12

ELECTROCHEMISTRY

After completing this lesson, you will be able to:

- Define cathode, anode, electrode potential and S.H.E. (Standard Hydrogen Electrode).
- Define the standard electrode potential of an electrode.
- Give the characteristics of Redox reaction.
- Define cell potential, and describe how it is determined.
- Determine the oxidation number of an atom of any element in a pure substance
- Define oxidation and reduction in terms of a change in oxidation number
- . Use the oxidation-number change method to balance redox equation.
- Balance redox reaction into oxidation and reduction half reaction.
- When given an unbalanced redox equation, use the half r3eaction method to balance the equation
- Identify the substance oxidized and the substance reduced in a dry cell.
- Describe the reaction that occurs when a lead storage battery is recharged.
- Explain how a fuel cell produces electrical energy.
- Use the activity series of metals to predict the products of single replacement reactions.

Reading

INTRODUCTION

Electrochemistry deals with wide range of important phenomena, many of which depend on the transfer of electrons from one substance to another. **Electrochemistry is the branch of chemistry, which deals with inter-conversion of electrical energy and chemical energy.** Electrochemical processes are redox (oxidation - reduction) reactions in which the energy released by a spontaneous reaction is converted to electricity or in which electrical energy is used to cause a non-spontaneous reaction to occur. Redox reaction involves transfer of electrons from one substance to another. It deals with efficient sources of energy such as batteries, fuel cells etc. Chemistry of these devices will be discussed in this chapter.

12.1 OXIDATION - REDUCTION CONCEPTS

When happens when an unprotected iron object is left in moist atmosphere for few days,? What type of chemical change occurs?

You have learned in your grade IX-X, the definition of oxidation and reduction in terms of loss or gain of oxygen or hydrogen or electrons. Here we will discuss oxidation and reduction in terms of loss or gain of electrons by a chemical reaction in which this change can be observed with naked eyes.

Example 12.2

Calculate the oxidation number of Cr in $K_2 Cr_2 O_7$

Solution

K_2	Cr_2	O_7	
(+1) 2 +	(x) 2 +	(-2) 7	
+ 2 +	2x -	14	= 0
+	2x -	12	= 0
		2 x	=12
		x	= 12/2
		x	= 6

Thus oxidation number of Cr in $K_2 Cr_2 O_7$ is +6.

I-A = +1
II-A = +2
III-A = +3

F = -1
O = -2
H = -1 (with metal)
H = +1 (with non-metal)

Example 12.3

What is the oxidation state of S in SO_4^{-2} ion.

Solution

In SO_4^{-2} ion oxidation state of O is –2. If x is the oxidation state of S then,

x	+	4(-2)	=	-2
x	-	8	=	-2
		x	=	6

Self Check Exercise 12.1

Identify the compound in which oxidation number of Fe is +3

FeO, Fe_3O_4, Fe_2O_3.

Oxidation-Reduction in Terms of Change in Oxidation Number

We have already defined oxidation and reduction in terms of transfer of one or more electrons in section 12.1. We can also define oxidation and reduction in terms of change in oxidation number. For this purpose, consider the following reaction.

$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

Assign oxidation number to all the atoms involved in this reaction and write it over their symbols

$$\overset{0}{2N}a_{(s)} + \overset{0}{C}l_{2(g)} \longrightarrow \overset{+1}{2Na}\overset{-1}{C}l_{(s)}$$

Oxidation number of which element is increasing in this reaction? Oxidation numbers of which element is decreasing in this reaction.

Notice that the oxidation number of Na is zero because it is in the elemental form. In this reaction Na undergoes a change in oxidation number from zero in Na to +1 in NaCl. Thus this change can be accounted for by a loss of one electron per Na atom. This is oxidation.

$$\overset{0}{2Na}_{(s)} \longrightarrow \overset{+1}{2Na} + 2e^-$$

On the other hand, each Cl atom in Cl_2 molecule changes its oxidation number from zero in Cl_2 to –1 in NaCl. In this change gain of one electron per Cl atom occurs. This is reduction.

The Student should be guided to develop skills to interpret information in various ways.

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$\overset{0}{Cl_2} + 2e^- \longrightarrow 2\overset{-1}{Cl}$

Thus we can also define oxidation and reduction in terms of change in oxidation number.

Oxidation is an increase in oxidation number (a loss of electrons).

Reduction is a decrease in oxidation number (a gain of electrons).

Example 12.4

Identify the elements undergoing oxidation or reduction in terms of change in oxidation number in the following reaction which takes place in the combustion of natural gas.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O\ (l)$$

Solution

oxidation number to all the atoms involved in this reaction.

$$\overset{-4}{C}H_{4(g)} + 2\overset{0}{O}_{2(g)} \longrightarrow \overset{+4}{C}O_{2(g)} + 2\overset{2(+1)}{H_2}\overset{-2}{O}(l)$$

The C changes its oxidation number from –4 in CH_4 to +4 in CO_2. This is 8 electrons loss. This means C undergoes an increase in oxidation number. On the other hand, O changes its oxidation number from zero in O_2 to –2 in H_2O and CO_2. Each oxygen atom gains two electrons and therefore it is reduced.

We can say that,

i) C is oxidized because there has been an increase in its oxidation number.

ii) O is reduced because there has been a decrease in its oxidation number.

Example 12.5

Identify the substance oxidized and the substance reduced in the dry cell.

Solution

Following reaction can take place in dry cell.

At Anode, $Zn \longrightarrow Zn^{+2} + 2e^-$

At Cathode,

$$2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$$

Anode reaction indicates that Zn metal loses 2 electrons, therefore it undergoes oxidation. For determining the substance reduced, assign oxidation number to all the atoms involved in the reaction that occurs at cathode.

$$2[\overset{-3(+1)4}{N}H_4]^{+1} + 2\overset{(-2)2}{Mn}O_2 + 2e^- \longrightarrow \overset{2(+3)6}{Mn_2}\overset{(+1)3}{O_3} + 2\overset{2(-3)1}{N}H_3 + H_2\overset{-2}{O}$$

In this reaction Mn changes it oxidation number from +4 in MnO_2 to +3 in Mn_2O_3. This means that each Mn gains one electron, therefore undergoes reduction. Thus the substance reduced is Mn.

