CHEMISTRY

11

CH#10

Electrochemistry

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Chapter 10
ELECTROCHEMISTRY

The branch of Chemistry which deals with the Conversion (تبدیلی) of electrical energy into chemical energy and chemical energy into electrical energy is called **Electrochemistry**.

The interconversion of electrical and chemical energies take place in electrolytic cells and in galvanic or Voltaic cells.

Electric Current:- The flow of electrons is called electric current or electricity.

Conductor (موصل):- A substance through which electric current can pass is called conductor. e.g Iron, Copper, Silver etc. All metals are good conductor of electricity. It is due to free electrons present in metallic lattice.

Electronic Conduction:- The conduction (گزرجانا) of electricity due to free movement of electrons through a metal is called electronic conduction. It is simply called metallic conduction. In this case no transfer of material takes place.

Electrolyte:- A substance through which an electric current can pass in solution form or in molten form (پگھلی حالت) is called electrolyte (برق پاشیدہ). e.g NaCl, KBr, H_2SO_4, NaOH etc.

Electrolytic Conduction:- The flow of electric current through an electrolyte due to movement of ions and not due to electrons is called electrolytic conduction. In this case transfer of material takes place. e.g when we pass the electricity through fused پگھلا ہوا $PbCl_2$, then Pb and Cl_2 are produced

$$PbCl_2 \xrightarrow{Electricity} Pb + Cl_2$$

Ionization:- The splitting of a substance into positive and negative ions is called ionization.

e.g

$$NaCl \underset{}{\overset{Water}{\rightleftharpoons}} Na^{+} + Cl^{-}$$

$$PbBr_2 \underset{}{\overset{H_2O}{\rightleftharpoons}} Pb^{+2} + 2Br^{-}$$

Oxidation:- Removal of electrons from a substance is called oxidation. The addition of oxygen to a substance or removal of hydrogen from a substance is called oxidation.

e.g

$$Zn \longrightarrow Zn^{+2} + 2e^{-}$$

$$Pb \longrightarrow Pb^{+2} + 2e^{-}$$

Reduction:- عملِ تخفیف Gain (لینا) of electrons by a substance is called Reduction. The removal of oxygen or addition of hydrogen to a substance is called reduction

e.g

$$Cu^{+2} + 2e^{-} \longrightarrow Cu$$

$$2H^{+} + 2e^{-} \longrightarrow H_2$$

Oxidation Number or Oxidation State

The apparent charge on an atom in a molecule or ion is called oxidation number or oxidation state. It may be positive, negative or zero. e.g $\overset{+1}{Na}\overset{-1}{Cl}$, $\overset{0}{Zn}$, $\overset{+}{H}\overset{-}{Cl}$ etc.

Rules for assigning oxidation number

(i) Oxidation number of all elements in free state is zero. e.g H_2^{0}, $\overset{0}{Na}$, Mg^{0}, Zn^{0}

(ii) The oxidation number of hydrogen is +1 but in metal hydrides it is −1. e.g $\overset{+1}{Na}\overset{-1}{H}$

(iii) The oxidation number of oxygen is −2. But in peroxide it is −1, in super oxide it is −½.
The oxidation number of oxygen in OF_2 is +2

(iv) The oxidation number of halogens is −1 in binary compounds. e.g $\overset{+1}{Na}Cl^{-1}$, $\overset{+1}{K}\overset{-1}{I}$

(v) In neutral molecules the sum of the oxidation numbers of all elements is zero. e.g $\overset{+1}{K}\overset{+7}{Mn}\overset{-8}{O_4}$

(vi) In ions, the sum of all oxidation numbers is equal to the charge on the ion. e.g $[\overset{+6}{S}\overset{-8}{O_4}]^{-2}$

(vii) The more electronegative elements have negative oxidation number

(viii) The oxidation number of group IA, group IIA and group IIIA elements are +1, +2 and +3 respectively (بالترتیب)

EXAMPLE:-1 Calculation of oxidation number(O manganese in $KMnO_4$.

Solution:- oxidation number (O.N) of K =
oxidation number of Mn = x
oxidation number of O = −2

Sum of all oxidation numbers = 0

$$+1 + x + 4(-2) = 0$$
$$1 + x - 8 = 0$$
$$x - 7 = 0$$
$$x = 7$$

So oxidation number of Mn in $KMnO_4$ = +

EXAMPLE:-2 Calculation of oxidation number(O.N.) of sulphur in SO_4^{-2}.

Solution:- O.N of oxygen = −2

O.N of S = x
Charge on ion = −2

Sum of all oxidation numbers = −2

[O.N of S] + 4[O.N of O] = −2

$$x + 4(-2) = -2$$
$$x - 8 = -2$$
$$x = 8 - 2 \quad \text{or} \quad x = +6$$

So oxidation number of sulphur in SO_4^{-2} is

Balancing of Equations by Oxidation number Method

We can balance an equation by oxidation method with help of following steps.

(i) Write down skeleton equation of a redox r

(ii) Identify the elements which change their oxidation number during reaction

(iii) Record the oxidation number above the symbols of elements whose oxidation number has changed.

(iv) Indicate the change in oxidation by arrows with help of electrons gained or lost

(v) Equate the number of electrons gained or lost by multiplying with suitable digits

(vi) Balance the rest of equation by inspection method.

EXAMPLE:-3 Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

Solution:- (1) Write down oxidation No of each eleme

$$\overset{2(+1)\ 2(+6)\ 7(-2)}{K_2Cr_2O_7} + \overset{+1\ -1}{HCl} \longrightarrow \overset{+1\ -1}{KCl} + \overset{+3\ 3(-1)}{CrCl_3} + \overset{0}{Cl_2} + \overset{2(+1)}{H_2}O$$

(2) Identify the elements which change their O.N

The oxidation number of Cr changes from +6 to +.

The O.N of Cl changes from -1 to zero. In KCl and $CrCl_3$ the O.N of Cl remains same (-1)

We should write HCl twice on left hand side

Reduction

$$HCl + K_2\overset{+6}{Cr_2}O_7 + H\overset{-1}{Cl} \longrightarrow KCl + \overset{+3}{Cr}\overset{-1}{Cl_3} + \overset{0}{Cl_2} + H_2O$$

oxidation

(3) Two Cr atoms gained 6 electrons and two Cl atoms lost 2 electrons.

(4) We multiply HCl with 6, $CrCl_3$ with 2 and Cl_2 with 3. In this way those atoms are balanced, which have been oxidized or reduced.

$$HCl + K_2Cr_2O_7 + 6HCl \longrightarrow KCl + 2CrCl_3 + 3Cl_2 + H_2O$$

(5) Now we balance those Cl atoms which have not been oxidized or reduced. Here we multiply KCl with 2 and other molecule of HCl with 8

$$8HCl + K_2Cr_2O_7 + 6HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + H_2O$$

(6) Balance the rest of equation by inspection method. Multiply H_2O with 7, to balance H-atoms and O-atoms.

$$8HCl + K_2Cr_2O_7 + 6HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

or $$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

It is final balanced equation.

Balancing of Equation by Ion-Electron Method

In this method we eliminate (remove) all the unnecessary ions and retain only the essential ions. The general rules of this method are given below

(i) Write a skeleton equation which shows only the actually involved species in reaction

(ii) Split the equation into two half reactions. One is oxidation and other is reduction.

(iii) Those atoms, ions or molecules should be written which actually exist

(iv) Balance each half reaction separately.

(V) To balance oxygen and hydrogen atoms, we can add H_2O and H^+ ions in neutral and acidic medium. Similarly we can add $\bar{OH}$ ions and H_2O in alkaline medium. Oxygen atoms are balanced first.

(Vi) Multiply each half reaction by a suitable number so that total electrons lost or gained remain equal.

(vii) Add the two half reactions.

(viii) Check that total number of atoms and net charge should be equal on both sides of the equation.

Example 4 (Acidic medium)

Balance the equation for the reaction of HCl with $KMnO_4$ where Cl^- is oxidized to Cl_2 and MnO_4^- is reduced to Mn^{2+}. The skeleton equation which does not contain either H^+ or H_2O is

$$Cl^- + MnO_4^- \rightarrow Cl_2 + Mn^{2+}$$

Solution:- (1) Split the equation into two half reactions

$$\bar{Cl} \longrightarrow Cl_2 \quad \text{(oxidation)}$$

$$\bar{MnO_4} \longrightarrow Mn^{+2} \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction.

Multiply L.H.S by 2 and add $2\bar{e}$ on R.H.S to balance atoms and charges

$$2\bar{Cl} \longrightarrow Cl_2 + 2\bar{e} \quad \text{——(A)}$$

(3) Balancing of reduction half reaction

Add $4H_2O$ on R.H.S and $8H^+$ on L.H.S

$$\bar{MnO_4} + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$$

Now add $5\bar{e}$ on L.H.S to balance the charges

$$\bar{MnO_4} + 8H^+ + 5\bar{e} \longrightarrow Mn^{+2} + 4H_2O \quad \text{——(B)}$$

(4) Multiply eq(A) by 5 and eq (B) by 2 to

balance the charges and then add

$$10Cl^- \longrightarrow 5Cl_2 + 10e^-$$

$$2MnO_4^- + 16H^+ + 10e^- \longrightarrow 2Mn^{+2} + 8H_2O$$

$$10Cl^- + 2MnO_4^- + 16H^+ \longrightarrow 5Cl_2 + 2Mn^{+2} + 8H_2O$$

It is a balanced equation.

Example 5 (Basic medium)

Balance the following equation in basic aqueous solution by ion electron method.

$$MnO_4^{-1}(aq)\ C_2O_4^{2-}(aq) + H_2O \rightarrow MnO_2(s) + CO_2(g) + OH^-(aq)$$

Solution:- (1) Split the equation into two half reactions.

$$C_2O_4^{-2} \longrightarrow CO_2 \quad \text{(oxidation)}$$

$$MnO_4^{-1} \longrightarrow MnO_2 \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction.

Multiply R.H.S by 2 and add $2e^-$ on R.H.S

$$C_2O_4^{-2} \longrightarrow 2CO_2 + 2e^- \quad \text{---(A)}$$

(3) Balancing of reduction half reaction. Add $4OH^-$ on R.H.S and $2H_2O$ on L.H.S to balance H and O-atoms.

$$MnO_4^- + 2H_2O \longrightarrow MnO_2 + 4OH^-$$

Now add three on L.H.S to balance the charges

$$MnO_4^{-1} + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \quad \text{---(B)}$$

(4) Multiply eq.(A) by 3 and eq.(B) by 2 and then add.

$$3C_2O_4^{-2} \longrightarrow 6CO_2 + 6e^-$$

$$2MnO_4^{-1} + 4H_2O + 6e^- \longrightarrow 2MnO_2 + 8OH^-$$

$$3C_2O_4^{-2} + 2MnO_4^{-1} + 4H_2O \longrightarrow 6CO_2 + 2MnO_2 + 8OH^-$$

Electrochemical Cell and battery

An apparatus which consists of two electrodes dipped in an electrolyte and produces electric current due to chemical reaction is called electrochemical cell or simply a cell. e.g Dry cell, Daniel cell etc.

