



Notes

13

ELECTROCHEMISTRY

Electrochemistry 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.



OBJECTIVES

After reading this lesson you will be able to:

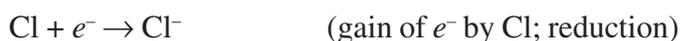
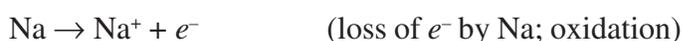
- understand oxidation and reduction in terms of electron transfer concept;
- calculate oxidation number (ON) of an atom in a molecule or ion;
- balance the chemical equation for redox reaction;
- explain electrolytic conduction, conductance and molar conductivity;
- describe the effect of dilution on conductivity and molar conductivity of an electrolyte;
- differentiate between electrolytic and Galvanic cell;
- state Faraday's laws of electrolysis;
- predict and justify the products of electrolysis of some common electrolytes;
- 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.



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13.1 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.

13.2 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 (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.

13.2.1 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.

- Oxidation number is taken as zero if atoms are present in elemental form. For example, O_2 , Na, P_4 are elemental forms. They have oxidation number zero.
- The oxidation number of a monatomic ion is the same as the charge present on it. For example, Na^+ , Mg^{2+} , Al^{3+} , Cl^- , S^{2-} will have oxidation no +1, +2, +3, -1, -2 respectively.
- The oxidation number of oxygen is -2 in almost all the compounds except (a) in peroxides e.g. Na_2O_2 , H_2O_2 where oxidation number is -1 and (b) super oxides (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 HCl the O.N. of H is +1 but in 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 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 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) H_2SO_4 (b) NO_3^- (c) ClO_4^- respectively will be calculated as

- (a)
- 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.
 - H_2SO_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 H_2SO_4 is +6.



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(b) 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 ClO_4^- $x - 8 = -1$

$$x = +7$$

13.3 BALANCING REDOX REACTION

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

- (a) Oxidation number method.
- (b) Ion electron method.

13.3.1 Balancing by Oxidation Number method

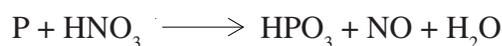
The steps involved in balancing redox reactions by this method are as follows:

1. Write the skeletal equation of reaction i.e. chemical equation without the stoichiometric coefficient.
2. Write the oxidation number of each atom above its symbol in the equation.
3. Identify the atoms undergoing change in oxidation number.
4. 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.
5. Equate the increase and decrease in oxidation number on the reactant side by multiplying the formulae of the oxidising and reducing agents suitably.
6. Balance the equation with respect to all the atoms except hydrogen and oxygen.
7. Finally balance H and O also.
8. If the reaction is taking place in acidic medium balance the O atoms by adding required number of H_2O molecule on the side where O atoms are less in number. Balance the H atoms by adding H^+ to the side deficient in H atoms.

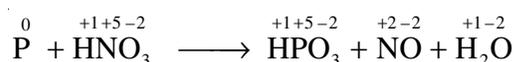
9. In the basic medium by add required number of negative charges by adding required number of OH^- ions to the side deficient in the magnitude of charges, then add H_2O molecules to balance OH^- ions.

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

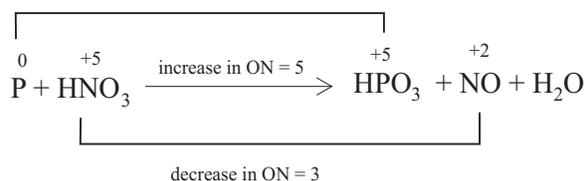
1. The skeletal equation is



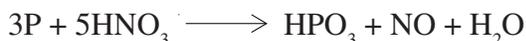
2. Write the oxidation number of each atom on the given skeletal equation



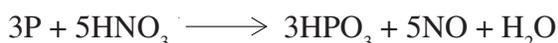
3. P and N are undergoing change in Oxidation Number.



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.

13.3.2 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.



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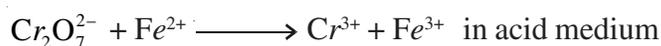


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- Balance the atoms, undergoing change in oxidation number in each half reaction.
- Calculate the total change in oxidation number in each half reaction which is equal to total number of electron transfer.
- Add total number of electron transfer as calculated above on the reactant side in reduction half and on the right hand side on the oxidation half reaction.
- Balance the charges by adding H^+ (for reactions in acidic medium) or OH^- (reactions basic medium) either on left or right of equation.
- Finally balance H and O by adding H_2O on the required side of the reaction.
- 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.

13.3.3 Example of Balancing

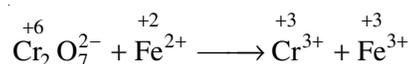
Example 13.1 : Balance the following skeletal reaction by ion electron method



Referring to the rules given :

Step I and II

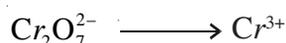
Write the oxidation number of the atoms above their symbol in the skeletal equation



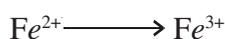
Step III : Oxidation number of Fe^{2+} is increasing; therefore it is undergoing oxidation and oxidation number of Cr is decreasing so it is undergoing reduction.

Step IV : Split the reactions in two half reactions

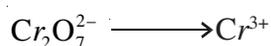
(a) Reduction half reaction



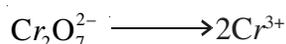
(b) Oxidation half reaction



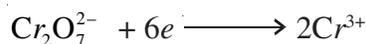
Balance the first reduction half reaction



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



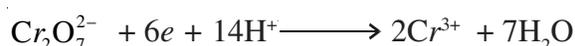
Step VI & VII : Write the total number of electron transfer taking place. Here each atom undergoes change in ON by 3 therefore two Cr atoms undergoes change in Oxidation Number by 6.



Step VIII : Balance the charge by adding H^+ on the left side



Step IX : Balance the H and O by adding H_2O on either side

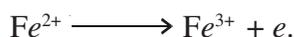


Balancing the oxidation half reaction

According to the steps as followed for reduction half reaction

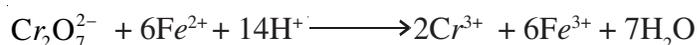
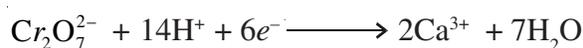
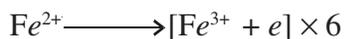


- (i) Atoms are balanced on both side so we go to next step, that is number of electron transfer taking place



- (ii) Balance the charge and it is balanced.

Step X : Add the two half reactions

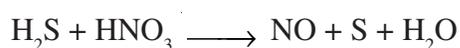


INTEXT QUESTIONS 13.1

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.

