- Give the units of conductance and conductivity.  
.....
- List factors affecting the conductance of an electrolyte.  
.....
- Draw a graph showing variation in molar conductivity of weak and strong electrolytes.  
.....
- Write the expression for molar conductivity at infinite dilution for  $\text{Al}_2(\text{SO}_4)_3$ .  
.....

**15.6 Electro Chemical Cell**

An electrochemical cell is a device used for the interconversion of electrical and chemical energy. An electrochemical cell contains two electrodes (cathode and anode) and an electrolyte.

They are of two types; based on the nature of conversion of energies

- Electrolytic cell (Faradaic cell)
- Galvanic cell (Voltaic cell)

## 15.7 Electrolytic Cell

An electrolytic cell consists of two electrodes connected to a battery as shown in Fig 15.4.

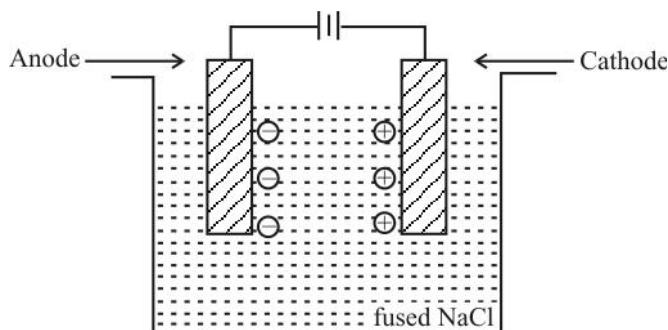


Fig. 15.4 : Electrolytic cell

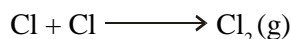
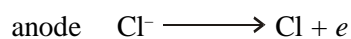
In an electrolytic cell electrical energy is converted into chemical energy. The process of decomposition of an electrolyte into its ions when an electric current is passed through it, is called electrolysis.

When electricity is passed through an electrolyte, a chemical change i.e. decomposition of the electrolyte into ions takes place at the electrode. Oxidation and reduction reactions occur in the cell.

In the electrical field  $\text{Cl}^-$  ions migrate to the +ve electrode (anode) and undergo oxidation by losing electrons.  $\text{Na}^+$  ions will go to -ve electrode (cathode) and undergo reduction.

The process can be represented as :

oxidation at



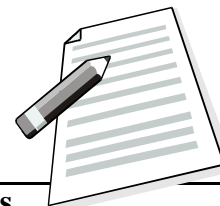
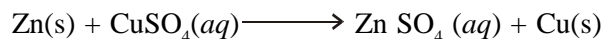
### 15.7.1 Galvanic Cell

Such cells are called voltaic cells. In such a cell chemical energy is converted into electrical energy. Dry cells, car batteries and button cells used in wrist watches are all examples of this type of cell. They are energy producing devices.

### 15.7.2 Redox Reaction and Galvanic Cell

You have already learnt that when electricity is passed through a solution, redox reaction takes place. Now we shall learn how redox reaction can be used to produce electricity.

When a Zinc rod is dipped in  $\text{CuSO}_4$  solution, a reaction starts in the solution.



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## Chemical Dynamics



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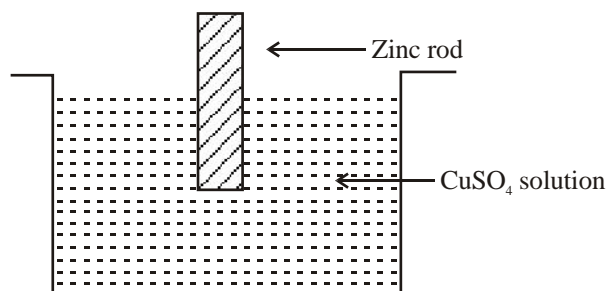
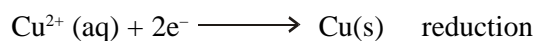
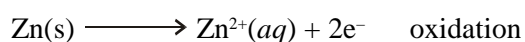


Fig. 15.5 : Redox reaction

It is an example of redox reaction. The two **half reactions** are



In this **redox reaction** the electrons given by zinc rod have been directly consumed by  $\text{Cu}^{2+}$  ion. But, if somehow we make the electrons given by Zinc rod to flow through a wire to reach  $\text{Cu}^{2+}$  ions, we shall be producing electric current. To do so, the reaction is carried out in the electrochemical cell as shown Fig. 15.6 :