Self Check Exercise 12.2

Use the oxidation number change method to identify the atoms undergoing oxidation or reduction in the following redox reactions.

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$$

$$C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O(l)$$

12.1.3 Balancing Redox Equations by Oxidation Number Change Method

It is based on the principle that in any redox reaction, the total number of electrons lost by one element must be equal to the total number of electrons gained by another element. This method can be understood by the following example.

Example 12.6

Balance the following equation by oxidation number method.

$$P + HNO_3 + H_2O \longrightarrow H_3PO_4 + NO$$

Solution

Step1: Assign oxidation number to all the atoms involved in the equation.

$$\overset{0}{P} + \overset{+1+5(+2)3}{HNO_3} + \overset{(+1)2-2}{H_2O} \longrightarrow \overset{3(+1)+5(-2)4}{H_3PO_4} + \overset{+2-2}{NO}$$

Step2: Identify the elements undergoing a change in oxidation number

The P goes from zero to +5 oxidation state in H_3PO_4 . This is a 5 electron change. N in HNO_3 goes from +5 to +2 oxidation state in NO. This is 3 electron change.

Step3: Draw a bridge between the same atoms whose oxidation number have changed, Indicate this change by the number of electrons gained or lost by each element.

$$\overset{0}{P} + \overset{+5}{NHO_3} \longrightarrow H_3\overset{+5}{P}O_4 + \overset{+2}{NO}$$

$+3\bar{e}$ (gained) $\quad -5\bar{e}$ (lost)

Step4: Equalize the number of electrons lost and gained by multiplying the two numbers, by a small whole number which produces a common number. Use these multipliers as coefficients of the respective substance.

To balance a $3e^-$ gain against a $5e^-$ loss, we need to multiply $3e^-$ gain by 5 and $5e^-$ loss by 3. This will equalize the number of electrons gained and lost.

$$\overset{0}{P} + \overset{+5}{NHO_3} \longrightarrow H_3\overset{+5}{P}O_4 + \overset{+2}{NO}$$

$+3\bar{e} \times 5 = +15\bar{e}$ (gained) $\quad -5\bar{e} \times 3 = -15\bar{e}$ (lost)

Multiply the coefficients of P and that of H_3PO_4 by 3. Whereas multiply coefficients of HNO_3 and NO by 5.

$$3P + 5HNO_3 + H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Now the coefficient of H_3PO_4 and NO should not be changed hereafter it.

Step5: Balance the rest of the equation by inspection method. Balance the atoms other than oxygen and hydrogen first, then oxygen atoms and finally hydrogen atoms.

The student should be guided to demonstrate this knowledge in various ways.

To balance oxygen atoms multiply coefficient of H_2O by 2.

$$3P + 5HNO_3 + 2H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Inspect the equation, it is balanced.

Self Check Exercise 12.3

Using the oxidation number method balance the following equation.

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

12.1.4 Breaking a Redox Reaction into Oxidation and Reduction Reactions

A redox reaction in aqueous reaction can be separated into two half-reactions. One, half reaction represents oxidation and the other represents reduction. A **half-reaction** is the part of an overall redox reaction that represents, separately, either an oxidation or a reduction. Consider the following reaction which is used to analyze iron ore for its iron content.

$$MnO_4^{-1} + Fe^{+2} \xrightarrow{Acid} Fe^{+3} + Mn^{+2}$$

Step1: Write oxidation number of all the atoms involved in this reaction

$$\left[\overset{+7\ (-2)4}{MnO_4}\right]^{-1} + Fe^{+2} \xrightarrow{Acid} Fe^{+3} + Mn^{+2}$$

Identify and write equation for the half-reactions.

Notice that the Mn goes from +7 oxidation state in MnO_4^- to +2. The reduction half-reaction must involve species containing Mn.

$MnO_4^{-1} \longrightarrow Mn^{+2}$ (Reduction half – reaction)

Iron goes from+2 to +3 oxidation state. The oxidation half-reaction must involve Fe^{+2} and Fe^{+3}.

$Fe^{+2} \longrightarrow Fe^{+3}$ (Oxidation half – reaction)

Example 12.7

Split the following reaction into half-reactions.

$$SO_2 + MnO_4^{-1} \longrightarrow SO_4^{-2} + Mn^{+2}$$

Solution:

decrease in oxidation number (reduction)

$$\overset{+4\ (-2)2}{SO_2} + \left[\overset{+7\ (-2)4}{Mn\ O_4}\right]^{-1} \longrightarrow \left[\overset{+6\ (-2)4}{SO_4}\right]^{-2} + Mn^{+2}$$

Increase in oxidation number (oxidation)

Reduction half reaction:

$$MnO_4^{-1} \longrightarrow Mn^{+2}$$

Oxidation half reaction:

$$SO_2 \longrightarrow SO_4^{-2}$$

The student should be guided to employ this knowledge to illustrate the concepts.

Self Check Exercise 12.4

Split the following reactions into two half reactions:

(i) $Mn^{+2} + PbO_2 \longrightarrow MnO_4^{-1} + Pb^{+2}$

(ii) $Br_2 + SO_2 \longrightarrow SO_4^{-2} + Br^{-1}$

(iii) $NO + MnO_4^{-1} \longrightarrow NO_3^{-1} + MnO_2$

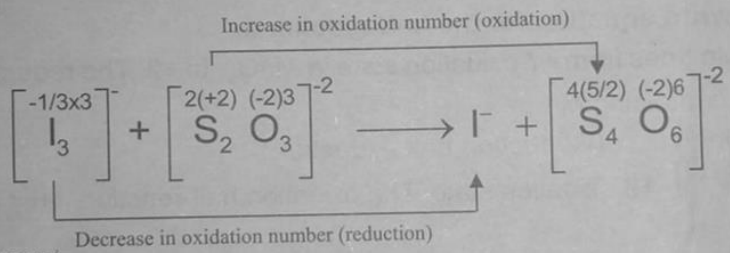
12.1.5 Half Reaction Method to Balance a Redox Reaction

A powerful technique for balancing redox reactions involves dividing these reactions into separate oxidation and reduction half reactions. We then balance the half-reaction, one at a time. And combine them so that electrons are neither created nor destroyed in the reaction.