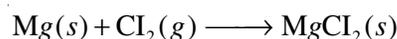
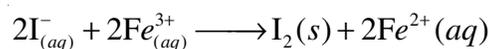


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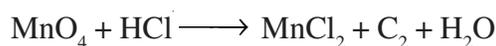
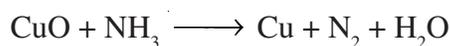


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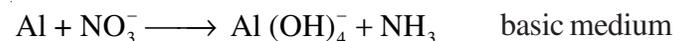
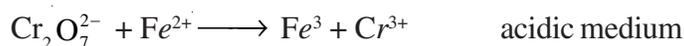
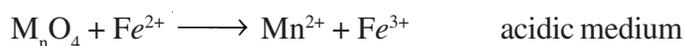
4. Write the half reaction for the following



5. Balance the equation by oxidation number method



6. Balance the following by ion electro half reaction method



13.4 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 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.

13.4.1 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 cm², the resistance R of the electrolyte is found to be directly proportional to l and inversely proportional to A i.e.

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

or

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

Where ρ “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⁻¹ 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,

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

or

$$L = k \frac{A}{l}$$

and

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

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

13.4.2 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.



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

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

The conductivities of some substances are given in the table.

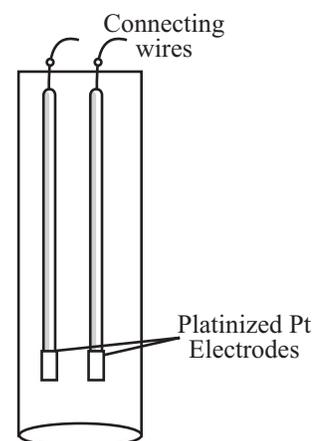


Fig. 13.1 : Conductivity Cell

Table 13.1 : The values of conductivity of some selected substances at 298 K

Substance	k/S cm^{-1}	Substance	k/S cm^{-1}
Pure water	6.0×10^{-8}	Silver metal	6.1×10^5
0.1 M HCl	3.5×10^{-2}	Mercury metal	1.0×10^4
0.1M NaCl	9.2×10^{-3}	Glass	1.0×10^{-14}
0.1M CH_3COOH	4.7×10^{-4}		
0.1M NH_4OH	3.4×10^{-4}		

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

13.4.3 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 λ_m and is related to K by the relation.

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

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

13.5 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 :
- Weak or strong electrolyte :** A weak electrolyte furnishes fewer ions therefore it has lower conductivity than a strong electrolyte of same concentration.
 - 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.
 - 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 :**
- 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 cm^3 of the solution. When the solution is diluted the number of ions per cm^3 also decreases, hence k decreases.

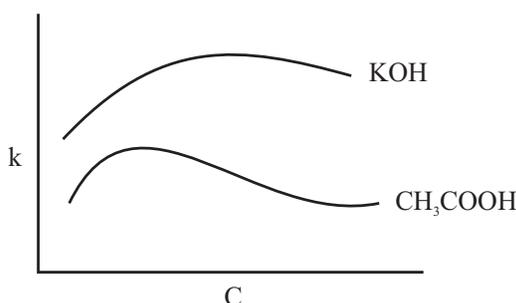


Fig. 13.2 : Variation of conductivity with concentration

- Variation of Molar and Equivalent conductivity with concentration:** As the solution is diluted its molar conductivity increases. λ_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 λ_m is a resultant of two factors. On decreasing the concentration both k and M decreases. Of the two (k) tries to decrease λ_m while the other factor (M) tries to increase it. Since the decrease in M is much more, the net result is that λ_m increases. However, strong and weak electrolyte as show different type of behaviour on dilution (Fig. 13.3)

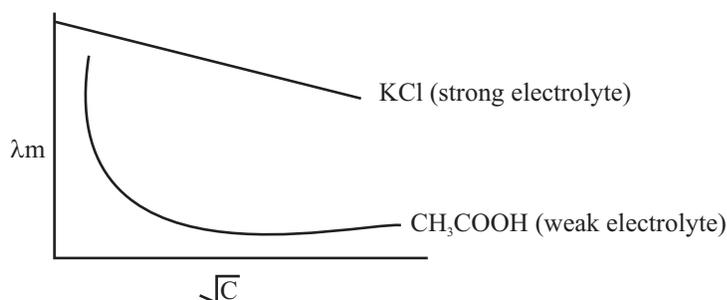


Fig. 13.3 : Variation of molar conductivity with concentration

From the Fig. 13.3 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 CH_3COOH , there is a gradual increase in λ_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.

13.5.1 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 A_xB_y the molar conductivity at infinite dilution is written as

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

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

Example 13.2 : Λ^0 for NaCl, HCl and CH_3COONa are 126.0, 426.0 and 91.0 $\text{S cm}^2 \text{mol}^{-1}$ respectively. Calculate Λ^0 for CH_3COOH .

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 13.2

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

13.6 ELECTRO CHEMICAL CELLS

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.

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

- (a) Electrolytic cell (Faradaic cell)

In electrochemical cells, a battery is used to carry out redox reactions on the electrodes of the cell. Thus, these cells convert electrical energy into chemical energy.



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(b) Galvanic cell (Voltaic cell)

In galvanic cells an emf is developed as a result of redox reaction occurring on the electrodes. These cells convert chemical energy into electrical energy.

13.7 ELECTROLYTIC CELLS OR FARADAY CELLS

An electrolytic cell consists of two electrodes connected to a battery as shown in Fig 13.4.

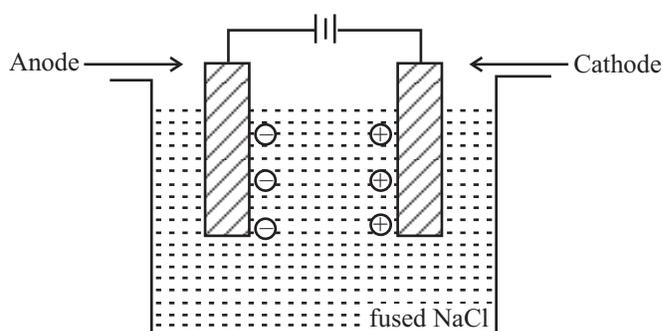


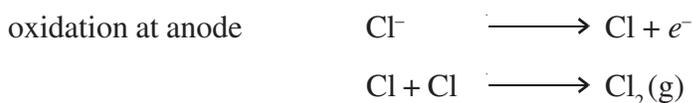
Fig. 13.4 : Electrolytic cell

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 Cl^- ions migrate to the +ve electrode (anode) and undergo oxidation by losing electrons. Na^+ ions will go to -ve electrode (cathode) and undergo reduction.

The process can be represented as :



13.7.1 Faraday's Laws of Electrolysis

Michael Faraday studied the quantitative aspects of electrolysis and expressed the results of his study in the form of the following two laws which are known as the Faraday's laws of electrolysis.