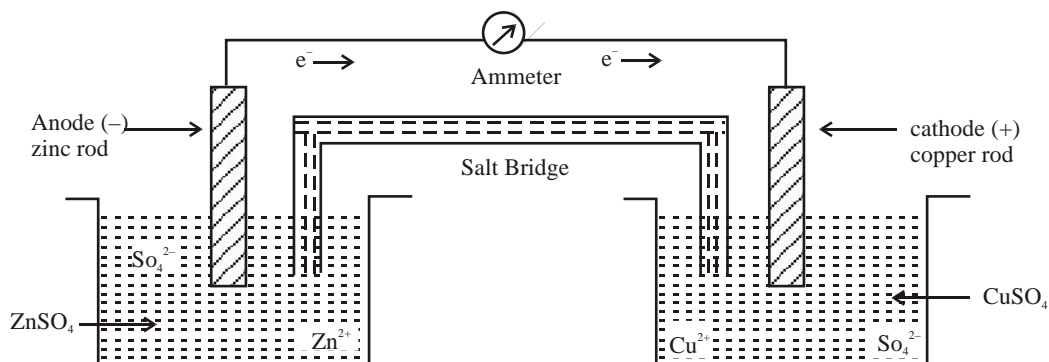
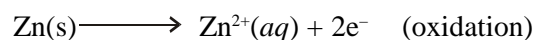


Fig. 15.6 : Daniell cell having zinc and copper electrodes

The redox reaction in the electro chemical cell has been modified Zinc rod is dipped in zinc sulphate solution in one beaker while copper rod is dipped in another beaker containing  $\text{CuSO}_4$  solution. The two solutions are connected through a **salt bridge** and the two metals are connected to an ammeter with the help of wire. We find electrons move through the wire from zinc to copper rod.

A metal dipped in its own salt solution is called as **half cell**. Zinc rod dipped in-zinc sulphate solution is oxidation half cell because oxidation takes place.



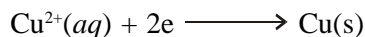
The released electrons are taken up by zinc rod and it becomes negatively charged.

Copper in copper sulphate is reduction half cell. Copper acts as cathode and reduction take place here. Copper rod becomes positively charged. Copper gains electrons and in



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this process, becomes positively charged.



Here the electrons will move from negatively charged electrode to positively charged copper electrode.

### Flow of electrons in the external circuit

The electrons released at the anode during oxidation flow through the external circuit and reach the cathode where they are taken up for reduction. Thus in a galvanic cell the electrons always flow from anode to cathode while the conventional positive current flows in the opposite direction i.e. from cathode to anode. Since the electric current always move in a closed circuit salt bridge is used to make electrical contact between the two half cells.

### 15.7.3 Salt Bridge

A salt bridge is a inverted U tube filled with a concentrated solution of an inert electrolyte like KCl or  $\text{NH}_4\text{NO}_3$  which does not take part in the cell reaction. The electrolyte is taken in the form of solution and mixed with agar-agar. The mixture is heated and filled in the U tube when hot. On cooling it sets into a jelly like mass and does not flow out, during its use. Salt bridge has two functions.

- (i) It completes the inner circuit. It acts as a contact between the two half cells without any mixing of electrolytes.
- (ii) It prevents accumulation of charges in two half cells and maintains electrical neutrality.

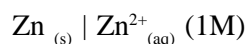
Cations and anions of the salt bridge move into two half cells and neutralise the excess charge. The anions move into oxidation half cell and neutralise the excess charge. The cations move into the reduction half cell and neutralise the charge.

In a Daniell cell a salt bridge is replaced by a porous pot, to make the cell more handy to use.

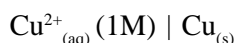
### 15.7.4 Symbolic Representation of Galvanic Cells

In the previous section the cell was a Zn-Cu cell. But any two suitable metals can be used to make the cell and everytime we do not always draw the diagrams showing the cell. It is represented in the symbolic form with the help of standard notation. The rules of notations are as follows :

1. Anode is written on the left hand side and cathode on the right hand side.
2. The metal electrode in the anode half cell is written by its symbol and this is followed by the cation (metal ion) along with its concentration in a small bracket. The metal and cations are separated by vertical line or a semicolon (:)



3. In the reduction half cell the anion along with its concentration is written first, then vertical line and then the metal



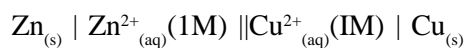
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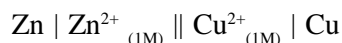
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4. A salt bridge is represented by two vertical lines.

Thus the Galvanic cell described above is written as



o r



## 15.8 Electrode Potential

Metal atoms have tendency to lose electrons and go into solution as metal ions. Electrode potential is a measure of the tendency of metal atoms to gain or loose electrons when in contact with a solution of its own ions.

When a metal strip M is immersed in a solution of its salt containing ions ( $\text{M}^{n+}$ ), one of the processes as shown in Fig. 15.7 (a) or (b) can occur.