Battery :- An apparatus which consists of two or more electric cells connected with each other and produces electric current is called battery. e.g Car battery and Ni–Cd battery etc. There are two types of cells.

i) Electrolytic cell (ii) Galvanic cell

(i) Electrolytic Cell :- An electrochemical cell in which an electric current is used to drive a non-spontaneous reaction is called electrolytic cell. e.g Nelson's cell and Down's cell.

(ii) Voltaic or Galvanic cell :-
An electrochemical cell in which a spontaneous redox reaction produces an electric current is called Voltaic or Galvanic cell.
e.g Daniel cell, Ni–Cd cell, fuel cells

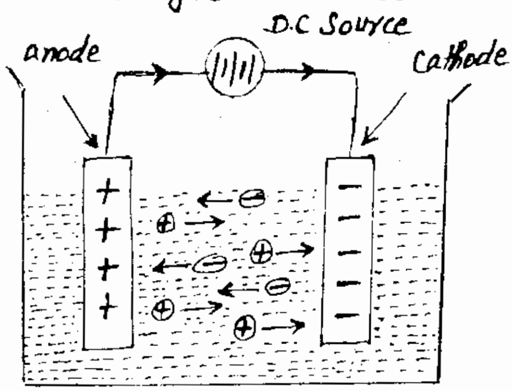
Electrolysis (برق پاشیدگی) :- The process in which a compound in solution or in molten پگھلی ہوئی state decomposes (پھٹ جانا) by passing electric current is called electrolysis. For example

$$2NaCl + 2H_2O \xrightarrow{\text{Electrolysis}} 2NaOH + H_2 + Cl_2$$

"The process in which a non spontaneous reaction takes place at the cost (expense) of electrical energy is called electrolysis.

Working of electrolytic Cell

Consider an electrolytic cell shown in figure



An electrolyte is taken in a container. Two electrodes are dipped in it. Then electrodes are connected to a direct current (D.C) source. When electric current passes, then positive ions move towards cathode and negative ions move towards anode. At the **anode** the negative ions give up electrons. Thus oxidation takes place at anode. At the **Cathode** positive ions pick up electrons. Thus reduction takes place at cathode. The oxidation and reduction reactions carry on simultaneously (بیک وقت). When electric supply is cut off, the reactions stop. The movement of ions due to passage of electric current is called electrolytic conduction. The electrochemical reactions which take place at electrodes by passing electric current through an electrolyte is called electrolysis. e.g.

$$\underset{(Fused)}{2NaCl} \xrightarrow{\text{Electric Current}} 2Na + Cl_2$$

In the electrolysis of a fused (molten پگھلا ہوا) salt, the products can be predicted from equation. In electrolysis of an aqueous solution, the products cannot be predicted from equation. The reason is that water has ability to show oxidation or reduction. Moreover some ions can not compete water during redox reactions.

Electrolysis of Fused Lead Chloride, $PbCl_2$

In electrolysis of fused $PbCl_2$, the lead and chlorine are produced. The mechanism of reaction is given below.

$$PbCl_2 \xrightarrow{\text{ionization}} Pb^{+2} + 2\bar{Cl}$$

The cations (Pb^{+2}) move towards cathode and take up electrons and show reduction. The anions ($\bar{Cl}$) move towards anode and give up electrons and show oxidation.

$$Pb^{+2} + 2\bar{e} \longrightarrow Pb_{(s)} \text{ (at cathode)}$$

$$2\bar{Cl} \longrightarrow Cl_2 + 2\bar{e} \text{ (at anode)}$$

Electrolysis of aqueous solution of $NaNO_3$

Consider the electrolysis of aqueous solution of $NaNO_3$

$$NaNO_{3(aq)} \xrightarrow{\text{ionization}} Na^+ + \bar{NO_3}$$

$$H_2O + H_2O \xrightarrow{\text{self ionization}} H_3O^+ + \bar{OH}$$

The cations (Na^+, H_3O^+) move towards cathode. The H_3O^+ (hydronium ion) shows easy reduction than Na^+. Thus Na^+ ions remain in solution.

$$H_3\overset{+}{O} + \bar{e} \longrightarrow H + H_2O$$
$$H + H \longrightarrow H_2 \quad \text{(at cathode)}$$

The anions $\bar{OH}$ and $\bar{NO_3}$ move towards anode. The $\bar{OH}$ ions show easy oxidation than $\bar{NO_3}$ ions

$$\bar{OH}_{(aq)} \longrightarrow OH + \bar{e}$$
$$4OH \longrightarrow O_2 + 2H_2O \quad \text{(at anode)}$$

Thus during electrolysis of aqueous $NaNO_3$, H_2 is produced at cathode, O_2 is produced at anode. The ions $\overset{+}{Na}$ and $\bar{NO_3}$ remain in solution. They are called spectator ions

Electrolysis Processes of industrial Importance

(i) Electrolysis of fused NaCl:- Sodium is extracted by electrolysis of fused NaCl. It is done in Down's Cell. In this cell iron cathode and graphite anode are dipped in molten NaCl.

image from book and HCn

$$2NaCl_{(s)} \longrightarrow 2\overset{+}{Na} + 2\bar{Cl}$$
$$2\overset{+}{Na} + 2\bar{e} \longrightarrow 2Na \quad \text{(at cathode)}$$
$$2\bar{Cl} \longrightarrow Cl_2 + 2\bar{e} \quad \text{(at anode)}$$

Sodium deposits on cathode and Cl_2 is produced as a by product on anode. more from book

(ii) Electrolysis of aqueous NaCl:- The electrolysis of aqueous NaCl gives Caustic Soda (NaOH). It is done in Nelson cell or Castner-Kellner cell or Hg-cell

In this cell anode is made of Titanium and Cathode is made of Steel or Mercury

$$2NaCl \rightleftharpoons 2Na^{+} + 2Cl^{-}$$

$$2Cl^{-} \longrightarrow Cl_2 + 2e^{-} \quad \text{(at anode)}$$

Now H_2O shows easy reduction than Na^{+} ions

$$2H_2O + 2e^{-} \longrightarrow H_2 + 2OH^{-} \quad \text{(at cathode)}$$

The overall reaction is

$$2NaCl + 2H_2O \longrightarrow H_2 + Cl_2 + 2Na^{+} + 2OH^{-}$$

Hence electrolysis of aqueous NaCl gives NaOH as main Product and H_2, Cl_2 as by Products.

(iii) We extract Mg and Ca by electrolysis of their fused Chlorides. e.g

$$MgCl_2 \longrightarrow Mg^{+2} + 2Cl^{-}$$

$$Mg^{+2} + 2e^{-} \longrightarrow Mg \quad \text{(at cathode)}$$

$$2Cl^{-} \longrightarrow Cl_2 + 2e^{-} \quad \text{(at anode)}$$

(iv) We can extract Aluminium by electrolysis of fused mixture of bauxite ($Al_2O_3 \cdot 2H_2O$) and cryolite, Na_3AlF_6. The Process is called Hall-Beroult Process. The reactions are given below

$$Al_2O_3 \longrightarrow 2Al^{+3} + 3O^{-2}$$

$$Al^{+3} + 3e^{-} \longrightarrow Al \quad \text{(at cathode)}$$

$$2O^{-2} + C \text{ (anode)} \longrightarrow CO_2 + 4e^{-} \quad \text{(at anode)}$$

(V) Electrolysis Process is used for electroplating. In this Process one metal is deposited on the surface of another metal. Generally electroplating of copper, silver, Gold, Nickel and Chromium can be done. e.g In electroplating of copper following reactions occur.

$$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2\bar{e} \text{ (at anode)}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu \text{ (at cathode)}$$

(Vi) Electrolysis is used for Purification of copper. Anode is made of impure copper. The cathode is made of thin sheet of pure copper. The solution of $CuSO_4$ is used as electrolyte. During electrolysis Cu^{+2} ions from anode go to solution and then Pure Cu deposits on cathode. The impurities are left at anode.

$$Cu \longrightarrow Cu^{+2} + 2\bar{e} \text{ (at anode)}$$

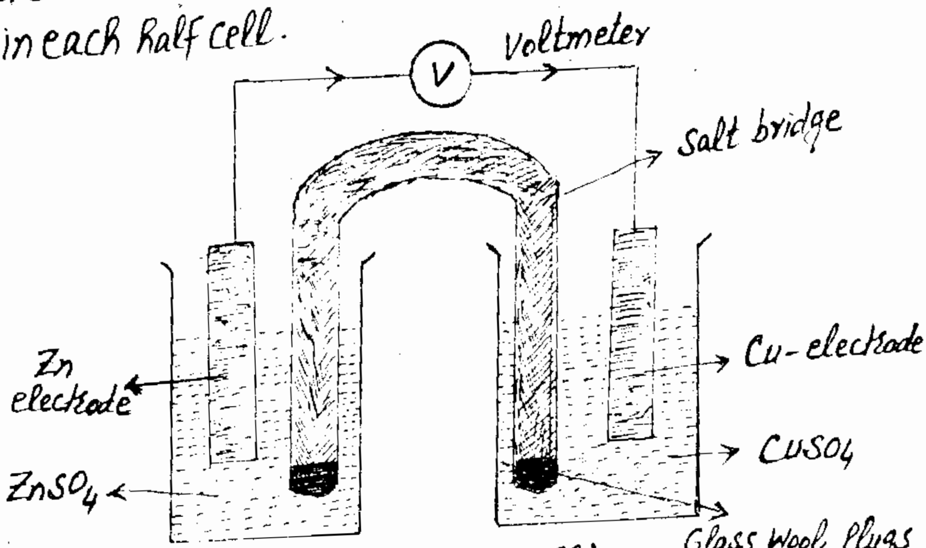
$$Cu^{+2} + 2\bar{e} \longrightarrow Cu_{(s)} \text{ (at Cathode)}$$

(Vii) Anodized Aluminium:- When Aluminium is coated with a thin layer of oxide by electrolysis process, then it is called anodized aluminium. It does not show corrosion زنگ لگنا
It is used to absorb dyes

Voltaic or Galvanic Cell

A cell which Produces electrical energy at the cost of chemical energy is called Voltaic or Galvanic cell. OR An electrochemical cell in which a spontaneous redox reaction Produces an electric current is called Voltaic or Galvanic cell.

e.g Daniel cell. It consists of two half cells which are electrically connected. Half reaction takes place in each half cell.



(A Galvanic cell)

In left hand side cell a zinc strip (جست) is dipped in 1M $ZnSO_4$ solution. It acts as anode. In right hand side cell, a copper strip is dipped in 1M $CuSO_4$ solution. It acts as cathode. The two solutions are connected by a salt bridge.