The steps involved in this method can be understood by considering the following reactions used to determine the amount of the tri-iodide ion (I_3^-) in a solution by titration.

$$I_3^- + S_2O_3^{-2} \longrightarrow I^- + S_4O_6^{-2}$$

Step1: Break the reaction into oxidation and reduction half-reactions. (as discussed in section 12.1.4)



Reduction half-reaction:

$$I_3^- \longrightarrow I^-$$

Oxidation half-reaction:

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

Step2: Balance these half-reactions one at a time. It doesn't matter which half-reaction we balance first. Balance each half reaction in terms of both charge and mass. Let us start with the reduction half reaction.

$$I_3^- \longrightarrow I^-$$

There are 3 I atoms on the left side and one on the right side. So we will multiply co-efficient of I^- by 3. This will balance I atoms on both the sides.

$$I_3^- \longrightarrow 3I^-$$

Now balances charges. The right side has 3 mono negative charges corresponding to -3 charge. But the left side has only one uni negative charge(-1). Thus left side needs $2e^-$.

$$I_3^- + 2e^- \longrightarrow 3I^- \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Now balance oxidation half reaction.

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

To balance S atoms on both the sides, multiply co-efficient of $S_2O_3^{-2}$ by 2. This will also balance O atoms.

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

Now balance charges. The left side has two di negative charges corresponding to 2x(-2) = -4. The right side has -2 charge. Thus the right side needs $2e^-$.

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

Notice that both the half reaction are balanced in terms of both mass and charge.

Step3:Combine these half reactions so that electrons are neither created nor destroyed.

Reduction half reaction uses up $2e^-$ and oxidation half reaction produces $2e^-$, we can therefore obtain a balanced equation by simply adding equation (1) and equation (2)

$$I_3^- + 2e^- \longrightarrow 3I^-$$

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

$$I_3^- + 2e^- + 2S_2O_3^{-2} \longrightarrow 3I^- + S_4O_6^{-2} + 2e^-$$

Step4:Cancel Duplication of Species on both the sides.

Duplications are $2e^-$. Strike these out from both the sides.

$$I_3^- + 2S_2O_3^{-2} \longrightarrow 3I^- + S_4O_6^{-2}$$

Check, the overall reaction is balanced in terms of both charge and mass.

Self Check Exercise 12.5

Use the half reaction method to balance the following redox reactions.

(i) $Co + Cr^{+3} \longrightarrow Co^{+2} + Cr^{+2}$

(ii) $Au^{+3} + H_2 \longrightarrow H^+ + Au$

(iii) $Cl_2 + I^- \longrightarrow I_2 + Cl^-$

12.1.6 Half Reaction Method to Balance a Redox Reaction in Acid Solution

We can understand this method by the following example.

Example 12.8

Balance the following equation by half reaction method.

$$Cr_2O_7^{-2} + H_2SO_3 \longrightarrow Cr^{+3} + HSO_4^-$$

Solution

Step1:

Split the reaction into two half reactions.

Reduction half reaction:

$$Cr_2O_7^{-2} \longrightarrow Cr^{+3}$$

Oxidation half reaction:

$$H_2SO_3 \longrightarrow HSO_4^-$$

Step2:

Balance each half reaction. First consider reduction half reaction. Two Cr atoms on the left require 2 before Cr^{+3}

$$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$$

There are seven O atoms on the left and none on the right. So we will add 7 H_2O on the right side.

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

There are 14 H atoms on the right and none on the left, so we will add 14 H^+ on the left side.

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

Now balance charges. The left side has one di-negative and 14 mono-positive, corresponding to $-2 + 14 = +12$. The right side has two tri-positive corresponding to $+3 \times 2 = +6$. Thus left side needs $6e^-$.

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow Cr^{+3} + 7H_2O \qquad \text{---(1)}$$

In the other half reaction (Oxidation half reaction), S atoms are already balanced.

$$H_2SO_3 \longrightarrow HSO_4^-$$

Balance O – atoms. As there are three O – atoms on the left and four on the right, we will add one H_2O to the left.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^-$$

There are four H-atoms on the left and one on the right. We will add $3H^+$ to the right.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+$$

For charge, the left side is neutral but the right side has a net charge of (-1) + (+3) = +2. Thus we will add $2e^-$ to the right side.

$$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+ + 2e^- \qquad \text{-----(2)}$$

Step3:

Equalize the number of electrons transferred in the two half reactions and add half reactions. Reduction half reaction uses up $6e^-$ and oxidation half reaction produce $2e^-$. Therefore multiplying equation (1) by one and equation (2) by three and adding two equations we get.

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$$
$$3H_2SO_3 + 3H_2O \longrightarrow 3HSO_4^- + 9H^+ + 6e^-$$
$$\overline{Cr_2O_7^{-2} + 14H^+ + 3H_2SO_3 + 3H_2O + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O + 3HSO_4^- + 9H^+ + 6e^-}$$

Step4:

Cancel the duplication. Duplications are $6e^-$, $3H_2O$ and $9H^+$. Strike these out from both sides.

$$Cr_2O_7^{-2} + 5H^+ + 3H_2SO_3 \longrightarrow 2Cr^{+3} + 4H_2O + 3HSO_4^-$$

Example 12.9

Use the half reaction method to balance the following reaction that takes place in acidic medium.

$$MnO_4^- + H_2O_2 \longrightarrow Mn^{+2} + O_2$$

Solution:

Step1:

Split the reaction into two half-reactions.