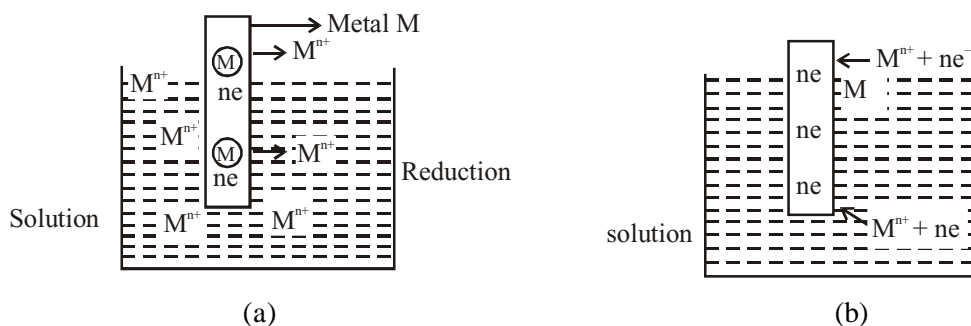
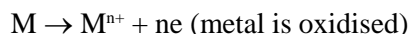


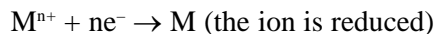
Fig. 15.7 : Metal placed in a solution of its ions

- (i) The dissolution process where atoms of metal electrode M may loose some electrons to the electrode and enter the solution as  $\text{M}^{n+}$

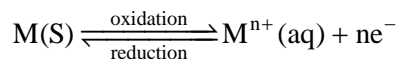


The metal electrode gets negative charge and the solution gets extra positive charge.

- (ii) The deposition process where metal cations  $\text{M}^{n+}$  from the solution may come in contact with the metal strip, gain some electrons and get converted into metal atoms M, which get deposited on the surface of metal strip. Separation of charges take place and a potential is developed called electrode potential.

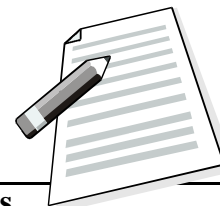


The electrode reaction reaches an equilibrium as represented below



Electrode potential is the potential developed at the interface between metal and its salt solution; when a metal is dipped in its own salt solution.





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### 15.8.1 Standard Electrode Potential

An electrode is said to be in the standard state if the concentration of the electrolyte is one molar and the temperature is 298K. Then its electrode potential is called standard electrode potential and denoted by  $E^\circ$ . If any gas is used to make the electrode then the pressure of the gas should be 1 bar.

## 15.9 Measurement of Electrode Potential

It is not possible to measure single electrode potential. It is because the reaction taking place at the electrodes is oxidation or reduction and these reactions do not take place in isolation. It can be measured with respect to a reference electrode. The electrode used as reference electrode is standard hydrogen electrode (SHE).

### 15.9.1 Standard Hydrogen Electrode

Standard Hydrogen Electrode (SHE) consists of a container, containing 1M HCl solution kept at 298K. A wire containing Platinum electrode coated with platinum black is immersed in the solution. Pure hydrogen gas is bubbled in the solution at 1 bar pressure.

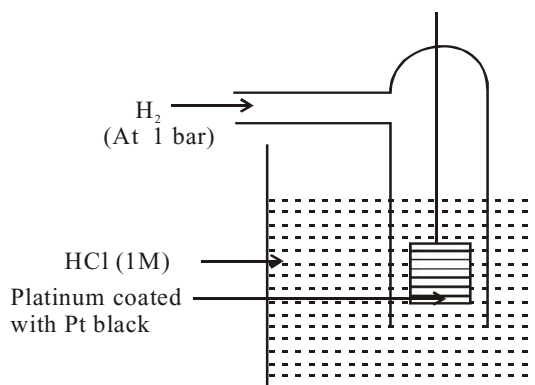
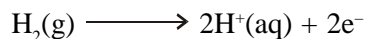


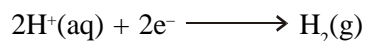
Fig. 15.8 : Standard Hydrogen electrode

The potential of SHE ( $E^\circ$ ) is taken as zero volt at all temperatures.