Following reactions take place in the cell

$$Zn \longrightarrow Zn^{+2} + 2\bar{e} \quad \text{(at anode)}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu \quad \text{(at cathode)}$$

Because Zn is more active than Cu. So it loses electrons and shows oxidation. The Cu^{+2} ions gain electrons and show reduction. The overall cell reaction is

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2} + Cu \quad E^\circ = 1.1\,V$$

The electrons flow from anode to cathode in outer circuit. Thus due to flow of electrons, an electric current is produced. Hence we may say that voltaic cell acts as a source of electric current. This electric current can be used to light روشن کرنا a bulb, drive a motor and so on. The voltaic cell can be represented as follows.

$$Zn_{(s)} / Zn^{+2}_{(aq)} 1M \,||\, Cu^{+2}_{(aq)} 1M / Cu_{(s)}$$

The two parallel (متوازی) lines in the centre indicate a salt bridge.

Function of Salt Bridge

A salt bridge consists of a U-shaped glass tube containing aqueous solution of KCl in gel. It is sealed at two ends by glass wool plugs. It has following functions.

(i) It keeps electrical contact of two half cells.

(ii) It prevents (روکنا) direct mixing of two solutions because by direct mixing of two solutions the half cells are destroyed.

(iii) It maintains electrical neutrality in two solutions.

(iv) It prevents any net charge accumulation جمع ہونا in either solution because it allows excess ions to diffuse from one solution to other solution. If diffusional exchange of ions does not take place, the net charge accumulates in solutions. Thus flow of electrons in outer circuit stops and redox reaction would stop.

Reversibility of Voltaic Cell:-

When we connect two electrodes of voltaic cell to a D.C source, then it becomes a reversible cell. Now copper strip acts as anode and Zn strip acts as cathode. The flow of electrons is also in reverse direction. In this way a reverse non-spontaneous reaction takes place. Following reactions occur in the cell

$$Cu_{(s)} \longrightarrow Cu^{+2} + 2\bar{e} \quad \text{(at anode)}$$

$$Zn^{+2} + 2\bar{e} \longrightarrow Zn \quad \text{(at cathode)}$$

Net reaction is

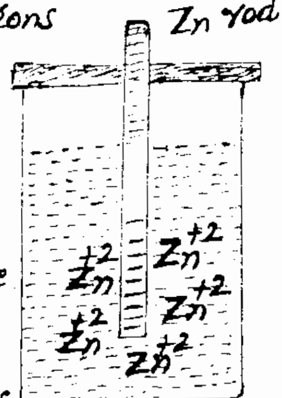
$$Cu + Zn^{+2} \longrightarrow Cu^{+2} + Zn$$

Now the cell is working like an electrolytic cell because external electric current is driving a non-spontaneous reaction.

(8) Electrode Potential

When a metal electrode is dipped into the solution of its own ions, then a potential difference is set up between them. It is called electrode potential. It indicates the tendency of the ions to get reduction.

When a metal electrode is dipped into 1M solution of its own ions at 298K and 1 atm pressure, then potential set up is called standard electrode potential or standard reduction Potential. It is represented by E^o. The standard electrode potential of Hydrogen has been fixed as zero. We can explain electrode potential in terms of an equilibrium attained between metal atoms and its ions. For example a rod of Zinc is dipped in solution of $ZnSO_4$. Some atoms of Zn give electrons to piece of Zn. Thus Zn^{+2} ions go into solution and electrons accumulate (جمع ہونا) on the rod. At the same time Zn^{+2} ions already present in solution take up electrons from Zn rod and deposit as neutral atoms.

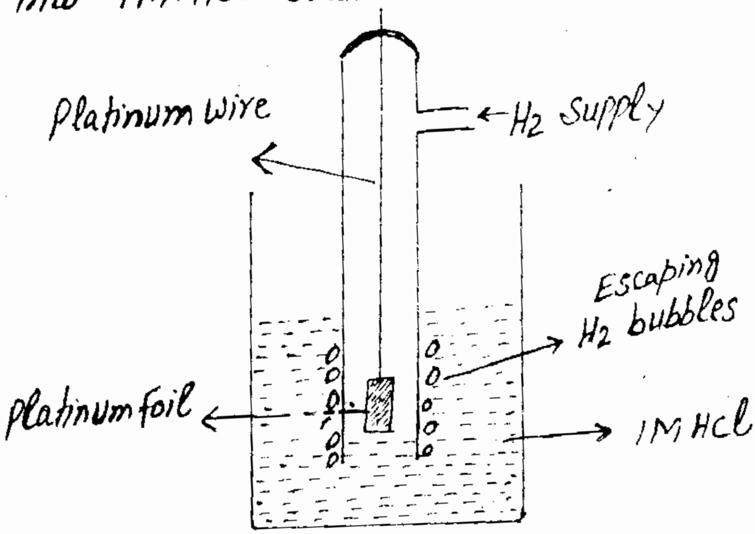


At equilibrium state, the two processes take place at same rate. Thus there is no further change in potential difference. This equilibrium is represented as

$$Zn_{(s)} \rightleftharpoons Zn^{+2} + 2e^-$$

Standard Hydrogen electrode (SHE)

A standard hydrogen electrode is used as standard (معیار) for the measurement of electrode potential. It consists of a Platinum foil which is coated (تہہ لگانا) with black platinum. It is connected to a Platinum wire and placed in a glass tube. This glass tube is suspended into 1M HCl solution



(Standard Hydrogen Electrode)

Pure H_2 gas at 1 atm Pressure is bubbled into 1M HCl solution. The H_2 gas absorbs on Platinum foil. An equilibrium is attained between hydrogen and its ions. The Potential of SHE is arbitrarily taken as zero. SHE may act as cathode or anode. It depends upon nature of electrode connected with it. SHE acts as anode when

connected with a metal having higher value of reduction Potential. e.g Cu. In this case H_2 has greater tendency to lose electrons.

$$H_2 \longrightarrow 2H^+ + 2\bar{e} \text{ (oxidation at anode)}$$

SHE acts as cathode when connected with a metal having lower value of reduction Potential. e.g Zn. In this case hydrogen has greater tendency to gain electrons

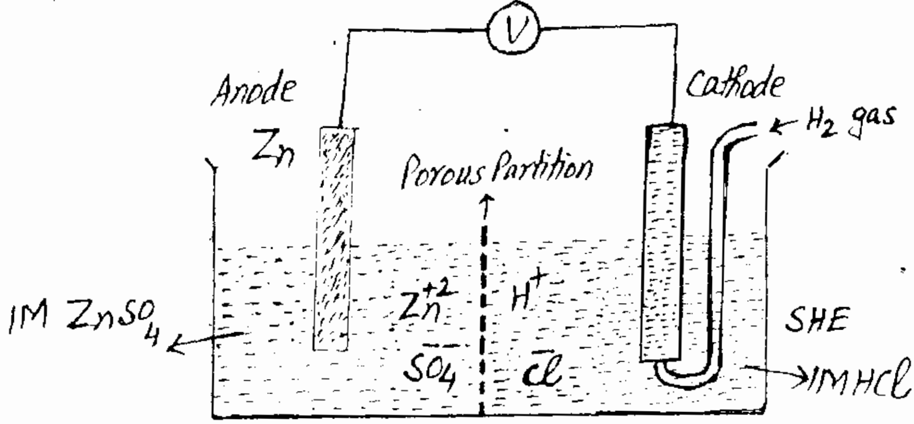
$$2H^+ + 2\bar{e} \longrightarrow H_2 \text{ (reduction at cathode)}$$

(8)

Measurement of Electrode Potential

We can not measure absolute electrode Potential. The relative electrode Potential is measured. A galvanic cell is ~~set up~~ established between a metal electrode and standard Hydrogen electrode (SHE). The two solutions are separated by a Porous Partition or salt bridge containing a conc solution of KOH. Because Potential of SHE is zero so voltmeter reading gives electrode Potential of metal electrode. (8)

Electrode Potential of Zinc:- A Zn-electrode is dipped in 1M $ZnSO_4$ solution. A galvanic cell is ~~set up~~ established between Zinc electrode and SHE. The two solutions (1M $ZnSO_4$, 1M HCl) are separated by Porous Partition under the standard conditions.



The reading on voltmeter gives electrode Potential of Zn. It is 0.76 Volts. It means that Zn has greater tendency to give up electrons than that of Hydrogen by 0.76 volts. In this arrangement Zn electrode acts as anode and SHE acts as Cathode.

Following reactions take place on electrodes

$$Zn \longrightarrow Zn^{+2} + 2\bar{e} \quad \text{(at anode)}$$

$$2H^{+} + 2\bar{e} \longrightarrow H_2 \quad \text{(at Cathode)}$$

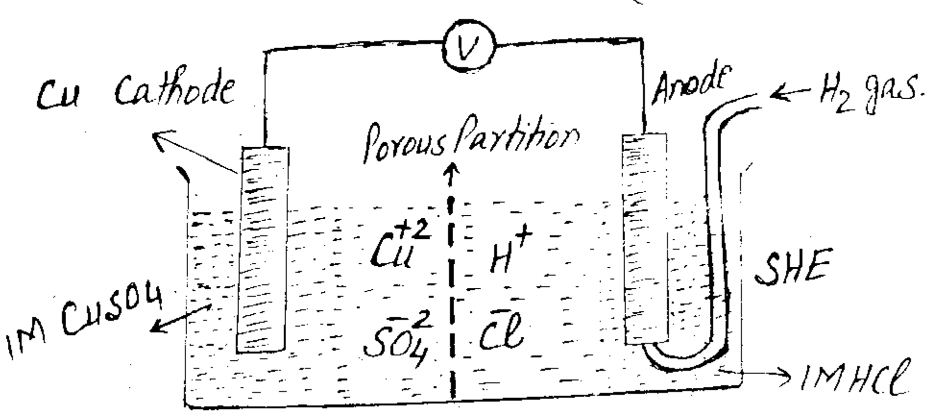
Electrode Potential of Copper:- We measure electrode potential of copper as follows.

A copper electrode is dipped in 1M $CuSO_4$ solution. Then a galvanic cell is ~~set up~~ established between Cu-electrode and SHE at 25°C. The two solutions are separated by a porous partition. It is shown in figure.

The reading on voltmeter gives electrode potential of copper. It is 0.34 volts. It means that hydrogen has greater tendency to give up electrons by 0.34 volts. Following reactions take place in the cell.

$$H_2 \longrightarrow 2H^{+} + 2\bar{e} \quad \text{(At anode)}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu \quad \text{(At Cathode)}$$



Electrochemical Series

The list of elements arranged in the order of their standard electrode potential on the hydrogen scale is called electrochemical series. This series can be arranged on the basis of oxidation or reduction potentials. The International Union of Pure and Applied Chemistry (IUPAC) has recommended (سفارش کرنا) the reduction mode. By changing the mode, the magnitude of potential does not change but the signs are reversed (الٹ جانا). The electrochemical series arranged on the basis of standard reduction potentials is given below.