(I) Faraday's First Law of Electrolysis

It states that the mass of a substance liberated during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte taken as a solution or as melt.

Mathematically, if w is the mass of a substance liberated or discharged on passing Q coulomb of electricity

$$w \propto Q$$

and

$$w = zQ \quad (1)$$

where z , the constant of proportionality is called **electrochemical equivalent** of the substance

The quantity of electricity passed, Q , is related to the strength of the current passed in amperes I , and the time in seconds, t .

$$Q = I.t$$

\therefore

$$w = zIt \quad (2)$$

Electrochemical equivalent, z , of a substance is its mass liberated or deposited on passing 1 coulomb ($Q = 1$) charge or one ampere ($I = 1$) current for one second ($t = 1$).

(II) Faraday's Second Law of Electrolysis

This law relates the masses of different substances liberated or discharged by passing the same amount of electricity. It states that when the same quantity of electricity is passed through different electrolytes (taken in different electrolytic cells which are connected in series) the masses of different substances liberated are proportional to their chemical equivalent masses. Equivalent mass of any substance undergoing a redox reaction (oxidation or reduction) is related to its molar mass as.

$$\text{Equivalent mass} = \frac{\text{Molar mass}}{\text{Number of electrons lost or gained}}$$

Let w_A and w_B be the masses of two substances liberated in two electrolytic cells connected in series, then:

$$\frac{w_A}{w_B} = \frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}}$$



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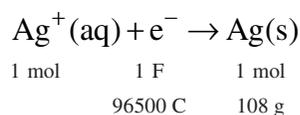


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Example 13.3: What is the mass of silver deposited when 500 coulomb electricity is passed through a solution of AgNO_3 ? (Atomic mass of $\text{Ag} = 108 \text{ u}$)

Solution:

Silver is deposited on cathode according to the reaction



Thus, 1 mole of electrons (1 Faraday) or 96500 coulombs of electricity are required to produce 108 g of silver

96500 C produce 108 g of Ag

500 C would produce $\frac{108 \times 500}{96500} = 0.56 \text{ g}$ of Ag

Example 13.4: On passing electric current for some time, it was found that 32.4 g Ag had deposited on cathode in a cell filled with AgNO_3 . How much would a copper cathode of another electrolytic cell containing CuSO_4 solution weigh after the electrolysis if it was connected in series to the AgNO_3 cell? The mass of the copper cathode before electrolysis was 27.33 g, Equivalent masses:

$$\text{Ag} = 108 \text{ g}; \text{Cu} = 31.75 \text{ g}$$

Solution:

According to the Faraday's second law of electrolysis

$$\frac{\text{Mass of copper deposited}}{\text{Mass of silver deposited}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

$$\frac{\text{Mass of copper deposited}}{32.4 \text{ g}} = \frac{31.75 \text{ g}}{108 \text{ g}}$$

$$\text{Mass of copper deposited} = \frac{31.75 \text{ g} \times 32.4 \text{ g}}{108 \text{ g}} = 9.53 \text{ g}$$

Mass of copper cathode before electrolysis = 27.33g

$$\begin{aligned} \text{Mass of copper cathode after electrolysis} &= 27.33 + 9.53 \\ &= 36.86 \text{ g} \end{aligned}$$

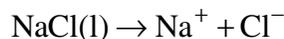
13.7.2 Products of Electrolysis

During electrolysis, cations are reduced at cathode and anions are oxidized at anode and a chemical reaction occurs in a non-spontaneous direction. The minimum potential required for any electrode process to occur is called its **discharge potential** or **decomposition potential**. Discharge potential is *equal to* the electrode potential for cathodic (*reduction*) process and *equal in magnitude but opposite in sign* to the electrode potential for anodic (*oxidation*) process. At any electrode that process (oxidation or reduction) would occur which is the easiest. The reduction of that ion would occur which has highest reduction potential and the oxidation of that ion would occur which has the smallest reduction potential in highest oxidation potential.

In many cases, the actual discharge potential exceeds the expected value. The difference between the two is known as **over potential**. Over potential is commonly observed when gaseous products are formed and depends upon the nature of cathode. Over potential for the discharge of H₂ gas is zero on a platinum cathode but it is 1.5 V on mercury cathode. Due to over potential the process which occur may not be the one which otherwise is the easiest. Let us take some, examples now.

1. Electrolysis of molten NaCl (Pt electrodes).

Molten NaCl furnishes its own cations and anions

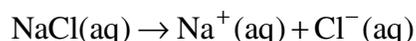


So only one process is possible at anode and cathode



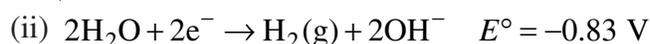
2. Electrolysis of aqueous NaCl (Pt electrodes)

Dissolved NaCl ionizes in its solution as



At Cathode

At cathode it is not only Na⁺ ions that can be reduced, but H₂O also can be reduced. The two possible reduction processes are:



Out of these, the reduction potential of water is much greater than that of Na⁺. Therefore only H₂ gas is evolved at cathode. (However, if **mercury cathode**



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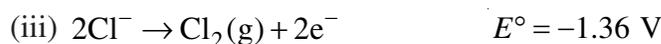


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is used, due to large over potential of discharge of H_2 , Na^+ ions are reduced and Na is produced which reacts with water to produce NaOH and H_2 . It is used for manufacture of NaOH)

At anode

At anode, Cl^- ions and H_2O both can get oxidized:



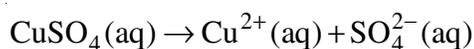
Oxidation potential of water is slightly greater than that of Cl^- so its oxidation should be easier. But due to *over potential* for discharge of O_2 , it becomes more difficult and Cl_2 gas is evolved at anode. Thus the electrolysis of aqueous NaCl occurs as:



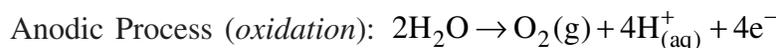
H_2 is evolved at cathode and Cl_2 at anode.

3. Electrolysis of aqueous CuSO_4 (Pt electrodes)

CuSO_4 ionizes in its aqueous solution as



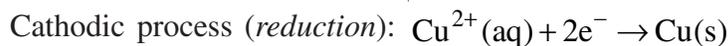
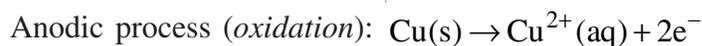
At cathode, copper is deposited because reduction of Cu^{2+} is easier than that of water and at anode O_2 is evolved as oxidation of water is easier than that of SO_4^{2-} ions.



Thus copper is discharged at cathode and $\text{O}_2(\text{g})$ at anode.