Standard hydrogen electrode may act as anode or cathode depending upon the nature of the other electrode. If it acts as anode, the oxidation reaction taking place is



If it acts as cathode then the reduction half reaction occurring is



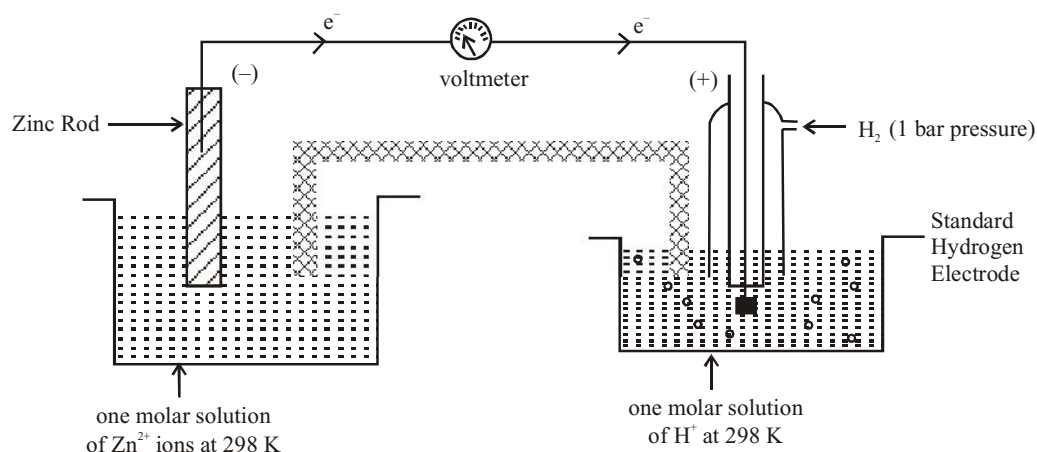
### 15.9.2 Measurement of Standard Electrode Potential

(i) **Determination of magnitude :** The standard electrode potential of an electrode can be measured by combining it with standard hydrogen electrode. To illustrate, let us take the example for the measurement of standard electrode potential of zinc electrode. A zinc strip is dipped in 1M  $\text{ZnSO}_4$  solution and it is connected to Standard Hydrogen electrode. The cell emf is found to be 0.76 V.

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**Fig. 15.9 :** Measurement of standard electrode potential of  $\text{Zn}/\text{Zn}^{2+}$  electrode

When copper electrode i.e. copper dipped in 1M  $\text{CuSO}_4$  solution is connected to standard hydrogen electrode then the cell emf is 0.34 .

(ii) **Sign of electrode potential**

The galvanic cell formed by the combination of SHE and electrode under study, the polarity of the electrode is determined with the help of a voltmeter. In case the given electrode is found to be positive electrode, its electrode potential is given the positive sign and if it is negative then it is given the negative sign. In the case of zinc connected to SHE the polarity is negative but in case of copper it is positive.

## 15.10 Electrochemical Series and its Applications

### 1510.1 Cell emf and Potential difference

The difference in potential of the two electrodes (or half cells) of a galvanic cell, when measured in the open circuit is called the cell electromotive force or cell emf. When it is measured in a closed circuit with some external load it is called potential difference.

Cell emf can be measured by using a potentiometer. It depends on the nature of electrodes, concentration of electrolyte and the temperature.

### 15.10.2 Standard cell emf

The emf of a cell has a standard value if both its half cells are in their standard states. It is denoted by  $E^\circ$  cell.

### 15.10.3 Cell emf and electrode potential

The standard cell emf is related to the standard electrode potentials of its anode and cathode.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= E^\circ_{\text{Right}} - E^\circ_{\text{left}} \end{aligned}$$

Cell emf is related to the electrode potentials of its anode and cathode

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{right}} - E_{\text{left}} \end{aligned}$$



Notes

### 15.10.4 Electrochemical Series

Standard potential of a large number of electrodes have been measured and they have been listed in the increasing order of electrode potential in a series called electro chemical series. The table 15.2 gives the standard reduction potentials of some electrodes.

**Table 15.2 : Standard Electrode Potentials and Electrochemical Series**

<i>Element</i>	<i>Electrode reaction</i>	<i>E°(V)</i>
Li	$\text{Li} + \text{e}^- \rightarrow \text{Li}$	-3.045
K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925
Cs	$\text{Cs}^+ + \text{e}^- \rightarrow \text{Cs}$	-2.923
Ba	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.906
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.866
Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.363
Al	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.662
H <sub>2</sub>	$\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.829
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.763
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.440
Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403
Pb	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.310
Co	$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.280
Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.250
Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.136
Pb	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.126
Fe	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
H <sub>2</sub>	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{SHE})$	0
Cu	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	+0.153
S	$\text{S}_4\text{O}_6^{2-} + 2\text{e}^- \rightarrow 2\text{S}_2\text{O}_3^{2-}$	+0.170
Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.337
I <sub>2</sub>	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.534
Fe	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	+0.77
Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799
Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.854
Br <sub>2</sub>	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.066
O <sub>2</sub>	$\text{O}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	+1.230
Cr	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.330
Cl <sub>2</sub>	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.359
Au	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.498
Mn	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.510
F <sub>2</sub>	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.870

## Chemical Dynamics



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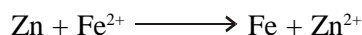
The most active metal lithium is placed at the top and the most active non metal fluorine at the bottom. Thus we find that lithium is the most powerful reducing agent and fluorine is most powerful oxidising agent.