Element	Electrode Reaction	Standard Reduction Potential
Li	$Li^{+} + e^{-} \longrightarrow Li$	−3.045
K	$K^{+} + e^{-} \longrightarrow K$	−2.925
Ca	$Ca^{+2} + 2e^{-} \longrightarrow Ca$	−2.87
Na	$Na^{+1} + e^{-} \longrightarrow Na$	−2.714
Mg	$Mg^{+2} + 2e^{-} \longrightarrow Mg$	−2.37
Al	$Al^{+3} + 3e^{-} \longrightarrow Al$	−1.66
Zn	$Zn^{+2} + 2e^{-} \longrightarrow Zn$	−0.76
Fe	$Fe^{+2} + 2e^{-} \longrightarrow Fe$	−0.44
Pb	$Pb^{+2} + 2e^{-} \longrightarrow Pb$	−0.126
H_2	$2H^{+1} + 2e^{-} \longrightarrow H_2$	0.000
Cu	$Cu^{+2} + 2e^{-} \longrightarrow Cu$	+0.34
I_2	$I_2 + 2e^{-} \longrightarrow 2I^{-}$	+0.535
Ag	$Ag^{+} + e^{-} \longrightarrow Ag$	+0.7994
Hg	$Hg^{+2} + 2e^{-} \longrightarrow Hg$	+0.885
Br_2	$Br_2 + 2e^{-} \longrightarrow 2Br^{-}$	+1.08
Cl_2	$Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}$	+1.36
Au	$Au^{+3} + 3e^{-} \longrightarrow Au$	+1.50
F_2	$F_2 + 2e^{-} \longrightarrow 2F^{-}$	+2.87

In this series Lithium is at the top and Fluorine is at the bottom. All elements above SHE have negative reduction Potential and elements below SHE have Positive reduction Potentials

Applications of Electrochemical Series.

(i) Feasibility (Spontaneity) of a redox Reaction

By electrochemical series we can check the feasibility or spontaneity (خودبخود ہونا) of a redox reaction.

If sum of E° values of two half cell reactions is Positive, then reaction will be feasible

e.g

$$Zn \longrightarrow Zn^{+2} + 2\bar{e}, \quad E^\circ = +0.76 \text{ Volts}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu, \quad E^\circ = +0.34 \text{ Volts}$$

The overall reaction is

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu, \quad E^\circ = +1.10 \text{ Volts}$$

The E° of full reaction is Positive, so it is energetically feasible. If sum of E° values of two half cell reactions is negative, then reaction will not be feasible.

e.g

$$Cu_{(s)} \longrightarrow Cu^{+2} + 2\bar{e}, \quad E^\circ = -0.34 \text{ Volts}$$

$$Zn^{+2} + 2\bar{e} \longrightarrow Zn_{(s)}, \quad E^\circ = -0.76 \text{ Volts}$$

$$Cu + Zn^{+2} \longrightarrow Cu^{+2} + Zn, \quad E^\circ = -1.10 \text{ Volts}$$

As E° of full reaction is negative, so it is not feasible.

(ii) Voltage or Electromotive force (emf) of cells

The force with which electrons move in external

Circuit is called voltage or emf of a cell. It indicates the tendency of a cell reaction to take place. It is calculated as follows

$$Zn_{(s)} \longrightarrow Zn^{+2} + 2\bar{e}, \quad E^{\circ}_{oxi} = +0.76 \text{ Volts}$$

$$Cu^{+2} + 2\bar{e} \longrightarrow Cu_{(s)}, \quad E_{red} = +0.34 \text{ Volts}$$

The overall reaction is

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu, \quad E^{\circ}_{cell} = E^{\circ}_{oxi} + E^{\circ}_{red}$$

$$E^{\circ}_{cell} = E^{\circ}_{oxi} + E_{red}$$

$$= 0.76 + 0.34$$

$$= 1.10 \text{ Volts}$$

(iii) Reaction of metals with dilute acids

A metal will react with dilute acid and displace the H_2 if it has very low reduction potential or it is above the hydrogen in electrochemical series

e.g $\quad Mg + 2HCl \longrightarrow MgCl_2 + H_2$

$\quad Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

The metals with high reduction potential (below SHE) do not liberate (خارج کرنا) H_2 from acids

e.g Ag, Au, Cu, Pt, Hg etc.

(iv) Displacement of one metal by another:-

A metal will displace another metal from its salt solution if it is above the second metal in electrochemical series. e.g Fe can displace Cu from $CuSO_4$ but Zn can not displace Mg from aqueous solution of $MgSO_4$.

$Fe + CuSO_4(aq) \longrightarrow FeSO_4 + Cu$

$Zn + MgSO_4(aq) \longrightarrow$ No reaction.

(V) Chemical reactivity of metals

Reactivity of metal depends upon its tendency to lose electron to form Positive ion. Thus metals with Smaller reduction Potential have greater tendency to lose electron. So they are more reactive.
e.g Alkali metals (Li, Na, K, Rb) are highly reactive.
The metals with high (Positive) reduction Potential are less reactive because they have little tendency to lose electrons. e.g Coinage metals (سکے بنانے والی) like Ag, Au and Cu are the least reactive.

(Vi) Oxidizing or Reducing agents:-

If an element has low (negative) reduction Potential then it has greater tendency to lose electron. Thus it will act as reducing agent (تخفیفی عامل)
e.g Li is the strongest reducing agent.
Similarly an element with high (Positive) reduction Potential has greater tendency to gain electrons. Thus it will act as oxidizing agent. e.g In the electrochemical Series, Fluorine is the strongest oxidizing agent.

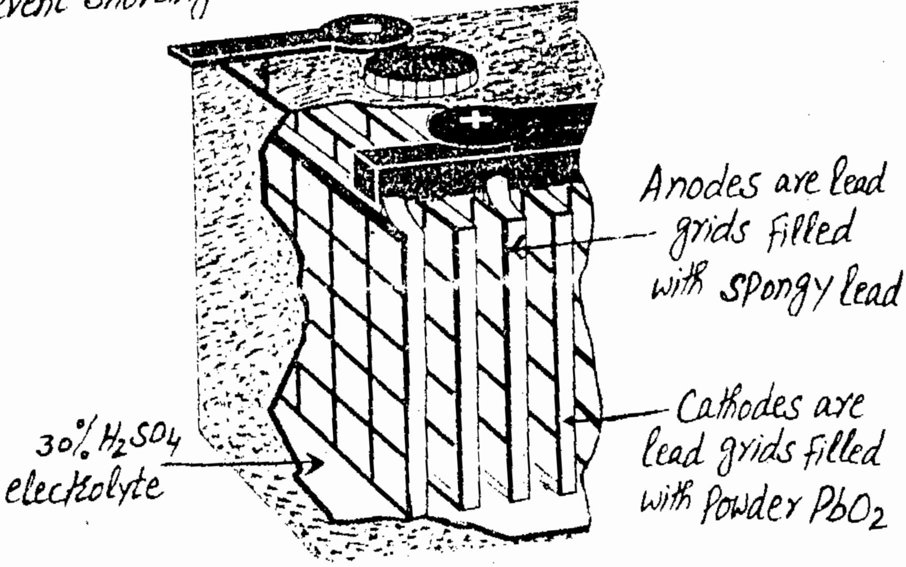
(Vii) As Cathode or Anode:- An element with low value of reduction Potential acts as anode and that with high reduction Potential acts as a Cathode.
e.g In Daniel Cell, Zn is anode and Cu is Cathode

Modern Batteries and Fuel Cells

Those cells which can not be recharged are called **Primary Cells**. e.g. dry cell, alkaline battery, silver battery, Mercury battery. Those cells which can be recharged are called **Secondary Cells** or storage cells. e.g Lead accumulator, Ni–Cd battery and fuel cells etc.

Lead Accumulator (Rechargeable)

It is commonly used as a car battery. It is secondary or storage cell. It consists of six cells. Each cell provides 2 volts. The six cells are connected in series. The anodes are made of lead grids (جالیاں) packed with spongy lead. The cathodes are made of lead grids packed with powdered lead oxide, PbO_2. They are dipped in 30% H_2SO_4 solution which is $\approx 4.5M$. Fibre glass sheets are present between the grids to prevent shorting.



Lead Accumulator

Discharging:- At the anode the lead atom loses two electrons and form Pb^{+2} ion. The Pb^{+2} ions Combine with SO_4^{-2} ions to form $PbSO_4$. The $PbSO_4$ deposits (جمع ہونا) on anode.

$$Pb + SO_4^{-2} \longrightarrow PbSO_4 + 2\bar{e} \text{ (At Anode)}$$

The electrons from anode go to external circuit as electric current. This electric current is used for starting the engine and for lighting system of Car. At the Cathode, the PbO_2, SO_4^{-2} ions, H^+ ions and electrons show following reaction

$$PbO_2 + 4H^+ + SO_4^{-2} + 2\bar{e} \longrightarrow PbSO_4 + 2H_2O \text{ (At Cathode)}$$

Like anode, the $PbSO_4$ is also produced on cathode. Because $PbSO_4$ is insoluble in 30% H_2SO_4. So it deposits on both the electrodes. When both the electrodes are covered with $PbSO_4$, then cell can not produce current.

Recharging:- In recharging of the cell we connect (جوڑنا) the anode and cathode of the external circuit to the anode and cathode of the cell. So the current flows in reverse direction and recharging of the cell takes place. Following reactions take place during the recharging of the battery

At the cathode

$$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{-2} \text{ (reduction)}$$

overall reaction = ? from Book

At the anode

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{-2} + 2e^- \text{ (oxidation)}$$

I PbO_2
II MnO_2
III Ag_2O
IV NiO_2

During the process of discharging the concentration of H_2SO_4 decreases. So its density decreases from $1.25\ g\ cm^{-3}$ to $1.15\ g\ cm^{-3}$. During the process of recharging the concentration of acid again increases. Thus its density increases to initial value of $1.25\ g\ cm^{-3}$. At the same time the voltage of cell which was dropped during the discharging, returns to around 2 volts.

Alkaline Battery:- It is a dry alkaline cell in which Zn and MnO_2 (manganese dioxide) are reactants. A Zinc rod acts as anode and MnO_2 acts as cathode. The electrolyte contains KOH. It is the reason that battery is alkaline. The battery is enclosed in a steel container. This battery delivers more current and has longer life than a common dry cell (خشک سیل)
The voltage of this battery is 1.5V
Following reactions take place in the battery.

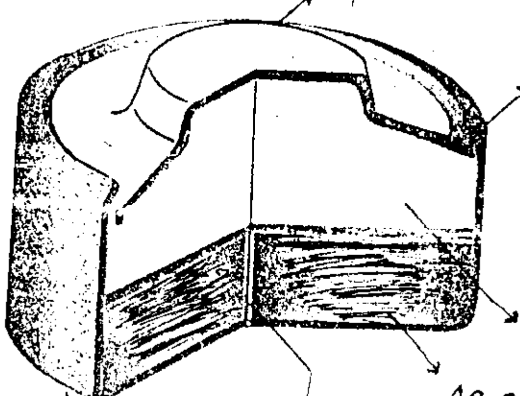
$$Zn + 2\bar{O}H \longrightarrow Zn(OH)_2 + 2\bar{e} \quad \text{(at anode)}$$

$$2MnO_2 + H_2O + 2\bar{e} \longrightarrow Mn_2O_3 + 2\bar{O}H \quad \text{(at cathode)}$$

overall reaction Book

Silver Oxide Battery

It is a tiny (چھوٹی) and expensive battery. It is used in electronic watches, electronic calculators and auto-exposure cameras. It is shown below.