4. Electrolysis of aqueous CuSO_4 (Cu electrodes)

When copper electrodes are used, oxidation of Cu (from electrode) is easier than oxidation of H_2O or SO_4^{2-} ions. However at cathode, reduction of Cu^{2+} ions occurs as the reduction of water is more difficult even on copper electrode



This process is used for electrolytic refining of copper in its metallurgy.

13.8 GALVANIC CELLS OR 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.

13.8.1 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 CuSO_4 solution, a reaction starts in the solution.

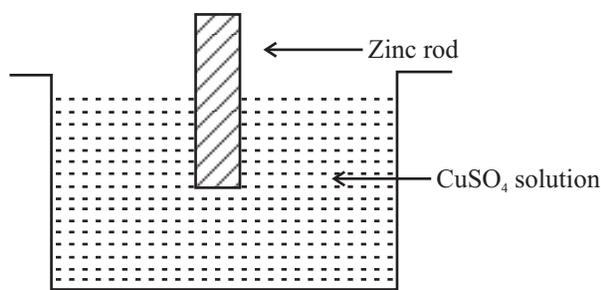
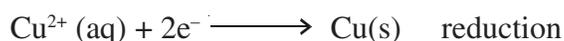
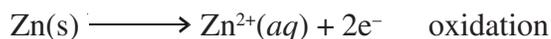


Fig. 13.5 : Redox reaction

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 Cu^{2+} ion. But, if somehow we make the electrons given by Zinc rod to flow through a wire to reach Cu^{2+} ions, we shall be producing electric current. To do so, the reaction is carried out in the electrochemical cell as shown Fig. 13.6 :

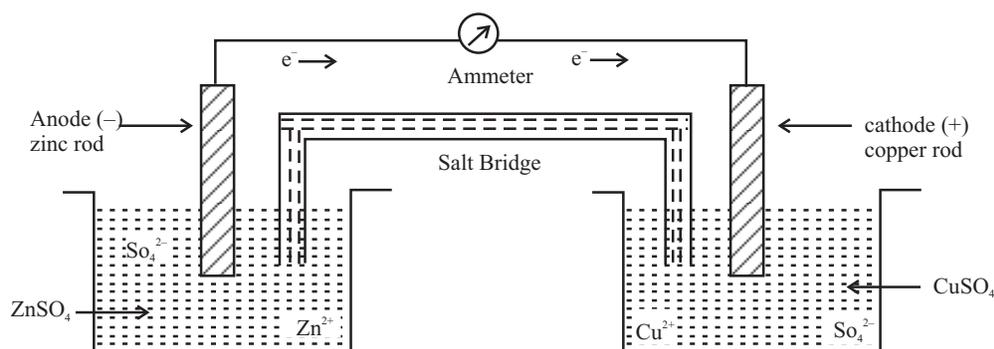


Fig. 13.6 : Daniell cell having zinc and copper electrodes



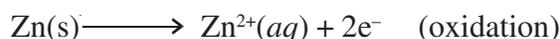
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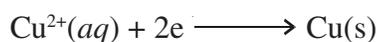
The redox reaction in the electro chemical cell has been modified. Zinc rod is dipped in zinc sulphate solution in one beaker while copper rod is dipped in another beaker containing CuSO_4 solution. The two solutions are connected through a **salt bridge** and the two metals are connected to an ammeter 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 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.

13.8.2 Salt Bridge

A salt bridge is a inverted U tube filled with a concentrated solution of an inert electrolyte like KCl or NH_4NO_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.

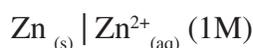
Cations and anions of the salt bridge move into two half cells and neutralise the excess charge. The anions move into oxidation half cell and neutralise the excess charge. The cations move into the reduction half cell and neutralise the charge.

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

13.8.3 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

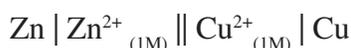


4. A salt bridge is represented by two vertical lines.

Thus the Galvanic cell described above is written as



or



13.9 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 lose 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 (M^{n+}), one of the processes as shown in Fig. 13.7 (a) or (b) can occur.

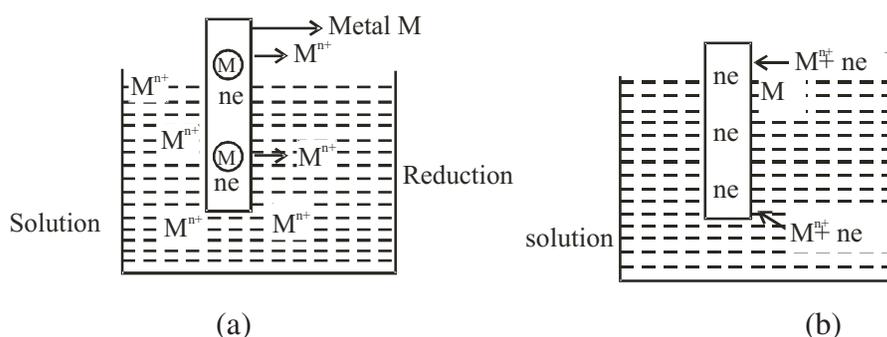


Fig. 13.7 : Metal placed in a solution of its ions

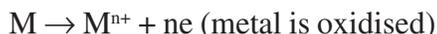


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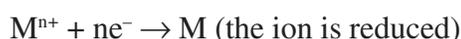
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- (i) The dissolution process where atoms of metal electrode M may lose some electrons to the electrode and enter the solution as M^{n+}

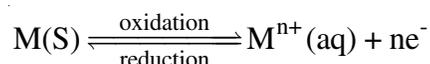


The metal electrode gets negative charge and the solution gets extra positive charge.

- (ii) The deposition process where metal cations 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.

13.9.1 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° . If any gas is used to make the electrode then the pressure of the gas should be 1 bar.

13.10 MEASUREMENT OF ELECTRODE POTENTIAL

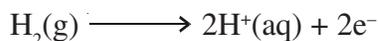
It is not possible to measure single electrode potential. It is because the reaction taking place at the electrodes is oxidation or reduction and these reactions do not take place in isolation. It can be measured with respect to a reference electrode. The electrode used as reference electrode is standard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

13.10.1 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 1bar pressure.

The potential of SHE (E°) 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

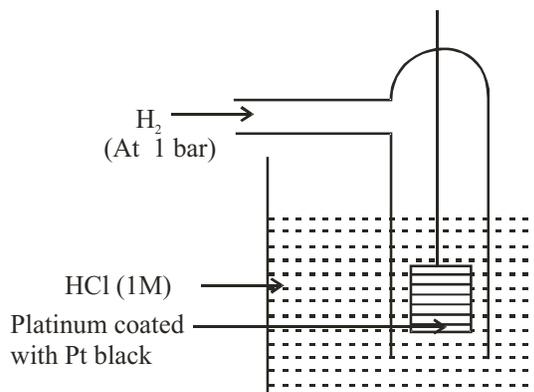
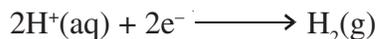


Fig. 13.8 : Standard Hydrogen electrode

13.10.2 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 ZnSO_4 solution and it is connected to Standard Hydrogen electrode. The cell emf is found to be 0.76 V.