Reduction half reaction:

$$MnO_4^- \longrightarrow Mn^{+2}$$

Oxidation half reaction:

$$H_2O_2 \longrightarrow O_2$$

Step2:

Balance each half reaction. First consider reduction half reaction.

$$MnO_4^- \longrightarrow Mn^{+2}$$

Mn atoms on both the sides are already balanced. There are four O atoms on the left side and non on the right, so we will add four $4H_2O$ on the right side.

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

There are 8 H atoms on the right side and non on the left so, we will add 8 H^+ on the left side.

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

Step3:

Now balance charges. The left side has one uni-negative and 8 mono-positive charges corresponding to $-1+8 = +7$. The right side has one di-positive corresponding to +2. Thus left side needs $5e^-$.

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

Now consider oxidation half-reaction.

$$H_2O_2 \longrightarrow O_2$$

O atoms on both sides are equal. There are 2H atoms on the left side and non on the right side. So we will add $2H^+$ on the right side

$$H_2O_2 \longrightarrow O_2 + 2H^+$$

Now balance charges. The left side is neutral whereas the right side has two mono positive charge corresponding to $+1x2 = +2$. Thus the right side needs $2e^-$.

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^- \quad \text{.....(2)}$$

Step4:

Reduction half reaction uses up $5e^-$ and oxidation half reaction produces $2e^-$. Therefore, multiply equation (1) by 2 and equation (2) by 5 and then add these equations.

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

$$5H_2O_2 \longrightarrow 5O_2 + 10H^+ + 10e^-$$

$$2MnO_4^- + 16H^+ + 10e^- + 5H_2O_2 \longrightarrow 2Mn^{+2} + 8H_2O + 5O_2 + 10H^+ + 10e^-$$

Step5:

Strike out duplications from both the sides.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{+2} + 8H_2O + 5O_2$$

Self Check Exercise 12.6

1. Balance each of the following half reactions that take place in acidic medium.

a) $NO_3^{1-} \longrightarrow NO_2$

b) $IO_3^{1-} \longrightarrow I_2$

c) $ClO_4^{1-} \longrightarrow ClO^{3-}$

2. Balance the following reactions by half–reaction method, which take place in acidic medium.

a) $NO_3^- + Br^- \longrightarrow NO + Br_2$

b) $Ce^{+4} + H_3AsO_3 \longrightarrow Ce^{+3} + H_3AsO_4$

c) $S_3O_8^{-2} + Cr_2^{+3} \longrightarrow SO_4^{-2} + Cr_2O_7^{-2}$

d) $MnO_4^- + C_2O_4^{-2} \longrightarrow Mn^{+2} + CO_2$

12.2 ELECTRODE, ELECTRODE POTENTIAL AND ELECTROCHEMICAL SERIES

12.2.1 The Galvonic Cell

In section 12.1 than have learned that, when a Zn rod is dipped into a copper(II) sulphate solution, zinc atoms are oxidized to zinc ions and copper (II)ions are reduced to copper metal, which deposits on the zinc rod. Following reaction occurs:

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

In this reaction, electrons flow directly from the zinc rod to Cu^{+2} ions in solution. However, if the electrons transfer from Zinc rod to the copper ions in solution could be directed through an external circuit, the spontaneous redox reaction could be used to generate electric current. But when a zinc rod is dipped in zinc sulphate solution in one container is connected by a copper wire with the copper metal and the copper rod dipped in copper (II) sulphate solution in a separate container, no current flows through the external circuit. However, when the two solutions are connected with a tube (**salt bridge**) filled with a solution of an electrolyte such as KCl, KNO_3 or Na_2SO_4, current flows through external circuit.

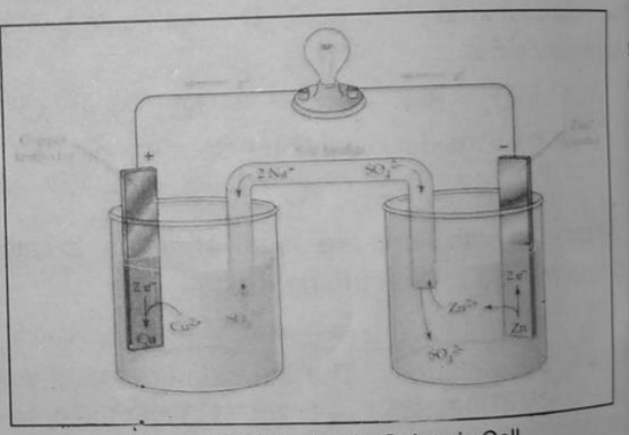


Figure 12.1: A simple Galvanic Cell

The **salt bridge** allows the movement of ions from one solution to the other without mixing of the two solutions and maintains electrical neutrality in each half-cell. (See Fig 12.1)

In one half-cell oxidation takes place and is called as oxidation half-cell or **anode**. Whereas in the other half-cell reduction takes place is called as reduction half-cell or **cathode**. Reaction

The Students should be guided to express, ability to explain or discuss concepts.

taking place in oxidation half-cell is called oxidation half reaction and the reaction taking place in reduction half-cell is called reduction half reaction.

Zn has greater tendency to lose electrons than Cu. Therefore, Zn electrode acquires negative charge relative to Cu electrode. The electrons flow from Zn electrode through the external circuit to Cu electrode. The following half-cell reactions occur at the two electrodes.

At anode:

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^- \qquad \text{(Oxidation half reaction)}$$

At cathode:

$$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \qquad \text{(Reduction half reaction)}$$

Over all cell reaction

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

An electrochemical cell in which spontaneous redox reaction produces an electric current is known as galvanic or voltaic cell.