The Cathode is made of Silver Oxide, Ag_2O and anode is made of Zinc metal. The voltage of this battery is about (تقریباً) 1.5V. Here NaOH or KOH is used as an electrolyte. Following reactions occur in the battery.

$$Zn_{(s)} + 2\bar{O}H_{(aq)} \longrightarrow Zn(OH)_2 + 2\bar{e} \quad \text{(at anode)}$$

$$Ag_2O + H_2O + 2\bar{e} \longrightarrow 2Ag_{(s)} + 2\bar{O}H \quad \text{(at cathode)}$$

The overall reaction is

$$Zn_{(s)} + Ag_2O_{(s)} \longrightarrow ZnO_{(s)} + 2Ag_{(s)}$$

Nickel Cadmium Cell (Rechargeable)

It is a strong cell widely used in NICAD or Nickel Cadmium battery. The anode is made of Cadmium. It shows oxidation in the alkaline electrolyte. The cathode is made of NiO_2. It shows reduction

$$Cd + 2\bar{OH} \longrightarrow Cd(OH)_2 + 2\bar{e} \text{ (at anode)}$$

$$NiO_2 + 2H_2O + 2\bar{e} \longrightarrow Ni(OH)_2 + 2\bar{OH} \text{ (at cathode)}$$

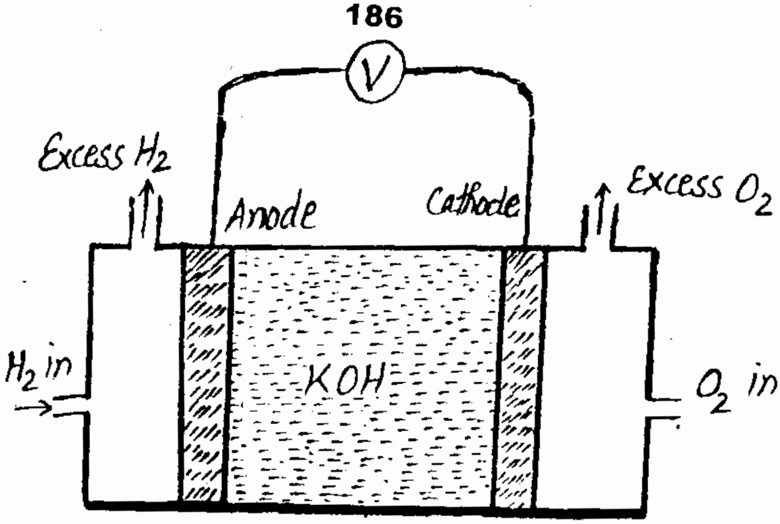
The overall reaction is

$$Cd + NiO_2 + 2H_2O \longrightarrow Cd(OH)_2 + Ni(OH)_2$$

The Ni—Cd cell is used in rechargeable electronic calculators, electrical shutters and power tools. It is more expensive مہنگا than the lead storage battery

Fuel Cells (Rechargeable)

A fuel cell is a type of cell in which chemical energy is converted into electrical energy. In this cell fuel gases (گیسی ایندھن) such as hydrogen and oxygen react to produce electrical energy. The electrodes are made of porous (مسام دار) Carbon. They are hollow (کھوکھلی) tubes of porous carbon filled by platinum. The platinum acts as catalyst. The KOH is used



(Hydrogen – Oxygen fuel cell)

as an electrolyte. The hydrogen shows oxidation and oxygen shows reduction.

$$[H_2 + 2\bar{O}H \longrightarrow 2H_2O + 2\bar{e}] \times 2 \quad \text{(at anode)}$$

$$O_2 + 2H_2O + 4\bar{e} \longrightarrow 4\bar{O}H \quad \text{(at Cathode)}$$

The overall reaction is

$$2H_2 + O_2 \longrightarrow 2H_2O$$

When supply of fuel gases stops, the working of cell stops. The fuel cell works at a temperature so that produced water forms vapours. This fuel cell is used in space vehicles. The water vapours condense (کثیف ہونا) and liquid water is used by an astronaut (خلا نورد).

A number of cells are connected together to generate many kilowatts of power.

EXERCISE

Q.1 Multiple choice questions. For each question there are four possible answers a, b, c and d. Choose the one you consider correct.

(i) The cathodic reaction in the electrolysis of dil H_2SO_4 with Pt electrodes is
(a) Reduction (b) Oxidation
(c) Both oxidation and reduction (d) Neither oxidation or reduction

(ii) Which of the following statements is correct about galvanic cell?
(a) Anode is negatively charged (b) Reduction occurs at anode
(c) Cathode is positively charge (d) Reduction occurs at cathode

(iii) Stronger the oxidizing agent, greater is the:
(a) oxidation potential (b) reduction potential
(c) redox potential (d) E.M.F of cell

(iv) If the salt bridge is not used between two half cells, then the voltage.
(a) Decrease rapidly (b) Decrease slowly
(c) Does not change (d) Drops to zero

(v) If a strip of Cu metal is placed in a solution of $FeSO_4$
(a) Cu will be precipitated out (b) Fe is precipitated out
(c) Cu and Fe both dissolve (d) No reaction take place

Answer: (i) a (ii) d (iii) b (iv) d (v) b

Q.2 Fill in the blank.

(i) The oxidation number of O-atom is ______ in OF_2 and is ______ in H_2O_2.

(ii) Conductivity of metallic conductors is due to the flow of ______ while that of electrolytes is due to flow of ______.

(iii) Reaction taking place at the ____ is termed as oxidation and at the ________ is called as reduction.

(iv) ______is set up when a metal is dipped in its own ions.

(v) Cu metal _____ on the Cu-cathode when electrolysis is performed for $CuSO_4$ solution with Cu-cathodes.

(vi) The reduction potential of Zn is ______ volts and its oxidation potential is ______ volts.

(vii) In a fuel cell, ______ react together in the presence of _______.

Answer: (i) +2, -1 (ii) electrons, ions (iii) anode, cathode (iv) electrode potential (v) deposits (vi) -0.76, +0.76 (vii) H_2 & O_2, KOH

Q.3 Mark the following statements true or false.

(i) In electrolytic conduction, electrons flow through the electrolyte.

(ii) In the process of electrolysis, the electrons in the external circuit flow from cathode to anode.

(iii) Sugar is a non-electrolyte in solid form and when dissolved in water will allow the passage of an electric current.

(iv) A metal will only allow the passage of an electric current when it is in cold state.

(v) The electrolytic products of aqueous copper (II) chloride solution are copper and chlorine.

(vi) Zinc can displace iron form its solution.

(vii) S.H.E. acts as cathode when connected with Cu-electrode.

(viii) A voltaic cell produces electrical energy at the expense of chemical energy.

(ix) Lead storage battery is not a reversible cell.

(x) Cr changes its oxidation number when $K_2Cr_2O_7$ is reacted with HCl.

Answer: (i) false (ii) false (iii) false (iv) false (v) true (vi) true (vii) false (viii) true (ix) false (x) true

Q.4 (a) Explain the term oxidation number with examples.

(b) Describe the rules used for the calculation of oxidation number of an element in molecules and ions giving examples.

(c) Calculate the oxidation number of chromium in the following compounds.

(i) $CrCl_3$ (ii) $Cr_2(SO_3)_3$ (iii) K_2CrO_4 (iv) $K_2Cr_2O_7$
(v) $Cr0_3$ (vi) Cr_2O_3 (vii) $Cr_2O_7^{-2}$

(d) Calculate the oxidation numbers of the elements underlined in the following compounds.

(i) $Ca(\underline{Cl}O_3)_2$ (ii) $Na_2\underline{C}O_3$ (iii) $Na_3\underline{P}O_4$ (vi) $H\underline{N}O_3$
(v) $Cr_2(\underline{S}O_4)_3$ (vi) $H\underline{P}O_3$ (vii) $K_2\underline{Mn}O_4$

Ans. (a) See Page No.____________, (b) See Page No.____________

(C):— i) $CrCl_3$

O.N of Chromium $= x$
O.N of Chlorine $= -1$

$$[\text{O.N of Cr}] + 3[\text{O.N of Cl}] = 0$$

$$x + 3(-1) = 0$$

$$x - 3 = 0 \quad \text{or} \quad \boxed{x = 3}$$

(ii) $Cr_2(SO_4)_3$

O.N of Cr $= x$
O.N of S $= +6$
O.N of O $= -2$

$$2[\text{O.N of Cr}] + 3[\text{O.N of S}] + 3\times4[\text{O.N of O}] = 0$$

$$2x + 3(6) + 12(-2) = 0$$

$$2x + 18 - 24 = 0 \quad \text{or} \quad 2x = 6 \quad \text{or} \quad \boxed{x = 3}$$

(iii) K_2CrO_4

O.N of K $= 1$, O.N of Cr $= x$
O.N of O $= -2$

$2[O.N\ of\ K] + O.N\ of\ Cr + 4[O.N\ of\ O] = 0$

$2[1] + x + 4(-2) = 0$ or $2 + x - 8 = 0$

$x - 6 = 0$ or $\boxed{x = 6}$

(iv) $K_2Cr_2O_7$

O.N of K = 1 , O.N of Cr = x

O.N of O = -2

$2[O.N\ of\ K] + 2[O.N\ of\ Cr] + 7[O.N\ of\ O] = 0$

$2(1) + 2x + 7(-2) = 0$

$2 + 2x - 14 = 0$ or $2x - 12 = 0$

$\boxed{x = 6}$

(v) CrO_3

O.N of Cr = x

O.N of O = -2

$x + 3[O.N\ of\ O] = 0$

$x + 3(-2) = 0$ or $x - 6 = 0$ or $\boxed{x = 6}$

(vi) Cr_2O_3

O.N of Cr = x

O.N of O = -2

$2[O.N\ of\ Cr] + 3[O.N\ of\ O] = 0$

$2[x] + 3[-2] = 0$

or $2x - 6 = 0$ or $2x = 6$ or $\boxed{x = 3}$

O = −2
Cl = −1
Na = +1
K = +1
[illegible] 5

(vii) $Cr_2O_7^{-2}$

O.N of Cr = x

O.N of O = -2

$2[O.N\ of\ Cr] + 7(O.N\ of\ O) = -2$

$2[x] + 7(-2) = -2$

$2x - 14 = -2$

$2x = 14 - 2$ or $2x = 12$

$\boxed{x = 6}$

(d) (i) $Ca(\underline{Cl}O_3)_2$ NaCl $+1+x=0$, $x=-1$

O.N of Cl = x   O.N of Ca = 2

O.N of O = −2

O.N of Ca + 2[O.N of Cl] + 2×3[O.N of O] = 0

$+2+2x+6(-2)=0$

$2+2x-12=0$ $2x=10$ or $x=5$

(ii) $Na_3\underline{P}O_4$

O.N of Na = 1 , O.N of P = x

O.N of O = −2

3[O.N of Na] + [O.N of P] + 4[O.N of O] = 0

$3(1)+x+4(-2)=0$

$3+x-8=0$ or $x-5=0$ or $x=5$

(iii) $Cr_2(\underline{S}O_4)_3$

O.N of Cr = +3 , O.N of S = x

O.N of O = −2

2[O.N of Cr] + 3[O.N of S] + 3×4[O.N of O] = 0

$2[3]+3x+12(-2)=0$

$6+3x-24=0$ or $3x-18=0$

$3x=18$ or $x=6$

(iv) $K_2\underline{Mn}O_4$

O.N of K = 1 , O.N of Mn = x

O.N of O = −2

2[O.N of K] + [O.N of Mn] + 4[O.N of O] = 0

$2(1)+x+4(-2)=0$ or $2+x-8=0$

or $x-6=0$ or $x=6$

(V) $Na_2\underline{C}O_3$

O.N of Na = +1

O.N of C = x , O.N of O = −2

2[O.N of Na] + (O.N of C) + 3[O.N of O] = 0

$2[1] + x + 3(-2) = 0$ or $2 + x - 6 = 0$

or $x - 4 = 0$ or $x = 4$

(Vi) $H\underline{N}O_3$

O.N of H = 1, O.N of N = x

O.N of O = −2

(O.N of H) + (O.N of N) + 3(O.N of O] = 0

$1 + x + 3(-2) = 0$ or $1 + x - 6 = 0$

or $x - 5 = 0$ or $x = 5$

(Vii) $H\underline{P}O_3$

O.N of H = +1, O.N of P = x

O.N of O = −2

(O.N of H) + (O.N of P) + 3(O.N of O) = 0

$1 + x + 3(-2) = 0$ or $1 + x - 6 = 0$

or $x - 5 = 0$ or $x = 5$

Q.5 Describe the general rules for balancing a redox equation by oxidation number method.