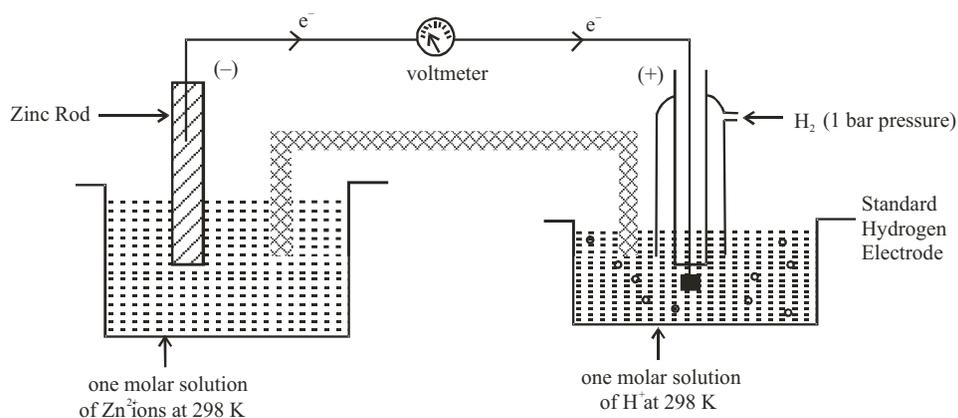


Fig. 13.9 : Measurement of standard electrode potential of Zn/Zn^{2+} electrode

When copper electrode i.e. copper dipped in 1M CuSO_4 solution is connected to standard hydrogen electrode then the cell emf is 0.34 .



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(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.

13.11 ELECTROCHEMICAL SERIES AND ITS APPLICATIONS

13.11.1 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.

13.11.2 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° cell.

13.11.3 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

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

13.11.4 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 13.2 gives the standard reduction potentials of some electrodes.

Table 13.2 : Standard Electrode Potentials and Electrochemical Series

Element	Electrode reaction	$E^\circ(V)$
Li	$\text{Li} + e^- \rightarrow \text{Li}$	- 3.045
K	$\text{K}^+ + e^- \rightarrow \text{K}$	- 2.925
Cs	$\text{Cs}^+ + e^- \rightarrow \text{Cs}$	- 2.923
Ba	$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	- 2.906
Ca	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	- 2.866
Na	$\text{Na}^+ + e^- \rightarrow \text{Na}$	- 2.714
Mg	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	- 2.363
Al	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	- 1.662
H_2	$\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	- 0.829
Zn	$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	- 0.763
Fe	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	- 0.440
Cd	$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	- 0.403
Pb	$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	- 0.310
Co	$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	- 0.280
Ni	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	- 0.250
Sn	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	- 0.136
Pb	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	- 0.126
Fe	$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$	- 0.036
H_2	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{SHE})$	0
Cu	$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$	+ 0.153
S	$\text{S}_4\text{O}_6^{2-} + 2e^- \rightarrow 2\text{S}_2\text{O}_3^{2-}$	+ 0.170
Cu	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+ 0.337
I_2	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+ 0.534
Fe	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+ 0.77
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+ 0.799
Hg	$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$	+ 0.854
Br_2	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+ 1.066
O_2	$\text{O}_2 + 4\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$	+ 1.230
Cr	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+ 1.330
Cl_2	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+ 1.359
Au	$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+ 1.498
Mn	$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+ 1.510
F_2	$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+ 2.870

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.

13.11.5 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.



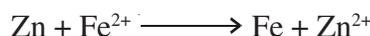
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Example 13.5 : Predict the redox reaction between zinc and iron. Given E^0 of Zn^{2+}/Zn is -0.763 and E^0 for Fe^{2+}/Fe is -0.44 V.

The E^0 value of Zn^{2+}/Zn is lower than Fe^{2+}/Fe . It means Zn has a greater reducing power than Fe or zinc can undergo oxidation more quickly than Fe. Zinc will reduce 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

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

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

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

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

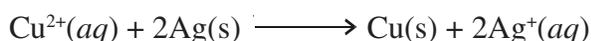
$$= 0.80 + 2.365$$

$$= 3.165 \text{ V}$$

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

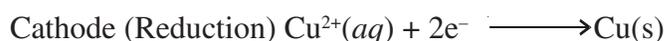
The feasibility of a redox reaction can be predicted by calculating E^0 cell for the redox reaction. The redox reaction is broken in two half reactions : oxidation half reaction acts as anode and reduction half acts as cathode. The positive E^0 cell indicates the redox reaction is possible.

Example 13.3 : Predict whether the following reaction is feasible or not?



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

The given redox reaction can be written as two half reactions



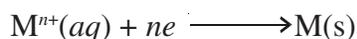
$$\begin{aligned}
 E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\
 &= E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Ag}^{+}/\text{Ag}} \\
 &= 0.34 \text{ V} - 0.80 \text{ V} \\
 &= -0.46 \text{ V}
 \end{aligned}$$

The $-ve$ E° value indicates that the above reaction will never take place and silver cannot displace Copper from a solution of 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 HCl or H_2SO_4 but metals like Copper, silver etc cannot displace hydrogen from acid.

13.12 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 :

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

where

E = Electrode potential

E° = 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 M^{n+} ion

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

Therefore,

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



Notes



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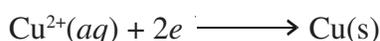
If we put the values of R, T and F in equation (i)

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

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

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

For example : For copper electrode as half cell



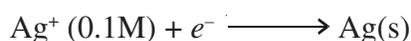
here $n = 2$.
$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = + 0.34\text{V}$$

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

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 13.7 : Calculate the reduction potential for the following half cell at 298 K



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

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

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

$$= 0.80 - 0.0591 \log 10$$

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

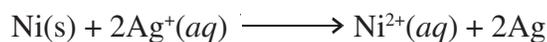
13.12.1 Nernst Equation for Cell emf

For a general cell reaction :



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

Thus, for the cell reaction :

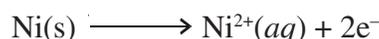


$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

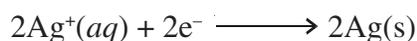
Note: Only the ions are written in the fraction as concentration of pure solid or liquid is taken as unity.