## 15.10.5 Applications of Electrochemical Series

- (i) **It helps to predict a redox reaction.** A given ion will oxidise all the metals below it and a given metal will reduce ions of any metal placed above it in the series.

**Example :** Predict the redox reaction between zinc and iron. Given  $E^0$  of  $\text{Zn}^{2+} / \text{Zn}$  is  $-0.763$  and  $E^0$  for  $\text{Fe}^{2+} / \text{Fe}$  is  $-0.44 \text{ V}$ .

The  $E^0$  value of  $\text{Zn}^{2+}/\text{Zn}$  is lower than  $\text{Fe}^{2+}/\text{Fe}$ . It means Zn has a greater reducing power than Fe or zinc can undergo oxidation more quickly than Fe. Zinc will reduce  $\text{Fe}^{2+}$  ions and itself undergoes oxidation. The given reaction between Zn and Fe will take place as shown.

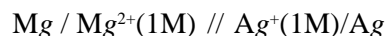


- (ii) **It helps to calculate the emf of a galvanic cell.**

$$E^0 \text{ cell} = E^0 \text{ cathode} - E^0 \text{ anode.}$$

$E^0$  cell should always be positive. If  $E^0$  cell comes as  $-ve$  it means the cell cannot work and electrodes should be interchanged.

**Example :** Predict the  $E^0$  for the cell



From the table

$$E^0 \text{ cell} = E^0 \text{ cathode} - E^0 \text{ anode}$$

$$E^0 \text{Mg}^{2+}/\text{Mg} = -2.365\text{V and}$$

$$E^0 \text{Ag}^+/\text{Ag} = 0.80\text{V}$$

$$E^0 \text{ cell} = 0.80 - (-2.365)\text{V}$$

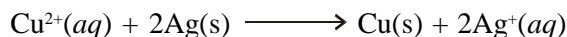
$$= 0.80 + 2.365$$

$$= 3.165 \text{ V}$$

- (iii) **It helps to predict the feasibility of a redox reaction**

The feasibility of a redox reaction can be predicted by calculating  $E^0$  cell for the redox reaction. The redox reaction is broken in two half reactions : oxidation half reaction acts as anode and reduction half acts as cathode. The positive  $E^0$  cell indicates the redox reaction is possible.

**Example 15.3 :** Predict whether the following reaction is feasible or not?

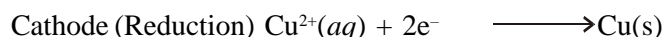
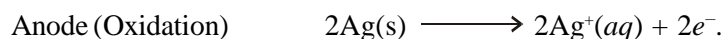


Given  $E^0 \text{Ag}^+/\text{Ag} = 0.80\text{V}$  and  $E^0 \text{Cu}^{2+}/\text{Cu} = 0.34\text{V}$

The given redox reaction can be written as two half reactions



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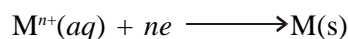
$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ &= E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Ag}^+/\text{Ag}} \\ &= 0.34 \text{ V} - 0.80 \text{ V} \\ &= -0.46 \text{ V} \end{aligned}$$

The  $-ve E^0$  value indicates that the above reaction will never take place and silver cannot displace Copper from a solution of  $\text{Cu}^{2+}$  ion. Instead the reverse reaction would be feasible.

(iv) **It helps to predict whether a metal can liberate hydrogen from acids.** Any metal which is above hydrogen in the electro chemical series can liberate hydrogen from acid since it is a better reducing agent than hydrogen. Thus metals like, Zinc, Magnesium, Calcium etc can displace hydrogen from  $\text{HCl}$  or  $\text{H}_2\text{SO}_4$  but metals like Copper, silver etc cannot displace hydrogen from acid.

### 15.11 Nernst Equation for Electrode Potential

Nernst equation relates electrode potential to the concentration of ions in the electrolyte. An electrode reaction is always written as reduction reaction. Let us take a general example for a metal M.



The Nernst equation for its electrode potentials is :

$$E = E^0 - \frac{2.303 RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{n+}]} \quad (i)$$

where

$E$  = Electrode potential

$E^0$  = Standard electrode Potential (Reduction)

$R$  = gas constant in  $\text{JK}^{-1} \text{mol}^{-1}$

$T$  = Temperature in Kelvin

$F$  = Faraday constant

$n$  = number of electrons involved in the electrode reaction

$[\text{M}^{n+}]$  = molar concentration of  $\text{M}^{n+}$  ion

$[\text{M}]$  = concentration of pure solid metal taken as unity

Therefore,

$$E = E^0 - \frac{2.303 RT}{nF} \log \frac{1}{[\text{M}^{n+}]}$$

If we put the values of  $R$ ,  $T$  and  $F$  in equation (i)