Ans: (a) See page No. 159, 160

(b) Balance the following equations by oxidation number method

i. $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

ii. $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

iii. $Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$

iv $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

v $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Fe_2(SO)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$

vi $HNO_3 + HI \longrightarrow NO + H_2O + I_2$

vii $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

viii $HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$

ix $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$

Ans:- (i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

Write oxidation number of each element

$$\overset{0}{Cu} + \overset{+1\,+5\,-2(3)}{HNO_3} \longrightarrow \overset{+2\;\;+5\,-6}{Cu(NO_3)_2} + \overset{+4\,-4}{NO_2} + \overset{+2\;\;-2}{H_2O}$$

Identify the elements which Change oxidation number and mention the change by an arrow

$-2\bar{e}$ (oxidation)

$$\overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

$+1\bar{e}$ (reduction)

Cu lost 2 electrons and N gained 1-electron
To balance the loss and gain of electron, we multiply Cu with one and HNO_3 with 2

$$Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$$

Balance the rest of equation by inspection

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(ii) $Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$

Write oxidation number of each element

$$\overset{0}{Zn} + \overset{+1\,+5\,-2(3)}{HNO_3} \longrightarrow \overset{+2\;\;+5\,-2(3)}{Zn(NO_3)_2} + \overset{+2\;-2}{NO} + \overset{+1\;\;-2}{H_2O}$$

Identify the elements which Change their oxidation number

$-2\bar{e}$ (oxidation)

$$\overset{0}{Zn} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Zn}(NO_3)_2 + \overset{+2}{N}O + H_2O$$

$+3\bar{e}$ (reduction)

Zn lost 2 electrons and N gained 3 electrons
To balance the loss and gain of electron we multiply

Zn by 3 and HNO_3 by 2.

$$3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + NO + H_2O$$

Balance the rest of equation by inspection

$$3Zn + 4\times2\,HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

$$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

(iii) $Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$

Write oxidation number of each element

$$\overset{0}{Br_2} + \overset{+1\,-2\,+1}{NaOH} \longrightarrow \overset{+1\,-1}{NaBr} + \overset{+1\,+5\,-2}{NaBrO_3} + \overset{+1}{H_2}\overset{-2}{O}$$

Identify the elements which change their oxidation number and mention the change with an arrow

$-5e^-$ (oxidation)

$$\overset{0}{Br_2} + NaOH \longrightarrow \overset{+1\,-1}{NaBr} + Na\overset{+5}{Br}O_3 + H_2O$$

$+1e^-$ (reduction)

Because Br_2 involves oxidation and reduction, so we write two molecules of Br_2

$$Br_2 + Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$$

To balance the loss and gain of electrons we multiply Br_2 with 5

$$Br_2 + 5Br_2 + NaOH \longrightarrow NaBr + NaBrO_3 + H_2O$$

Balance the rest of equation by inspection

$$6Br_2 + 12NaOH \longrightarrow 10NaBr + 2NaBrO_3 + 6H_2O$$

or $3Br_2 + 6NaOH \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$

(iv) $MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$

Write oxidation number of each element

$$\overset{+4}{Mn}\overset{-2(2)}{O_2} + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Mn}\overset{-1}{Cl_2} + \overset{+1}{H_2}\overset{-2}{O} + \overset{0}{Cl_2}$$

Identify the elements which change their oxidation number and mention the change with arrows.

+2e⁻ (reduction)

$$\overset{+4}{Mn}O_2 + \overset{+1}{H}\overset{-1}{Cl} \longrightarrow \overset{+2}{Mn}Cl_2 + H_2O + \overset{0}{Cl_2}$$

−1ē (oxidation)

To balance loss and gain of electrons we multiply HCl by 2 and MnO_2 by 1

$$MnO_2 + 2HCl \longrightarrow MnCl_2 + H_2O + Cl_2$$

Now balance the remaining atoms by inspection

$$MnO_2 + 2\times2HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

or $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

(v) $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$

Write down oxidation number of each element

$$\overset{+2}{Fe}\overset{+6}{S}\overset{4(-2)}{O_4} + \overset{2(1)}{K_2}\overset{2(6)}{Cr_2}\overset{7(-2)}{O_7} + \overset{2(1)}{H_2}\overset{+6}{S}\overset{4(-2)}{O_4} \longrightarrow \overset{2(+3)}{Fe_2}(SO_4)_3 + \overset{2(+3)}{Cr_2}(SO_4)_3 + \overset{2(+1)}{K_2}SO_4 + \overset{2(+1)}{H_2}\overset{-2}{O}$$

Identify the elements which change their oxidation number and mention the change with arrow.

$-1e^-$ (oxidation)

$$\overset{+2}{Fe}SO_4 + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$$

$+3\bar{e}$ (reduction)

Fe lost 1 electron and Cr gained 3 electrons. To balance the loss and gain of electrons we multiply Fe with 3 and Cr with 1

$$3FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

Balance the rest species by general inspection method without disturbing multiplier as coefficient

$$2 \times 3FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

or $$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

(vi) $HNO_3 + HI \longrightarrow NO + H_2O + I_2$

Write oxidation number of each element

$$\overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} + \overset{+1}{H}\overset{-1}{I} \longrightarrow \overset{+2}{N}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O} + \overset{0}{I_2}$$

Identify the elements which change their oxidation number and mention the change with arrow.

$+3\bar{e}$ (reduction)

$$H\overset{+5}{N}O_3 + H\overset{-1}{I} \longrightarrow \overset{+2}{N}O + H_2O + \overset{0}{I_2}$$

$-1\bar{e}$ (oxidation)

N gained 3 electrons and Iodine lost 1 electro[n]. So we multiply HI with 3 and HNO_3 with 1

$$HNO_3 + 3HI \longrightarrow NO + H_2O + I_2$$

Balance the rest of equation by inspection method without disturbing multiplier as coefficient

$$2HNO_3 + 6HI \longrightarrow 2NO + 4H_2O + 3I_2$$

It is a balanced equation.

(vii) $$Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$$

Write oxidation number of each element

$$\overset{0}{Cu} + \overset{+1\,+6\,-2}{H_2SO_4} \longrightarrow \overset{+2\,+6\,-2}{CuSO_4} + \overset{+4\,-2}{SO_2} + \overset{+1\,-2}{H_2O}$$

Identify the elements which change their oxidation number and mention the change with arrow.

$-2e^-$ (oxidation)

$$\overset{0}{Cu} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$$

$+2e^-$ (reduction)

Cu lost 2 electrons and S gained 2-electrons
Loss and gain of electrons is same. So we balance the equation by general inspection method.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

(viii) $$HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

Write oxidation number of each element

$$\overset{+1\,-1}{HI} + \overset{+1\,+6\,-2}{H_2SO_4} \longrightarrow \overset{0}{I_2} + \overset{+4\,-2}{SO_2} + \overset{+1\,-2}{H_2O}$$

Identify the elements which change their oxidation number and mention the change with arrow.

$$\overset{-1}{HI} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + H_2O$$

$-1e^-$ (oxidation): $HI \to I_2$; $+2e^-$ (reduction): $H_2SO_4 \to SO_2$

To balance the loss and gain of electrons, we multiply HI with 2 and H_2SO_4 with 1.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

Balance the rest of equation by inspection method.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$$

(ix) $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$

Write oxidation number of each element

$$\overset{+1\ -1}{NaCl} + \overset{+1(2)+6-2(4)}{H_2SO_4} + \overset{+4-2(2)}{MnO_2} \longrightarrow \overset{+1(2)+6-2(4)}{Na_2SO_4} + \overset{+2+6-2(4)}{MnSO_4} + \overset{+1(2)-2}{H_2O} + \overset{0}{Cl_2}$$

Identify the elements which change their oxidation number and mention the change with arrow.

$$Na\overset{-1}{Cl} + H_2SO_4 + \overset{+4}{Mn}O_2 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + \overset{0}{Cl_2}$$

$+2e^-$ (reduction): $MnO_2 \to MnSO_4$; $-1e^-$ (oxidation): $NaCl \to Cl_2$

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To balance the loss and gain of electrons, we multiply NaCl with 2 and MnO_2 with 1

$$2NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$$

Balance the rest of equation by inspection method.

$$2NaCl + 2H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

It is a balanced equation.

Q.6 (a) Describe the general rules for balancing a redox equation by ion-electron method.

(b) Balance the following ionic equations by ion-electron method.