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

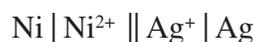
Anode reaction (oxidation)



Cathode reaction (reduction)

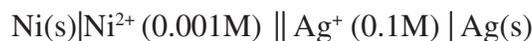


This can be represented in the form of a cell as



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

Example 13.8 : Calculate the EMF of the following cell at 298 K



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

From the given values first find

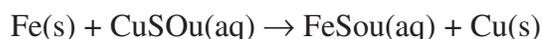
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.80 - (-0.25) \text{V} = 1.05\text{V}$$

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



INTEXT QUESTION 13.2

1. What type of process-spontaneous or non-spontaneous, occurs in (i) electrolytic cell (ii) galvanic cell.
2. Atomic mass of silver is 108 u. What is its electrochemical equivalent?
3. Why is salt bridge used for setting up of galvanic cells.
4. A galvanic cell is made in which the following reaction occurs.



Write down the cell notation, for this cell.

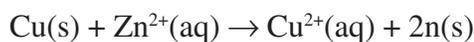


Notes



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5. Predict whether the following reaction is feasible or not?



$$\text{Given } E_{\text{Cu}^{2+}|\text{Cu}}^{\circ} = +0.34 \text{ V and } E_{\text{Zn}^{2+}|\text{Zn}}^{\circ} = -0.76 \text{ V}$$

13.13 BATTERIES AND FUEL CELLS

The cells and batteries (combination of 2 or more cells) that we use for various purposes from torch lights, cameras, watches to cars and bikes, are basically of three types: dry cells or primary cells, storage cells or secondary cells and fuel cells. A primary cell is the one that is consumed chemically when current is drawn from it. A secondary cell is the one which after discharge can be recharged by passing electricity through it and carrying out electrolysis. In fuel cells the oxidizing and reducing agents are fed continuously to the cell from outside.

(i) Dry cell (Primary cell)

It is the cell commonly used in torches transistor radios, portable music players, clock etc. It is also known as Leclanche cell after the name of its inventor. It consists of a zinc container which also acts as the anode and a carbon (graphite) rod which acts as the cathode. Around carbon rod, a moist paste of graphite, ammonium chloride and manganese dioxide is placed which acts as the electrolyte (Fig 13.10). The electrode reactions that occur are complex but can be written in simplified way as:

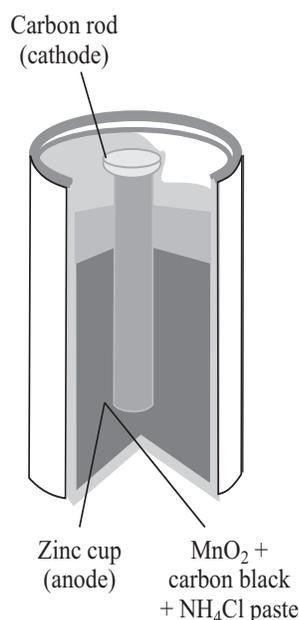
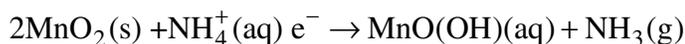


Fig. 13.10: Dry cell

Anodic process (*oxidation*): $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$

Cathodic process (*reduction*):



The ammonia gas evolved at cathode combines with Zn^{2+} ions produced at anode to give complex ion $[\text{Zn}(\text{NH}_3)_4]^{2+}$. A single dry cell has a potential of nearly 1.5V. It can be used only once and cannot be recharged.

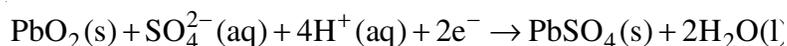
(ii) Lead Storage Battery (Secondary cell)

Lead storage batteries are used in automobiles (cars, bikes, trucks, buses etc) and in inverters.

A lead storage battery consists of alternate plates of anodes and cathodes. The anode consists of lead plate and the cathode of a grid of lead packed with lead dioxide (PbO_2). The electrolyte is an aqueous solution of sulphuric acid which is 38% or 3.7 M. (See Fig. 13.11) The reactions that occur at the electrodes during the discharge of the battery when it is used to draw current are:

Anodic process (*oxidation*): $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^{-}$

Cathodic process (*reduction*):



Net reaction: $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

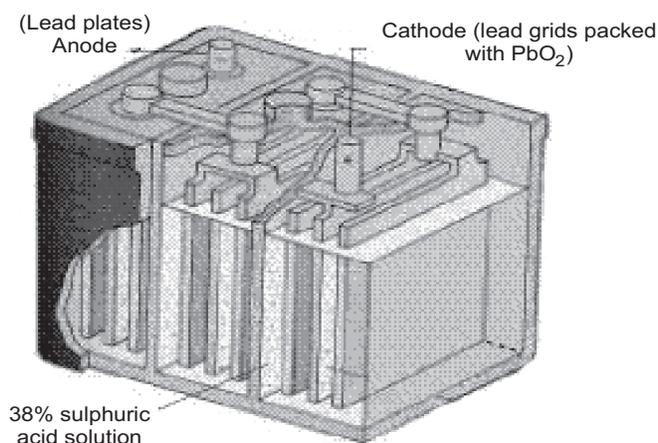


Fig. 13.11: Lead storage battery

The battery can be recharged by passing current through it. Now it acts like an electrolytic cell and the electrode reactions are reversed and the original reactants are regenerated. The battery can be charged and discharged a large number of times.



Notes



Notes

(iii) Fuel Cells

The maximum amount of electricity is produced by thermal power plants which use fossil fuel like coal or natural gas. Their efficiency is very low but these plants can be run continuously by constant feeding of the fuel. Galvanic cells have high efficiency but can be used only once and then have to be discarded, because reactants can not be fed into them continuously. Fuel cells combine the advantages of the two. They are efficient and can be used continuously. Most of the fuel cells are based on combustion reactions of fuels like hydrogen, methane, methanol etc which are fed continuously into fuel cells. One of the most successful fuel cells uses the combustion reaction of hydrogen (Fig. 13.12).