## Chemical Dynamics



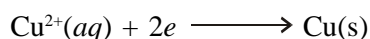
Notes

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad F = 96500 \text{ Coulomb}$$

$$T = 298 \text{ K}$$

we have 
$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad (ii)$$

For example : For copper electrode as half cell



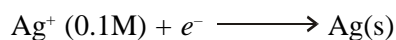
here  $n = 2$ . 
$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34\text{V}$$

$$E_{\text{Cu}^{2+}/\text{Cu}} = E_{\text{Cu}^{2+}/\text{Cu}}^0 - \frac{0.0591}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

Since  $E_{\text{Cu}^{2+}/\text{Cu}}^0$  is 0.34 V the equation becomes

$$= 0.34 - 0.0295 \log \frac{1}{[\text{Cu}^{2+}]}$$

**Example 15.4 :** Calculate the reduction potential for the following half cell at 298 K



$$E^0 = 0.80\text{V}$$

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[\text{Ag}^+]}$$

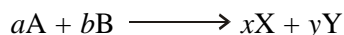
$$= 0.80 - \frac{0.0591}{1} \log \frac{1}{0.1}$$

$$= 0.80 - 0.0591 \log 10$$

$$= 0.80 - 0.0591 = 0.741\text{V}$$

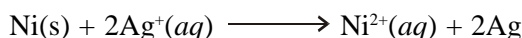
### 15.11.1 Nernst Equation for Cell emf

For a general cell reaction :



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b}$$

Thus, for the cell reaction :





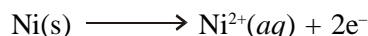
Notes

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

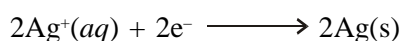
Note: Only the ions are written in the fraction as concentration of pure solid or liquid is taken as unity.

To determine the value of  $n$  the reaction is written in two half reactions.

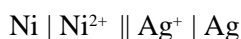
Anode reaction (oxidation)



Cathode reaction (reduction)

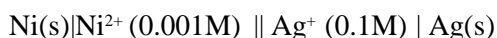


This can be represented in the form of a cell as



The value of  $n = 2$  as  $2\text{e}^{-}$  are exchange between anode and cathode

**Example 15.5 :** Calculate the EMF of the following cell at 298 K



$$E^{\circ}_{\text{Ni}^{2+} \mid \text{Ni}} = 0.25\text{V} \quad E^{\circ}_{\text{Ag}^+ \mid \text{Ag}} = 0.80\text{V}$$

From the given values first find

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= 0.80 - (-0.25) \text{ V} \\ &= 1.05\text{V} \end{aligned}$$

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \\ &= 1.05 - \frac{0.0591}{2} \log \frac{0.001}{(0.1)^2} \\ &= 1.05 - 0.0295 \log \frac{10^{-3}}{10^{-2}} \\ &= 1.05 + 0.0295 \log 10^{-1} \\ &= 1.0795 \text{ V} \end{aligned}$$

## 15.12 Cell EMF and Gibbs Energy

The maximum amount of work that a cell in its standard state can perform is given by

$$W_{\text{max}} = -n F E^{\circ}$$

## Chemical Dynamics



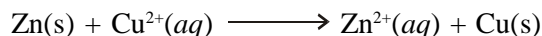
Notes

The significance of –ve sign is that the **work is done** by the cell. Since the maximum amount of useful work which a system can perform is equal to decrease in Gibbs energy thus

$$W_{max} = \Delta G^0 = -nFE^0$$

If  $\Delta G^0$  calculated is negative, then the cell reaction is spontaneous otherwise not.

**Example 15.6 :** Calculate the standard Gibb's energy  $\Delta G^0$  for the reaction occurring in Daniell cell



at 298 K. The  $E^0$  cell at this temperature is 1.1V. Is the reaction spontaneous.

For Daniell cell,  $n = 2$ .

**Solution :**

$$\Delta G^0 = -nFE^0$$

$$\Delta G^0 = -2 \times 96500 \times 1.1$$

$$= -212,300\text{J}$$

$$= -212.3\text{kJ}$$

Since  $\Delta E^0$  is –ve, the cell reaction is spontaneous



## Intext Questions 15.3

- Differentiate between electrolytic cell and galvanic cell.  
.....
- What is a salt bridge? What is the role of the salt bridge?  
.....
- What is electrochemical series? List any two applications of the series.  
.....
- With reference to the electrochemical series arrange the following metals in the order in which they displace each other from their salt solutions.  
Al, Cu, Ge, Mg, Zn, Ag  
.....