(i)	$Fe^{+3} + Sn^{+2}$	→	$Fe^{+2} + Sn^{+4}$	
(ii)	$MnO_4^{-1}(aq) + C_2O_4^{-2}(aq)$	→	$Mn^{+2}(aq) + CO_2(g)$	
(iii)	$Cr_2O_7^{-2} + Cl^{-1}$	→	$2Cr^{+3} + 3Cl_2$	
(iv)	$Cu + NO_3^{-1}$	→	$Cu^{+2} + 2NO_2$	
(v)	$Cr_2O_7^{-2} + Fe^{+2}$	→	$Cr^{+3} + Fe^{+3}$	(acidic media)
(vi)	$S_2O_3^{-2} + OCl^{-1}$	→	$Cl^{-} + S_4O_6^{-2}$	(acidic media)
(vii)	$IO_3^{-1} + AsO_3^{-3}$	→	$I^{-} + AsO_4^{-3}$	(acidic media)
(viii)	$Cr^{+3} + BiO_3^{-1}$	→	$Cr_2O_7^{-2} + 3Bi^{+3}$	(acidic media)
(ix)	$H_3AsO_3 + Cr_2O_7^{-2}$	→	$3H_3AsO_4 + 2Cr^{+3}$	(acidic media)
(x)	$CN^{-} + MnO_4^{-1}$	→	$CNO^{-} + MnO_2(s)$	(basic media)

Answer: (a) see page No 161, 162

(b) (i):- $Fe^{+3} + Sn^{+2} \longrightarrow Fe^{+2} + Sn^{+4}$

(1) Split the equation into two half reactions.

$$Sn^{+2} \longrightarrow Sn^{+4} \quad \text{(oxidation)}$$
$$Fe^{+3} \longrightarrow Fe^{+2} \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction. Add $2\bar{e}$ on R.H.S to balance the charges

$$Sn^{+2} \longrightarrow Sn^{+4} + 2\bar{e} \text{ ——— (A)}$$

(3) Balancing of reduction half reaction. Add $1\bar{e}$ on L.H.S to balance the charges

$$Fe^{+3} + 1\bar{e} \longrightarrow Fe^{+2} \text{ ——— (B)}$$

(4) Multiply eq (A) by 1 and eq (B) by 2 and then add.

$$Sn^{+2} \longrightarrow Sn^{+4} + 2\bar{e}$$
$$2Fe^{+3} + 2\bar{e} \longrightarrow 2Fe^{+2}$$

$$Sn^{+2} + 2Fe^{+3} \longrightarrow Sn^{+4} + 2Fe^{+2}$$

It is a balanced equation.

(ii) $M\bar{n}O_4 + C_2\bar{O}_4^{2} \longrightarrow Mn^{+2} + CO_2$

(1) Split the equation into two half reactions

$$C_2O_4^{-2} \longrightarrow CO_2 \text{ (oxidation)}$$

$$MnO_4^{-1} \longrightarrow Mn^{+2} \text{ (reduction)}$$

(2) Balancing oxidation half reaction. Multiply R.H.S by.

$$C_2O_4^{-2} \longrightarrow 2CO_2$$

Add $2\bar{e}$ on R.H.S to balance the charges

$$C_2O_4^{-2} \longrightarrow 2CO_2 + 2\bar{e} \text{ ——— (A)}$$

(3) Balancing reduction half reaction. Add $4H_2O$ on R.H.S and $8H^+$ on L.H.S

$$MnO_4^{-1} + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$$

Add $5\bar{e}$ on L.H.S to balance the charges on both side

$$MnO_4^{-1} + 8H^+ + 5\bar{e} \longrightarrow Mn^{+2} + 4H_2O \text{ ——— (B)}$$

(4) To balance loss and gain of electrons, multiply eq (A) by 5 and eq (B) by 2 and then add

$$5C_2O_4^{-2} \longrightarrow 10CO_2 + 10\bar{e}$$

$$2MnO_4^{-1} + 16H^+ + 10\bar{e} \longrightarrow 2Mn^{+2} + 8H_2O$$

$$5C_2O_4^{-2} + 2MnO_4^{-1} + 16H^+ \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$

It is a balanced equation

(iii) $Cr_2O_7^{-2} + Cl^{-1} \longrightarrow Cr^{+3} + Cl_2$

(1) split the equation into two half reactions

$$Cl^{-1} \longrightarrow Cl_2 \text{ (oxidation)}$$

$$Cr_2O_7^{-2} \longrightarrow Cr^{+3} \text{ (reduction)}$$

(2) Balancing of oxidation half reaction.
Multiply L.H.S by 2 and add $2\bar{e}$ on R.H.S

$$2\bar{Cl} \longrightarrow Cl_2 + 2\bar{e} \quad \text{------} (A)$$

(3) Balancing of reduction half reaction.
Multiply R.H.S by 2, add $7H_2O$ on R.H.S and add $14H^+$ on L.H.S to balance number of atoms

$$Cr_2O_7^{-2} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O$$

Add $6\bar{e}$ on L.H.S to balance charges

$$Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{+3} + 7H_2O \quad \text{------} (B)$$

(4) To balance loss and gain of electrons, multiply eq (A) by 3 and add it in eq (B)

$$6\bar{Cl} \longrightarrow 3Cl_2 + 6\bar{e}$$

$$Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{+3} + 7H_2O$$

$$6\bar{Cl} + Cr_2O_7^{-2} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$$

(iv) $Cu + \bar{NO_3} \longrightarrow Cu^{+2} + NO_2$

(1) split the equation into two half reactions.

$$Cu \longrightarrow Cu^{+2} \quad \text{(oxidation)}$$

$$\bar{NO_3} \longrightarrow NO_2 \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction.
Add $2\bar{e}$ on R.H.S to balance the charges

$$Cu \longrightarrow Cu^{+2} + 2\bar{e} \quad \text{------} (A)$$

(3) Balancing of reduction half reaction

Add [illegible] 2 [illegible] H.S and 2 H^+ on L.H.S

[illegible] H^+ [illegible] $\rightarrow NO_2 + H_2O$

Add [illegible] $\bar{e}$ on [illegible] S to balance the charges

$NO_3^- + 2H^+ + 1\bar{e} \longrightarrow NO_2 + H_2O$ —— (B)

(4) To balance loss and gain of electrons, multiply eq (B) by 2 and add it in eq (A)

$$2NO_3^- + 4H^+ + 2\bar{e} \longrightarrow 2NO_2 + 2H_2O$$

$$Cu \longrightarrow Cu^{+2} + 2\bar{e}$$

$$2NO_3^- + 4H^+ + Cu \longrightarrow 2NO_2 + 2H_2O + Cu^{+2}$$

(v) $Cr_2O_7^{-2} + Fe^{+2} \longrightarrow Cr^{+3} + Fe^{+3}$

(1) Split the equation into two half reactions.

$$Fe^{+2} \longrightarrow Fe^{+3} \quad \text{(oxidation)}$$

$$Cr_2O_7^{-2} \longrightarrow Cr^{+3} \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction

Add $1\bar{e}$ on R.H.S to balance the charges

$$Fe^{+2} \longrightarrow Fe^{+3} + 1\bar{e} \quad \text{—— (A)}$$

(3) Balancing of reduction half reaction

Multiply R.H.S by 2, Add $7H_2O$ on R.H.S

$14H^+$ on L.H.S to balance the atoms

$$Cr_2O_7^{--} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O$$

Add $6\bar{e}$ on L.H.S to balance the charges

$$Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{+3} + 7H_2O \quad \text{—— (B)}$$

(4) Multiply eq (A) by 6 and add it in eq (B)

$$6Fe^{+2} \longrightarrow 6Fe^{+3} + 6e^-$$

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$$

$$6Fe^{+2} + Cr_2O_7^{-2} + 14H^+ \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O$$

It is a balanced equation.

(Vi) $S_2O_3^{-2} + OCl^{-1} \longrightarrow Cl^- + S_4O_6^{-2}$ (acidic media)

(1) Split the equation into two half reactions.

$$S_2O_3^{-2} \longrightarrow S_4O_6^{-2} \quad \text{(oxidation)}$$

$$OCl^- \longrightarrow Cl^- \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction

Multiply L.H.S by 2 and add $2e^-$ on R.H.S

$$2S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2e^- \quad \text{---- (A)}$$

(3) Balancing of reduction half reaction.

Add H_2O on R.H.S and $2H^+$ on L.H.S

$$OCl^- + 2H^+ \longrightarrow Cl^- + H_2O$$

Add $2e^-$ on L.H.S to balance the charges

$$OCl^- + 2H^+ + 2e^- \longrightarrow Cl^- + H_2O \quad \text{------ (B)}$$

(4) Because loss and gain of electrons is equal, so add eq (A) and eq (B)

$$2S_2O_3^{-2} \longrightarrow S_4O_6^{-2} + 2e^-$$

$$OCl^- + 2H^+ + 2e^- \longrightarrow Cl^- + H_2O$$

$$2S_2O_3^{-2} + OCl^- + 2H^+ \longrightarrow S_4O_6^{-2} + Cl^- + H_2O$$

It is a balanced equation.

(vii) $IO_3^- + AsO_3^{-3} \longrightarrow I^- + AsO_4^{-3}$

(1) Split the equation into two half reactions

$$AsO_3^{-3} \longrightarrow AsO_4^{-3} \text{ (oxidation)}$$
$$IO_3^- \longrightarrow I^- \text{ (reduction)}$$

(2) Balancing of oxidation half reaction

Add H_2O on L.H.S and $2H^+$ on R.H.S

$$AsO_3^- + H_2O \longrightarrow AsO_4^- + 2H^+$$

Add $2e^-$ on R.H.S to balance the charges

$$AsO_3^- + H_2O \longrightarrow AsO_4^- + 2H^+ + 2e^- \quad \text{—— (A)}$$

(3) Balancing of reduction half reaction. Add $3H_2O$ on R.H.S and $6H^+$ on L.H.S

$$IO_3^- + 6H^+ \longrightarrow I^- + 3H_2O$$

Add $6e^-$ on L.H.S to balance the charges

$$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + 3H_2O \quad \text{—— (B)}$$

(4) Multiply eq (A) by 3 and then add it in eq (B)

$$3AsO_3^- + 3H_2O \longrightarrow 3AsO_4 + 6H^+ + 6e^-$$
$$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + 3H_2O$$

$$3AsO_3^- + IO_3^- \longrightarrow 3AsO_4^- + I^-$$

It is a balanced equation.

(viii) $Cr^{+3} + BiO_3^{-1} \longrightarrow Cr_2O_7^{-2} + Bi^{+3}$

(1) Split the equation into two half reactions

$$Cr^{+3} \longrightarrow Cr_2O_7^{-2} \quad \text{(oxidation)}$$

$$BiO_3^{-1} \longrightarrow Bi^{+3} \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction. Multiply L.H.S by 2, add $7H_2O$ on L.H.S and $14H^+$ on R.H.S

$$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2} + 14H^+$$

Now add $6\bar{e}$ on R.H.S to balance the charges

$$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \text{ ——— (A)}$$

(3) Balancing of reduction half reaction.

Add $3H_2O$ on R.H.S and $6H^+$ on L.H.S

$$BiO_3^{-1} + 6H^+ \longrightarrow Bi^{+3} + 3H_2O$$

Now add $2\bar{e}$ on L.H.S

$$BiO_3^{-1} + 6H^+ + 2\bar{e} \longrightarrow Bi^{+3} + 3H_2O \text{ ——— (B)}$$

(4) Multiply eq (B) by 3 and then add in eq (A)

$$3BiO_3^{-1} + 18H^+ + 6\bar{e} \longrightarrow 3Bi^{+3} + 9H_2O$$

$$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2} + 14H^+$$

$$3BiO_3^{-1} + 2Cr^{+3} + 4H^+ \longrightarrow 3Bi^{+3} + Cr_2O_7^{-2} + 2H_2O$$

It is a balanced equation.