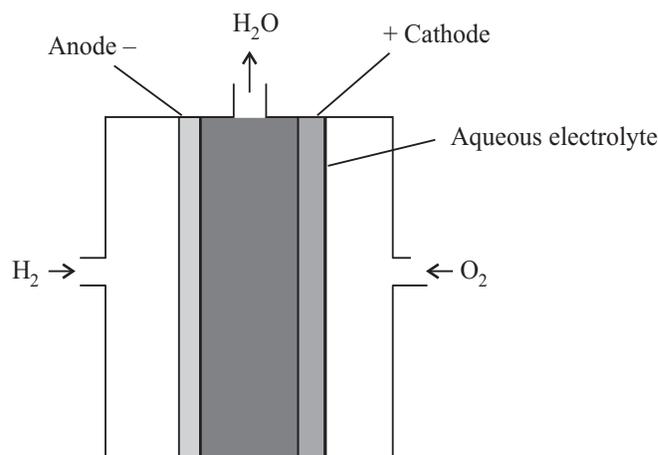
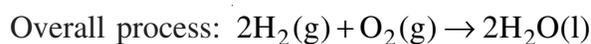
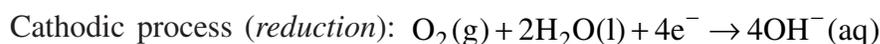


Figure 13.12: Hydrogen-oxygen fuel cell

The electrodes used in it are made of porous carbon impregnated with catalyst (finely divided Pt or Pd). The electrolyte used is an aqueous solution of KOH. Hydrogen gas is bubbled around the anode and oxygen gas around the cathode. The electrode process are:



The cell potential of this cell is 0.9V. It was used as a power source in Apollo space programme and water produced was used for drinking purpose by the crew of the spacecraft.

13.14 CELL EMF AND GIBBS ENERGY

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

$$W_{\text{max}} = -nFE^0$$

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 ΔG^0 calculated is negative, then the cell reaction is spontaneous otherwise not.

Example 13.9 : Calculate the standard Gibbs energy ΔG^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 ΔE^0 is –ve, the cell reaction is spontaneous



INTEXT QUESTIONS 13.4

1. Differentiate between electrolytic cell and galvanic cell.
2. What is a salt bridge? What is the role of the salt bridge?
3. What is electrochemical series? List any two applications of the series.
4. 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

13.15 CORROSION

Corrosion is the process of deterioration of metals due to their exposure to environment. It slowly forms a layer of oxides, basic carbonates or other salts on the surface of metals. Rusting of iron and tarnishing of silver objects are common examples of corrosion. Corrosion results in huge material loss resulting in damage to buildings, ships, bridges, machinery etc.

Corrosion is essentially an electrochemical process involving anodic oxidation of metals resulting in the formation of their ions and a cathodic process that



Notes



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consumes the electrons. Though rusting is a complex process. The following reactions can be considered to be taking place. One spot on the surface of iron becomes anode and undergoes *oxidation*.

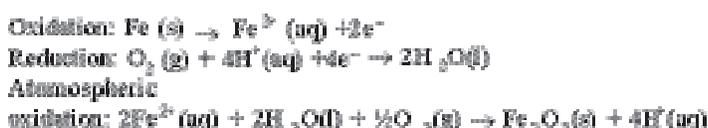
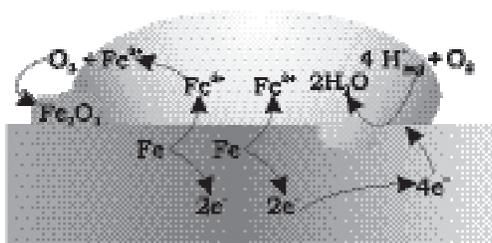
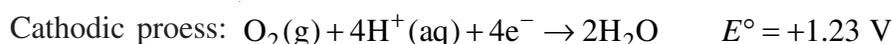


Fig. 13.13: Corrosion of iron



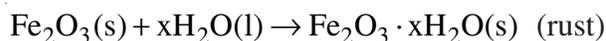
The electrons released here move through the metal to another place which acts like a cathode. Here the *reduction* of oxygen takes place in presence of H^+ ions.



The overall process is



The positive sign of E_{cell}° indicates that this reaction occurs spontaneously. Fe^{2+} ions formed here are further oxidized to Fe^{3+} ions by atmospheric oxygen to form rust



Rusting requires the combined effect of oxygen and water. It is accelerated by CO_2 and SO_2 (acidic conditions) and retarded by alkalis. It has been observed that completely homogeneous iron does not rust.

Protection against corrosion

There are two general methods used for protection of metallic objects against corrosion.

- application of protective layer to inhibit anodic process
- cathodic protection

(a) Use of Protective Layer

Many substances are used for applying a protective layer to prevent or limit corrosion:

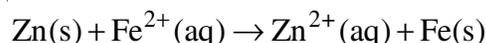
- (i) Machinery, tools and automobile engine parts are often protected by a thin film of oil or grease.
- (ii) Metallic doors, windows, coolers are painted with a suitable paint to prevent corrosion.
- (iii) In automobile industry, the chassis of vehicles is painted with phosphoric acid which reacts with iron to form an insoluble film of iron (III) phosphate.
- (iv) Iron containers are made from tin plated sheets. Tin is less reactive than iron and forms a protective layer. However, if tin layer is broken, rusting starts because iron is more electropositive than tin ($E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44\text{V}$ and $E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} = -0.14\text{V}$). In contact with each other and with atmosphere, iron becomes anode and tin becomes cathode and rusting of iron begins.

(b) Cathodic Protection

Cathodic protection of a metal can be done by coating it with a more reactive or more electropositive metal with smaller electrode potential.

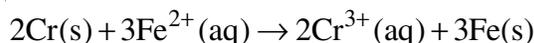
(i) Galvanisation:

Iron sheets or other objects are coated with a layer of zinc by dipping them in molten zinc or using electrolysis. Zinc layer is protected against corrosion by a firmly sticking layer of ZnO. Even when the zinc layer is broken, zinc being more electropositive than iron becomes the anode and iron ($E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{ V}$; $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44\text{ V}$) becomes the cathode, the cell reaction that occurs is



Thus, any Fe^{2+} ions formed as a result of atmospheric oxidation are reduced back to iron at the cost of zinc. Therefore, zinc coating becomes **sacrificial anode**.

(ii) Chromium plating (electroplating) is not only decorative, but also protects iron against rusting. Like zinc, chromium is also more electropositive than iron ($E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} = -0.74\text{ V}$; $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44\text{ V}$). Chromium itself is not affected by atmospheric oxygen. Its layer protects iron. Once this layer is broken, chromium becomes the anode and iron the cathode and the following reaction occurs:

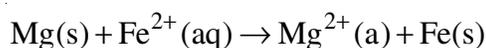


Notes



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(iii) Cathodic protection can also be provided by attaching, rather than coating, a piece of more reactive metal to the object to be protected. Ships, water pipes, iron tanks etc. are often protected against corrosion by connecting a piece of magnesium either directly or through a wire. Magnesium being more electropositive than iron ($E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -2.36\text{V}$; $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44\text{V}$) becomes sacrificial anode. The following reaction occurs in the cell formed.



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.
- 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 doesnot 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 ΔG^0 is related to the standard cell emf as $\Delta G^0 = -nFE^0$.