The electrode at which oxidation occurs is called the **anode.** Whereas, the electrode at which reduction occurs is called **cathode.**

12.2 Cell Potential

The cell potential for a galvanic cell is literally the potential of the cell to do work on its surroundings by driving an electric current through a wire. The work that can be accomplished when electrons are transferred through a wire depends upon the push or force behind the electrons.

By definition the force with which electrons are pushed to flow through the wire from anode to cathode is called the electromotive force or emf. It is measured is volts (V). The volt is the measure of energy that is capable of being extracted from the flowing electric charge. When the passage of one coulomb is able to accomplish one Joule of work, then emf is one volt. The emf produced by galvanic cell is called cell potential (E^0 cell). It depends upon the difference in the electrode potentials of the two half cells joined in series.

Thus the electrode with the more negative reduction potential acts as anode and the electrode with the more positive reduction potential acts as cathode. The net reaction that occurs in the galvanic cell under standard conditions can be constructed from standard reduction half-reactions. Since a redox reaction must include both an oxidation reaction and a reduction reaction, one of the half-cells must run an oxidation that supplies electrons for the reduction. Electrons always flow spontaneously from more negative electrical potential to more positive electrical potential. This means that, under standard conditions, electrons are produced by the reaction with the more negative standard potential and consumed by the reaction with the more positive standard potential. Thus under standard conditions (1 mol dm^{-3} concentration at 25 °C and 1 atm pressure), the reaction with more negative E° value occurs as oxidation (anode reaction). The reaction with more positive E° value occurs as reduction (cathode reaction). The

voltage of any cell under standard conditions can be calculated using tabulated standard reduction potentials (see table 12.1).

Any combination of two half-cells will produce a complete cell. The overall cell reaction is obtained by suitably combining the equations for the two half reactions. Standard cell potential E° cell or emf of cell is the algebraic difference between the respective standard reduction potentials of the two half-cells.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

The cell potential has positive value for any spontaneous redox reaction. The potential of a galvanic cell can be measured with a voltmeter. But a single half-cell potential or the **electrode potential** cannot be measured directly. This is because one half-cell reaction cannot occur without a simultaneous reaction in another half-cell. However, relative half-cell potential (electrode potential) can be determined by arbitrarily designating one half-cell reaction and its potential as the standard to which other half-cell potentials are compared. By international agreement, this reference half-cell is the **standard hydrogen electrode**, with the standard potential of 0.00V (for detail see section 12.2.3).

The standard electrode potential is defined as the tendency of a half-cell reaction to undergo reduction relative to the standard hydrogen electrode. It is potential difference developed when an electrode of an element is placed in a solution containing ions of that element when all the components are in their standard state i.e. 1 atm for gases, 1M for solutions, pure solid for electrode and at 25^0C.

A standard hydrogen electrode (SHE) consists of a platinum foil coated with finely divided platinum, surrounded by hydrogen gas at 1atm pressure in contact with IM HCl solution at 298K, as shown in Fig 12.2. Its electrode potential is arbitrarily chosen as zero at all temperatures.

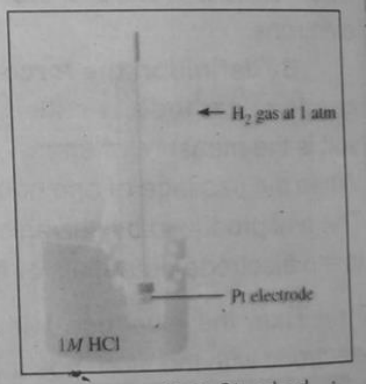


Figure 12.2: Standard Hydrogen Electrode

By convention, the half-cell potential for reduction of $H^+_{(aq)}$ to H_2 gas or the potential for the oxidation of H_2 to $H^+_{(aq)}$ in the standard Hydrogen half-cell is defined exactly 0.00V.

Reduction: (act as cathode)

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)} \qquad E^0_{H^+/H_2} = 0.00V$$

Oxidation: (act as anode)

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^- \qquad E^0_{H_2/H^+} = 0.00V$$

The symbol E^0 designates a standard potential i.e., the potential measured under standard conditions (1M concentration, 1 atm pressure and 25°C).

Table 12.1: Reduction potentials of some elements, ions and compounds

Reduction Half-reaction	E0 (Volts)	
$Li^+ + \bar{e} \rightleftharpoons Li$	-3.05	
$K^+ + \bar{e} \rightleftharpoons K$	-2392	
$Ba^{2+} + 2\bar{e} \rightleftharpoons Ba$	-2.90	
$Ca^{2+} + 2\bar{e} \rightleftharpoons Ca$	-2.76	
$Na^{1+} + 1\bar{e} \rightleftharpoons Na$	-2.71	• Oxidation
$Mg^{2+} + 2\bar{e} \rightleftharpoons Mg$	-2.38	(Anode)
$Al^{3+} + 3\bar{e} \rightleftharpoons Al$	-1.67	• Produce H_2
$Mn^{2+} + 2\bar{e} \rightleftharpoons Mn$	-1.03	with S.H.E
$2H_2O + 2\bar{e} \rightleftharpoons H_2 + 2OH^-$	-0.83	
$Zn^{2+} + 2\bar{e} \rightleftharpoons Zn$	-0.76	
$Cr^{3+} + 3\bar{e} \rightleftharpoons Cr$	-0.74	
$Fe^{2+} + 2\bar{e} \rightleftharpoons Fe$	-0.44	
$PbSO_4 + 2\bar{e} \rightleftharpoons Pb + SO_4^{2-}$	-0.36	
$Ni^{2+} + 2\bar{e} \rightleftharpoons Ni$	-0.25	
$Sn^{2+} + 2\bar{e} \rightleftharpoons Sn$	-0.14	
$Pb^{2+} + 2\bar{e} \rightleftharpoons Pb$	-0.13	
$Fe^{3+} + 3\bar{e} \rightleftharpoons Fe$	-0.04	
$2H^+ + 2\bar{e} \rightleftharpoons H_2$	0.00	
$AgCl + \bar{e} \rightleftharpoons Ag + Cl^-$	+0.22	
$Hg_2Cl_2 + 2\bar{e} \rightleftharpoons 2Hg + 2Cl^-$	+0.27	• Reduction
$Cu^{2+} + 2\bar{e} \rightleftharpoons Cu$	+0.34	(cathode)
$Cu^+ + 1\bar{e} \rightleftharpoons Cu$	+0.52	• Produce
$I_{2(aq)} + 2\bar{e} \rightleftharpoons 2I^-$	+0.54	H^+ with
$Fe^{3+} + \bar{e} \rightleftharpoons Fe^{2+}$	+0.77	S.H.E
$Ag^+ + \bar{e} \rightleftharpoons Ag$	+0.80	
$Br_{(aq)} + 2\bar{e} \rightleftharpoons 2Br^-$	+1.09	