## What You Have Learnt

- Oxidation is a process in which electrons are lost by an atom or ion.
- Reduction is a process in which electrons are gained by an atom or ion.
- Atoms or ions undergoing oxidation are reducing agents and atoms or ions undergoing reduction are oxidising agents.





Notes

- Oxidation number is the state of oxidation of an element in a compound, which is calculated by a set of rules. It is based on the concept that electrons in a covalent bond belong to the more electro negative element.
- Oxidation number of an atom in elemental form is zero. Otherwise the number is always written with positive or negative sign.
- A substance, if in its molten state or aqueous solution conducts current is called electrolyte and if it does not conduct electric current then it is called non-electrolyte.
- Ions carry charge in an electrolyte from one point to other. The conduction of electricity follows Ohm's law.
- Reciprocal of resistance and resistivity are called conductance and conductivity respectively.
- On dilution of a solution, its conductivity decreases while molar conductivity increases.
- Electrolysis is a process in which electrical energy is used to decompose an electrolyte into its ions and it is done in an electrolytic cell
- Electrochemical cell or Galvanic cell produce electricity due to oxidation and reduction reactions occurring in their half cells. Oxidation occurs at the anode (negative electrode) and reduction at the cathode (positive electrode).
- A galvanic cell can be written in symbolic form as Anode |Electrolyte| |Electrolyte| Cathode.
- The emf of a cell is the potential difference between two electrodes in the open circuit.
- When a metal is dipped in its own salt solution then the potential of metal with respect to solution is called electrode potential. This potential is measured with respect to a reference electrode called Standard Hydrogen electrode.
- Electrochemical series is the arrangement of electrodes in the order of their increasing electrode potential.
- The cell emf is related to the electrode potential (reduction)
 
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$
- The Nernst equation is
 
$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{Red}]}{[\text{Oxi}]}$$
- The standard Gibbs energy of the cell reaction  $\Delta G^0$  is related to the standard cell emf as  $\Delta G^0 = -nFE^0$ .



## Terminal Exercise

1. Calculate the Oxidation number of the elements written in bold letters

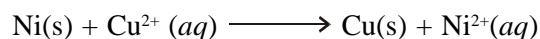


Chemical Dynamics



Notes

2. Balance the following reactions by oxidation number method
  - (a)  $\text{Fe}_2\text{O}_3 + \text{C} \longrightarrow \text{Fe} + \text{CO}$
  - (b)  $\text{C}_6\text{H}_6 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
3. Balance the following reactions by ion-electron method:
  - (i)  $\text{Zn} + \text{HNO}_3 \longrightarrow \text{Zn}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$
  - (ii)  $\text{ClO}_3^- + \text{Mn}^{2+} \longrightarrow \text{MnO}_2 + \text{Cl}^-$  in acidic medium
  - (iii)  $\text{Fe}(\text{OH})_2 + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}(\text{OH})_3 + \text{H}_2\text{O}$  in basic medium
4. Define the following and give its units:
  - (i) Conductivity
  - (ii) Molar conductivity
5. Draw a graph showing the variation in molar conductivity in a weak and a strong electrolytes with concentration.
6. Explain why the molar conductivity of an electrolyte increases with dilution while conductivity decreases on dilution.
7. The measured resistance of a conductance cell containing  $7.5 \times 10^{-3}\text{M}$  solution of KCl at  $25^\circ\text{C}$  was 1005 ohms. Calculate (a) Conductivity (b) Molar conductivity of the solution. Given the cell constant  $1.25 \text{ cm}^{-1}$ .
8. The conductivity of 0.05M solution of an electrolyte at 298 K is  $0.0025 \text{ cm}^{-1}$ . Calculate the molar conductivity.
9. Explain the term standard electrode potential. How is it determined experimentally.
10. Draw the diagram of the cell whose cell reaction is
 
$$\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$$
11. For the cell
 
$$\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Zn}^{2+} \mid \text{Zn}$$
  - (i) Draw the cell diagram
  - (ii) Identify anode and cathode
  - (iii) Write cell reaction
  - (iv) Write Nernst equation for the cell
  - (v) Calculate  $E^0$  use the data given the table 15.2
12. What are the functions of a salt bridge?
13. Using electro chemical series predict whether the following reaction is feasible or not



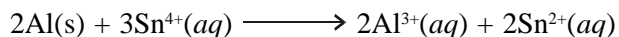


Notes

14. Explain with the help of electro-chemical series whether any reaction will take place when

- (i) Steam is passed over hot Cu.
- (ii) Tin is dipped in hydrochloric acid

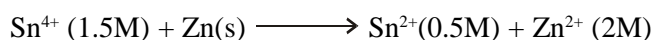
15. Calculate  $\Delta G^0$  for the reaction



16. Calculate emf of the cell



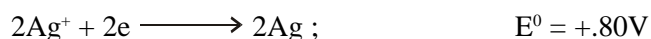
17. Calculate emf of the given cell reaction at 298k



18. The blue colour of  $\text{CuSO}_4$  is discharged when a rod of zinc is dipped in it? Explain.

19. Why oxidation cannot occur without reduction.

20. Knowing that



reason out whether 1M silver nitrate solution can be stored in copper vessel or 1M copper sulphate can be stored in silver vessel.