(ix) $H_3AsO_3 + Cr_2O_7^{-2} \longrightarrow H_3AsO_4 + Cr^{+3}$

(1) split the equation into two half reactions

$$H_3AsO_3 \longrightarrow H_3AsO_4 \quad \text{(oxidation)}$$

$$Cr_2O_7^{-2} \longrightarrow Cr^{+3} \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction. Add one H_2O on L.H.S and $2H^+$ on R.H.S

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+$$

Now add $2\bar{e}$ on R.H.S to balance the charges

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2\bar{e} \quad \text{---} (A)$$

(3) Balancing of reduction half reaction

Multiply R.H.S by 2, add $7H_2O$ on R.H.S and $14H^+$ on L.H.S

$$Cr_2O_7^{-2} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O$$

Now add $6\bar{e}$ on L.H.S to balance the charges

$$Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{+3} + 7H_2O \quad \text{---} (B)$$

(4) Multiply eq (A) by 3 and then add in eq (B)

$$3H_3AsO_3 + 3H_2O \longrightarrow 3H_3AsO_4 + 6H^+ + 6\bar{e}$$

$$Cr_2O_7^{-2} + 14H^+ + 6\bar{e} \longrightarrow 2Cr^{+3} + 7H_2O$$

$$3H_3AsO_3 + Cr_2O_7^{-2} + 8H^+ \longrightarrow 3H_3AsO_4 + 2Cr^{+3} + 4H_2O$$

It is a balanced equation.

(X) $C\bar{N} + MnO_4^{-1} \longrightarrow C\bar{NO} + MnO_2$ (basic media)

(1) Split the equation into two half reactions

$$C\bar{N} \longrightarrow C\bar{NO} \quad \text{(oxidation)}$$

$$M\bar{nO_4} \longrightarrow MnO_2 \quad \text{(reduction)}$$

(2) Balancing of oxidation half reaction. Add $2\bar{OH}$ on L.H.S and one H_2O on R.H.S to balance the

Oxygen atoms on both sides

$$\bar{CN} + 2\bar{OH} \longrightarrow C\bar{NO} + H_2O$$

Now add $2\bar{e}$ on R.H.S to balance the charges

$$\bar{CN} + 2\bar{OH} \longrightarrow C\bar{NO} + H_2O + 2\bar{e} \quad \text{---- (A)}$$

(3) Balancing of reduction half reaction

$$Mn\bar{O_4} \longrightarrow MnO_2$$

Add $4\bar{OH}$ on R.H.S and $2H_2O$ on L.H.S to balance oxygen atoms on both sides

$$Mn\bar{O_4} + H_2O \longrightarrow MnO_2 + 4\bar{OH}$$

Add $3\bar{e}$ on L.H.S to balance the charges

$$Mn\bar{O_4} + 2H_2O + 3\bar{e} \longrightarrow MnO_2 + 4\bar{OH} \quad \text{---- (B)}$$

(4) Multiply eq(A) by 3 and eq(B) by 2 and then add the two equations

$$3\bar{CN} + 6\bar{OH} \longrightarrow 3C\bar{NO} + 3H_2O + 6\bar{e}$$

$$2Mn\bar{O_4} + 4H_2O + 6\bar{e} \longrightarrow 2MnO_2 + 8\bar{OH}$$

$$3\bar{CN} + 2Mn\bar{O_4} + H_2O \longrightarrow 3C\bar{NO} + 2MnO_2 + 2\bar{OH}$$

It is a balanced equation

Q.7 Describe the electrolysis of molten sodium chloride and a concentrated solution of sodium chloride.

Ans. See on Page No. 167, 168

Q.8 What is the difference between single electrode potential and standard electrode potential? How can it be measured? Give its importance.

Ans. See on Page No. 172, 175

Q.9 Outline the important applications of electrolysis. Write the electrochemical reactions involved therein. Discuss the electrolysis of $CuSO_4$, using Cu-electrodes and $AgNO_3$ solution using Ag electrode.

Ans. See on Page No. 167, 168, 169

Electrolysis of $AgNO_3$:- During electrolysis of $AgNO_3$ solution following reactions take place.

$$Ag_{(s)} \longrightarrow Ag^+_{(aq)} + \bar{e} \quad \text{(at anode)}$$

$$Ag^+ + \bar{e} \longrightarrow Ag_{(s)} \quad \text{(at cathode)}$$

Q.10 Describe the construction and working of standard hydrogen electrode.

Answer:- see page No. 173, 174

Q.11 : Is the reaction $Fe^{3+} + Ag \rightarrow Fe^{2+} + Ag^+$ spontaneous? If not write spontaneous reaction involving these species.

Answer:- The reaction $Fe^{+3} + Ag \longrightarrow Fe^{+2} + Ag^+$ is non-spontaneous because emf of cell is negative.

$$Fe^{+3} + \bar{e} \longrightarrow Fe^{+2}, \quad E^\circ_{red} = -0.44\,V$$

$$Ag \longrightarrow Ag^+ + \bar{e}, \quad E_{oxi} = -0.799\,V$$

$$Fe^{+3} + Ag \longrightarrow Fe^{+2} + Ag^+, \quad E_{cell} = -1.239\,V$$

Since cell voltage or emf is negative, so reaction is non-spontaneous. By reversing the electrodes, the reaction becomes spontaneous.

$$Fe^{+2} + Ag^+ \longrightarrow Fe^{+3} + Ag$$

Q.12 Explain the difference between
(a) Ionization and electrolysis (b) Electrolytic cell and; voltaic cell
(c) Conduction through metals and molten electrolytes.

Answer:- see page No. 156, 157, 164, 165

Q.13 Describe a galvanic cell explaining the functions of electrodes and the salt bridge.

Ans:- See page No. 185

Q.14 Write comprehensive notes on:

(a) Spontaneity of oxidation reduction reactions

(b) Electrolytic conduction.

(c) Alkaline, silver oxide and nickel-cadmium batteries, fuel cell

(d) Lead accumulator, its desirable and undesirable features

Ans:- see page No 178, 184, 185.

Q15. Will the reaction be spontaneous for the following set of half reactions. What will be the value of E_{cell}?

i. Cr^{+3} (aq) +3$\bar{e}$ ⟶ Cr (s)

ii. MnO_2 (s) + 4H^+ +2e^- ⟶ Mn^{2+} (aq) + 2H_2O(l)

(Standard reduction pote...al for reaction (i) = -0.74V and for the reaction (ii) = +1.28V).

Ans:- We reverse the first half reaction

$$Cr_{(s)} \longrightarrow Cr^{+3} + 3\bar{e}, \quad E^\circ_{oxi} = 0.74V$$

$$MnO_2 + 4H^+ + 2\bar{e} \longrightarrow Mn^{+2} + 2H_2O, \quad E^\circ_{red} = 1.28V$$

$$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$$

$$= 0.74 + 1.28 = 2.02 V$$

Since E°_{cell} is positive, so cell reaction is spontaneous and E°_{cell} is 2.02V

Q16. Explain the following with reasons.

(a) A porous plate or a salt bridge is not required in lead storage cell.

(b) The standard oxidation potential of Zn is 0.76 V and its reduction potential is-0.76V.

(c) Na and K can displace hydrogen from acids but Pt,Pd and Cu can not.

(d) The equilibrium is set up between metal atoms of electrode and ions of metal in a cell.

(e) A salt bridge maintains the electrical neutrality in the cell.

(f) Lead accumulator is a chargeable battery.

(g) Impure Cu can be purified by electrolytic process.

(h) SHE acts as anode when connected with Cu electrode but as cathode with Zn electrode.

Answer:- (a) A salt bridge has two main functions

(i) It keeps electrical contact between two half cells.
(ii) It maintains electrical neutrality in two solutions by diffusional exchange of ions. Because in lead storage cell, both half cells are dipped in 30% H_2SO_4; So there is no need of electrical neutrality. Hence salt bridge is not required in lead storage battery.

(b):- According to recommendations of IUPAC, the standard electrode potential is given in reduction mode. By changing the mode, the magnitude of potential remains same but sign is reversed. It is the reason that

$$Zn^{+2} + 2\bar{e} \longrightarrow Zn_{(s)}, \quad \overset{\circ}{E}_{red} = -0.76V$$

$$Zn_{(s)} \longrightarrow Zn^{+2} + 2\bar{e}, \quad \overset{\circ}{E}_{red} = +0.76V$$

(c) Na and K have low value of reduction potential and they are above the hydrogen in electrochemical series. It is the reason they can displace H_2 from acids. On other hand Pt, Pd, and Cu have high value of reduction potentials and are below hydrogen in electrochemical series. ∴ Hence they do not displace H_2 from acids

(d) see page No. 173

(e) see page No. 171

(f) See page No. 182, 183

(g) see page No. 169

(h) See page No. 174

گلدستہ ڈاٹ پی کے کی جانب سے خوش آمدید

السلام علیکم ورحمتہ اللہ وبرکاتہ

مختصر تعارف

کافی عرصہ سے خواہش تھی کہ ایک ایسی ویب سائٹ بناؤں جس پر طالب العلموں کیلئے کچھ تعلیمی مواد جمع کر سکوں۔ اللہ تعالیٰ نے توفیق دی اور میں نے ایک سال کی محنت کے بعد ایک سائٹ "گلدستہ ڈاٹ پی کے" کے نام سے بنائی جو کہ قرآن و حدیث، اصلاحی، دلچسپ، تاریخی قصے واقعات، اُردو انگلش تحریریں، شاعری و اقوالِ زریں، F.Sc اور B.Sc کے مضامین کے آن لائن نوٹس، اسلامک، تفریحی، معلوماتی وال پیپرز، حمد و نعت، فرقہ واریت سے پاک اسلامی بیانات، پنجابی نظمیں و ترانے اور کمپیوٹر و انٹرنیٹ کی دنیا کے بارے میں ٹپس، آن لائن کمائی کرنے کے مستند طریقہ کار۔ کے ساتھ ساتھ اور بھی بہت سی چیزوں پر مشتمل ہے۔ اور انشاء اللہ میں مزید وقت کے ساتھ ساتھ اضافہ کرتا جاؤں گا۔ آپ کی قیمتی رائے کی ضرورت ہے۔ عدنان شفیق

اہم نوٹ

ذیل میں جو نوٹس مہیا کیے گئے ہیں وہ کئی گھنٹوں کی لگاتار محنت کے مرتب ہوئے ہیں۔ اور آپ کو بالکل مفت مہیا کر رہے کیے جا رہے ہیں۔آپ سے ان کی قیمت صرف اتنی سی متوقع ہے کہ ایک بار درودِ ابراھیمی اپنی زبان سے ادا کر دیں۔

اللَّهُمَّ صَلِّ عَلَىٰ مُحَمَّدٍ وَعَلَىٰ آلِ مُحَمَّدٍ كَمَا صَلَّيْتَ عَلَىٰ

إِبْرَاهِيمَ وَعَلَىٰ آلِ إِبْرَاهِيمَ إِنَّكَ حَمِيدٌ مَجِيدٌ

اللَّهُمَّ بَارِكْ عَلَىٰ مُحَمَّدٍ وَعَلَىٰ آلِ مُحَمَّدٍ كَمَا بَارَكْتَ عَلَىٰ

إِبْرَاهِيمَ وَعَلَىٰ آلِ إِبْرَاهِيمَ إِنَّكَ حَمِيدٌ مَجِيدٌ