$O_2 + 4H^+ + 4\bar{e} \rightleftharpoons 2H_2O$	+1.23
$MnO_2 + 4H^+ + 2\bar{e} \rightleftharpoons Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_7^{2-} + 14H^+ + 6\bar{e} \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_{2(g)} + 2\bar{e} \rightleftharpoons 2Cl^-$	+1.36
$2ClO_3 + 12H^+ + 5\bar{e} \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$8H^+ + MnO_4^- + 5\bar{e} \rightleftharpoons Mn^{2+} + 4H_2O$	+1.49
$PbO_2 + SO_4^{-2} + 4H^+ + 4\bar{e} \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$H_2O_2 + 2H^+ + 2\bar{e}\ s2H_2O$	+1.7
$S_2O_3^{-2} + 2\bar{e} \rightleftharpoons 2SO_4^{-2}$	+2.00
$F_2 + 2\bar{e} \rightleftharpoons 2F^-$	+2.87

12.2.4 Determination of Cell Potential

A cell reaction consists of two half reactions. Reduction takes place in the half-cell having greater value of reduction potential. Oxidation takes place in the half-cell having the smaller value of reduction potential. Equation of the half-cell reaction having smaller value of reduction potential is reversed and added to the equation of half-cell having greater value of reduction potential. Sum of these two equations represent cell reaction.

Example 12.10

Calculate E^0 cell for Zn-Cu cell and write cell reactions. Show direction of electron flow.

Solution

Half Cell reaction **Reduction potential**

i) $Zn^{++}_{(aq)} + 2\bar{e} \longrightarrow Zn_{(s)}$ - 0.76V

ii) $Cu^{++}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)}$ + 0.34V

Data indicates that the reduction potential of second half-cell is greater than the first. Hence reduction reaction will occur in second half-cell and oxidation in the first half-cell. Reverse the first equation and add it to the second equation to get cell reaction.

$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2\bar{e}$ (Oxidation half-reaction)

$Cu^{+2}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)}$ (Reduction half-reaction)

$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)}$ (Cell reaction)

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

$E^0_{cell} = E^0_{Cu} - E^0_{Zn}$

$E^0_{cell} = +0.34 - (-0.76)$

$E^0_{cell} = +1.10V$ s

Electrons will flow from anode to cathode i.e., from Zn electrode to Cu electrode.

Example 12.11

The standard reduction potentials for the following half reactions are:

$Ni^{+2}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$ $\quad E^0 = -0.25V$

$Mg^{+2}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$ $\quad E^0 = -2.38V$

Calculate E^0_{cell} for Ni-Mg cell, write cell reactions, show direction of electron flow and identify the anode of the cell.

Solution:

Data indicates that the reduction potential of first reaction is greater than that of the second reaction. Hence reduction will occur in the first reaction and oxidation in the second reaction. Reverse the second reaction and add it to the first reaction to get the cell reaction.

$Mg_{(s)} \longrightarrow Mg^{+2}_{(aq)} + 2e^-$ (Anode reaction)

$Ni^{+2}_{(aq)} + 2e^- \longrightarrow Ni_{(s)}$ (Cathode reaction)

$Mg_{(s)} + Ni^{+2}_{(aq)} \longrightarrow Mg^{+2}_{(aq)} + Ni_{(s)}$ (Cell reaction)

Thus Mg will act as anode and Ni as cathode. Electrons will flow from Mg to Ni.

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

$E^0_{cell} = E^0_{Ni} - E^0_{Mg}$

$= -0.25 - (-2.38)$

$= 2.13\ V$

Self Check Exercise 12.7

The standard reduction potentials for the following half-reactions are:

$Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ $\quad E^0 = +0.34V$

$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$ $\quad E^0 = +1.36V$

Estimate E^0_{cell} for Cu-Cl_2 cell, write cell reactions, choose cathode and show the direction of electron flow.

Feasibility of a Chemical Reaction

Whether a chemical reaction feasible or occurs spontaneously, can be inferred from the sign of the sum of E° values of the two half-cell reactions. If this value is positive, reaction occurs spontaneously or will be feasible. The negative value indicates that the reaction is not feasible.

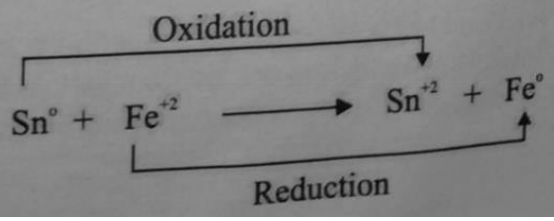
Example 12.12

Is the following reaction feasible?

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

The standard reduction potential values are $E^0_{Sn} = -0.14V$, $E^0_{Fe} = -0.44V$

Solution



It is clear from the above equation that oxidation of Sn and reduction of Fe is taking place. Sn is acting as anode and Fe as cathode. The above reaction consists of the following two half-cell reactions.

$$Sn \longrightarrow Sn^{+2} + 2\bar{e} \quad \text{(oxidation half reaction)}$$

$$Fe^{+2} + 2\bar{e} \longrightarrow Fe \quad \text{(reduction half reaction)}$$

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

$$E^0_{cell} = -0.44V - (-0.14V)$$

$$= -0.30$$

As E^0_{cell} is negative, therefore the given reaction is not feasible. However reverse reaction would be spontaneous.