Notes

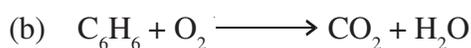
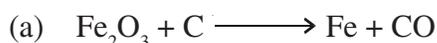


TERMINAL EXERCISE

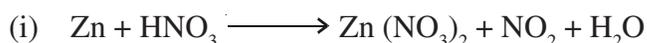
1. Calculate the Oxidation number of the elements written in bold letters



2. Balance the following reactions by oxidation number method



3. Balance the following reactions by ion-electron method:



4. Define the following and give its units:

(i) Conductivity

(ii) Molar conductivity



Notes

- Draw a graph showing the variation in molar conductivity in a weak and a strong electrolytes with concentration.
- Explain why the molar conductivity of an electrolyte increases with dilution while conductivity decreases on dilution.
- The measured resistance of a conductance cell containing $7.5 \times 10^{-3}\text{M}$ solution of KCl at 25°C was 1005 ohms. Calculate (a) Conductivity (b) Molar conductivity of the solution. Given the cell constant 1.25 cm^{-1} .
- The conductivity of 0.05M solution of an electrolyte at 298 K is 0.0025 cm^{-1} . Calculate the molar conductivity.
- How much aluminium will be deposited on passing a current of 25 A for 10 hr by electrolysis of molten Al_2O_3 ?
- Equivalent mass of an element is 94 g. What is its electrochemical equivalent?
- Two electrolytic cells A and B containing ZnSO_4 and CuSO_4 solutions respectively are connected in series on passing certain amount of electricity, 15.2 g of zinc was deposited in cell A. How much copper would be deposited in cell B?
- Explain the term standard electrode potential. How is it determined experimentally.
- Draw the diagram of the cell whose cell reaction is

$$\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$$
- For the cell

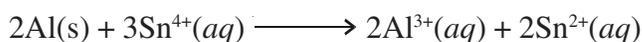
$$\text{Mg} \mid \text{Mg}^{2+} \parallel \text{Zn}^{2+} \mid \text{Zn}$$
 - Draw the cell diagram
 - Identify anode and cathode
 - Write cell reaction
 - Write Nernst equation for the cell
 - Calculate E^0 use the data given the table 13.2
- What are the functions of a salt bridge?
- Using electro chemical series predict whether the following reaction is feasible or not

$$\text{Ni(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Cu(s)} + \text{Ni}^{2+}(\text{aq})$$

17. 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

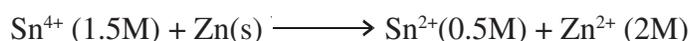
18. Calculate ΔG^0 for the reaction



19. Calculate emf of the cell



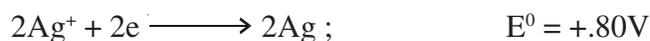
20. Calculate emf of the given cell reaction at 298k



21. The blue colour of CuSO_4 is discharged when a rod of zinc is dipped in it? Explain.

22. Why oxidation cannot occur without reduction.

23. 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.



Notes



ANSWERS INTEXT QUESTION

13.1

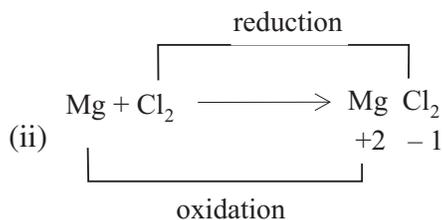
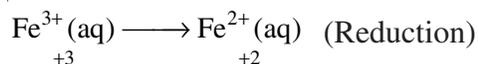
Oxidation Number

1. $-4, -3, +3, +2, +7, +5, 0, +5$
2. In oxidation O.N. increases
In reduction O.N. decreases
3. Oxidising agent HNO_3
reducing agent H_2S
4. $\text{I}^-(\text{aq}) \longrightarrow \text{I}_2(\text{s})$



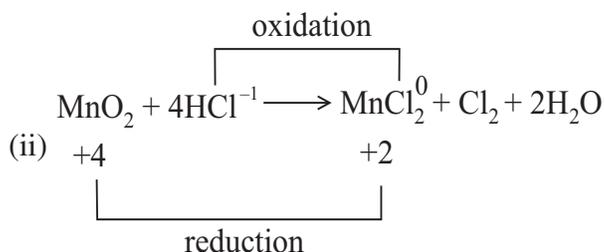
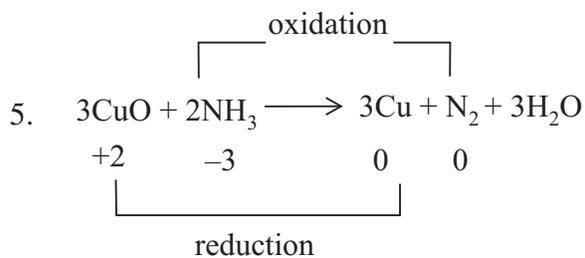
Notes

(i) oxidation



(iii) $\text{I}_2 \longrightarrow \text{HIO}_3$ oxidation

$\text{HNO}_3 \longrightarrow \text{NO}_2$ reduction



6. $\text{Bi} \longrightarrow \text{Bi}^{3+} + 3e^-$

(i) $[\text{NO}_3^- + 2\text{H}^+ + e^- \longrightarrow \text{NO}_2 + \text{H}_2\text{O}] \times 3$

$\text{Bi} + 3\text{NO}_3^- + 6\text{H}^+ \longrightarrow \text{Bi}^{3+} + 3\text{NO}_2 + 3\text{H}_2\text{O}$

(ii) $[\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}]$

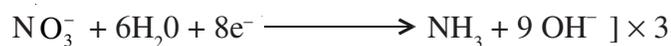
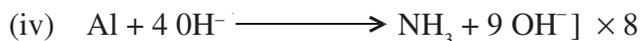
$[\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-] \times 5$

$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \longrightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

(iii) $[\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}]$

$[\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-] \times 6$

$\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$



13.2

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 1cm².
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⁻¹
4. Nature of electrolyte (strong or weak), valency of its ions, speed of ions, concentration and temperature.
5. See Fig. 13.2.
6. $\lambda_m^\infty \text{Al}_2(\text{SO}_4)_3 = 2\lambda_m^\infty \text{Al}^{3+} + 3\lambda_m^\infty \text{SO}_4^{2-}$

13.3

1. (i) non-spontaneous (ii) spontaneous
2. $1.12 \times 10^{-3} \text{ g c}^{-1}$
3. See section 13.8.2
4. $\text{Fe(s)} | \text{Fe SO}_4(\text{aq}) || \text{CuSO}_4(\text{aq}) | \text{Cu(s)}$
5. In feasible since $E^\circ = -1.10 \text{ V}$

13.4

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. 13.6.2
3. See sec. 13.8
4. $\text{Mg} > \text{Al} > \text{Zn} > \text{Fe} > \text{Cu} > \text{Ag}$.



Notes