## Answers Intext Question

### 15.1

#### Oxidation Number

1.  $-4, -3, +3, +2, +7, +5, 0, +5$

2. In oxidation O.N. increases

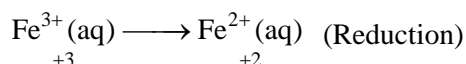
In reduction O.N. decreases

3. Oxidising agent  $\text{HNO}_3$

reducing agent  $\text{H}_2\text{S}$

4.  $\text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{s})$

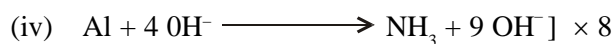
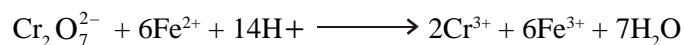
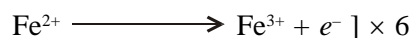
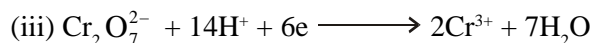
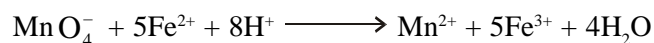
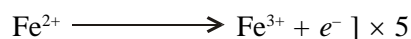
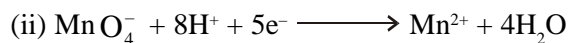
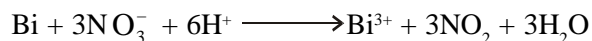
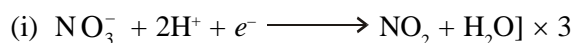
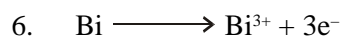
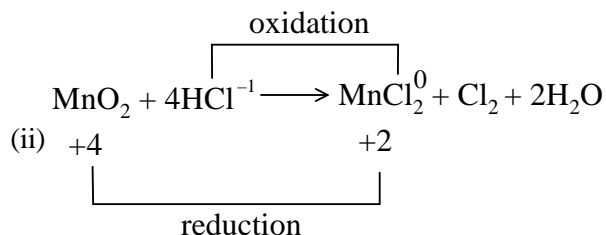
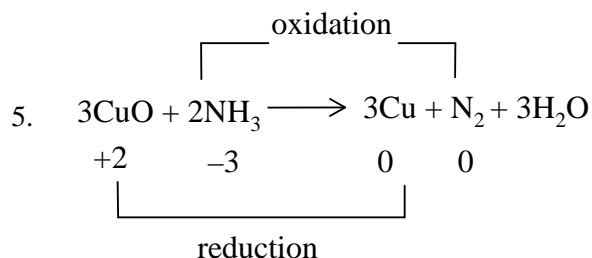
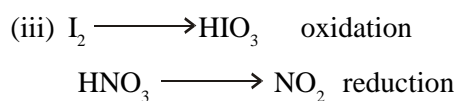
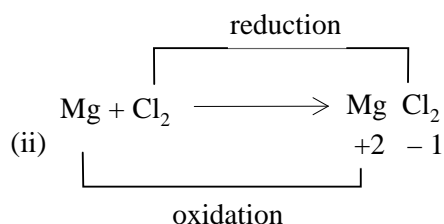
(i) oxidation



Chemical Dynamics

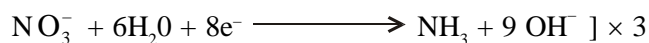


Notes





Notes

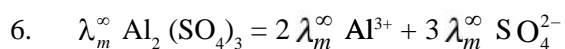


## 15.2

1. Electrolytes give ions in the solution and these ions conduct electricity by moving to their respective electrodes i.e. cations towards cathode and anions towards anode.
2. Specific conductance is the conductance of a solution taken in a cell in which two electrodes are 1cm apart and surface area of each one of them is 1cm<sup>2</sup>.

Equivalent conductance is the conductance of all the ions furnished by an equivalent of the electrolyte in a solution of given concentration.

3. Conductance S; specific conductance Scm<sup>-1</sup>
4. Nature of electrolyte (strong or weak), valency of its ions, speed of ions, concentration and temperature.
5. See Fig. 15.2.



## 15.3

1. In electrolytic cell electrical energy is used for carrying out redox reaction while in an electrochemical cell a redox reaction is used for producing electrical energy.
2. See sec. 15.6.2
3. See sec. 15.8
4. Mg > Al > Zn > Fe > Cu > Ag.