Self Check Exercise 12.8

Using emf data, argue on the following:

(i) Can Fe displace Cu from a solution of Copper (II) Sulphate.?

(ii) Can Iodine displace Bromine from aqueous solution of Potassium bromide?

Important Information

In modern dentistry, a material most commonly used to fill decaying teeth is known as dental amalgam. Dental amalgam actually consists of Ag, Sn and Hg, the standard electrode potential for this amalgam is +0.67V. Any person who bites a piece of Al foil (such as use for wrapping candies, biscuits etc) in such a way that the foil presses against a dental filling, will experience a momentarily sharp pain. This is because, an electro chemical cell has been created in the mouth, with Al as anode $E^o = -1.66V$, the filling as cathode and saliva as electrolyte. Contact between Al foil and filling short circuits the cell. This causes the weak current to flow between the electrodes. This current stimulates the sensitive nerve of the tooth, causing a sharp pain.

12.2.5 Electrochemical Series

Under the recommendation of international union of pure and applied chemistry (IUPAC) the half-cell reactions are given in the reduction reactions (Table 12.1) therefore E^0 values are known as reduction potentials. However, the value of oxidation potential for an electrode can be obtained by reversing the sign of reduction potential for that electrode. Note that the given reduction potential values relate to standard conditions only. i.e., IM solution of ions, 25^0C (298K) and I atm pressure. Changes in conditions will alter these values.

Such a list of arrangement of elements in the order of their standard electrode potential with reference to standard hydrogen electrode is called electrochemical series (Table 12.1).

12.2.6 Activity Series of Metals

A displacement or replacement reaction occurs when an element displaces another element which is a part of a compound. The general equation, $A + XY \longrightarrow X + AY$ in which an atom A replaces atom X in the compound XY illustrate this type of reaction.

For example, if Zn metal is placed in a blue solution of copper (II) sulphate, the blue color slowly fades away and grey metal is replaced by red orange Cu metal. In this reaction Cu ions in the solution are reduced to Cu metal and Zn atoms are oxidized to Zn ions (for details see section 12.1).

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

However, when copper metal is placed in zinc sulphate solution, no replacement reaction occurs. Table 12.1 shows that the standard reduction potential reaction of copper is greater than that of zinc.

This means that it is easy to oxidize Zn to its ions and reduce Cu^{+2} ions to its atoms. Thus Zn can place Cu^{+2} ions from its solution. For the same reason Mg and Al can also displace Cu^{+2} ions, but Ag cannot replace Cu^{+2} ions.

Similarly it is observed that metal like Na, K can displace H_2 from water but metals like Cu, Ag cannot displace H_2 from water. Metals are therefore, ranked according to their ability to replace other metals and hydrogen from their compounds. In this ranking metals and hydrogen are arranged in order of decreasing ease of oxidation to their respective ions in aqueous solution.

This arrangement is called **activity series** (see Table 12.2).

Table 12.2 **Activity series of common metals**

Increas in Reactivity

Li, K, Ba, Sr, Ca, Na	Very Active metals; React with cold water with the liberation of hydrogen gas; (K and Na react violently with water), They also react violently with acids
Mg, Al, Mn, Zn, Cr, Fe, Cd	Metals of intermediate activity: React with steam or with acids such as HCl with liberation of H_2
Co, Ni, Sn, Pb, H_2	Moderately active metals React slowly with HCL Do not react with water
Cu, Ag, Hg	Moderately noble metal; Do not react with water, HCl but react with oxidizing acids such as HNO_3
Pt, Au	Very noble metals; React only with aqua regia

Important point about the activity series are as follows:

1. Metals high on the list transfer electrons to metal cations lower on the list. The greate separation between the species the more vigorous will be the reaction. For exa

The student should be guided to argue his print of view of highlight the conclusion or inference.

when powdered barium is heated with lead (II) oxide, a replacement reaction occurs. This is because Ba is more active than Pb. Barium is oxidized to form barium oxide and lead is reduced to elemental lead.

$$Ba_{(s)} + PbO_{(s)} \longrightarrow BaO_{(s)} + Pb_{(s)}$$

On the other hand, when iron pellets are added to a solution of $MgCl_2$ no reaction will occur. This is because Fe is below Mg in the activity series.

2. Very active metals react with cold water to liberate Hydrogen. For example:

$$2Na_{(s)} + 2H_2O \longrightarrow NaOH_{(aq)} + H_{2(g)}$$

3. The less active metals react with steam and with non-oxidizing acid such as HCl. For example:

$$Mg_{(s)} + 2H_2O_{(s)} \longrightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$

$$Mg_{(s)} + HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$

Al reacts with hot water to a small degree. This is because Al forms a protective coating of Aluminum hydroxide and Aluminum oxide on its exposed surface. This protects metal from further reaction.

4. The moderately active metals such as Co, Ni, Sn, Pb do not react with steam. These metals react spontaneously with 1M HCl.

5. The metals below hydrogen in the activity series do not react with 1 M HCl. These metals are unable to reduce H^+ ions in 1M HCl solution. However, their 1M aqueous ions can be reduced by hydrogen gas at 1 atm. These metals are called as noble metals. The moderately noble metals Cu, Ag and Hg react only with oxidizing acids such as nitric acid and perchloric acids. The very noble metals do no react with these acids but react with aqua regia. For example

$$CuO_{(s)} + H_{2(g)} \longrightarrow Cu_{(s)} + H_2O_{(g)}$$

Example 12.13

Predict whether a replacement reaction will occur in the following instances. Defend your conclusion.

a) Magnesium ribbon is in a solution of silver nitrate.

b) A small piece of calcium is added to a beaker of water.

c) A copper wire is dipped in 1M HCl.

Solution

a) Magnesium is above Silver in the activity series. Thus Mg will displace Ag^+.

$$Mg_{(s)} + 2 + (Ag)^{+}_{(aq)} \longrightarrow Mg^{+2}_{(aq)} + 2Ag_{(s)}$$

b) Calcium being very active metal and above hydrogen in the activity list will react with cold water and will liberate hydrogen gas.

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

c) Copper metal is below hydrogen in the activity list, therefore no reaction will take place.

Self Check Exercise 12.9

Predict whether a reaction occurs in the following cases and write a net ionic equation for the reactions that occurs:

(i) An iron nail is placed in 1M HCl.
(ii) Lead(II) oxide is heated with powdered zinc.
(iii) Nickel wire is placed into a solution of silver nitrate.

12.3 TYPES OF ELECTRO-CHEMICAL CELLS

This section is based on your grade IX-X knowledge about electrochemical cells. You have already learnt to sketch these cells.

Devices, which convert electrical energy into chemical energy and vice versa, are known as electrochemical cells. There are two types of electrochemical cells.

1) Electrolytic cells.
2) Galvanic or voltaic cells.

In these cells electrical energy is used to drive many chemical processes. For example heavy industrial processes such as preparation of sodium hydroxide, metals, purification of nickel and copper, plating of noble metal on jewelry and instruments. The chemical process used in these cells is called electrolysis.

Electrolysis

Electrolysis is the production of a chemical reaction by means of an electric current. The apparatus for an electrolysis consist of an electrolytic cell containing the electrolyte either in molten state or in solution into which two electrodes are placed. The electrodes are connected with a battery. The current is carried from the battery through the wires by mean of electrons (metallic conduction). Within the cell the current is carried by the anions and cations of the electrolyte (Electrolytic conduction). The electrodes serve as a point where conduction changes from metallic to electrolytic or vice versa. At each electrode a chemical reaction takes place in which electrons are gained by the ions in solution at one electrode. Simultaneously electrons are released by some substance at the other electrode. These electrons are returned to the battery through the connecting wire. Thus oxidation-reduction reactions occur at the electrodes. The electrode at which oxidation occurs is called as anode. The electrode at which reduction occurs is called as cathode. The changes, which occur at the electrodes, depend on the relative oxidation–reduction tendencies of the substances involved. You have already learned many examples of electrolysis in grade IX-X. In this section we will discuss quantitative aspects of electrolysis.

The important quantitative aspects of electrochemistry are units, the relation between chemical change and electric current and the relation between tendency for chemical reaction to occur and voltage.

Units

The SI unit of charge is the **coulomb (C)**. It is the charge on 6.25×10^{18} electrons. Although the coulomb is the usual unit for measuring charge, the chemist finds that a more convenient unit is the **Faraday (F)**. It corresponds to the charge carried by the mole of electrons and amounts to 96487 C. The S1 Unit of current is the ampere, which is the amount of current flowing when one coulomb passes a given point in one second. Frequently, an ampere is referred as "a coulomb per second".

Relation Between Chemical Change And Electric Current

In 1833, Faraday described the results of his electrochemical investigations by stating the two principles of electrochemistry, which are now known as **Faraday's laws**. The first law of Faraday states that **"The amount of chemical reaction taking place at an electrode is directly proportional to the quantity of charge that flows through the electrode during the process."**

Second law of Faraday states that, **"If same quantity of charge is passed through different electrolytic cells, the chemical change in each case is proportional to the gram equivalent mass of each parent species".**

If several cells containing aqueous solutions are connected in series, as shown in figure 12.3 and if 96487 C of charge is passed through them, the electrode reactions proceed simultaneously and for 7.999g of O_2 produced from H_2SO_4, 1.008g of H_2, 107.9g of Ag, 31.77g of Cu and 32.5g of Zn are produced at the respective cathodes. These weights are the equivalent

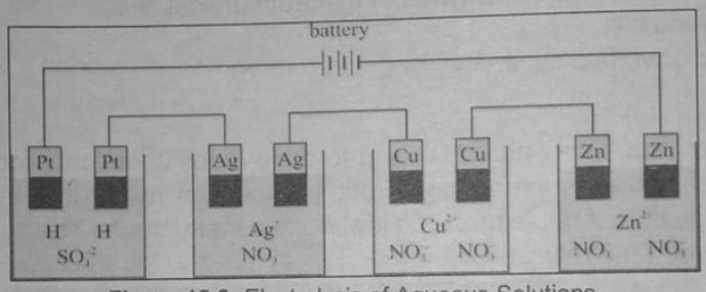


Figure 12.3: Electrolysis of Aqueous Solutions

weights of the respective elements.

It is therefore concluded that 96487 C is the charge on one mole of electrons. This quantity of charge is referred as one Faraday. Thus the quantity of the change that occurs in electrolysis can be determined from the number of Faraday's of charge, which passes. For most calculations, the value of the Faraday will be taken as 96500 C. **The amount of a substance produced during electrolysis by passing one Faraday of electricity is called its equivalent weight.**

Example 12.14

In the electrolysis of molten $ZnCl_2$, how much Zn can be deposited at the cathode by passage of 0.01 ampere for one hour?

Solution

0.01 Amp. for one hour = $0.01 \times 1 \times 60 \times 60$
= 36 C

96500C/Faraday = 3.7×10^{-4} Faraday

In molten Zinc chloride, the cathode reaction is

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

Which means that for every 2 Faraday of electricity used up, one mole of Zn is deposited. Thus,

3.7×10^{-4} Faraday $\times$ 1 Mole of Zn / 2 Faradays = 1.85×10^{-4} mole of Zn

As one mole of Zn is 63.37g.

Therefore 1.85×10^{-4} mole of Zn $\times$ 63.37g = 0.012g of Zn. (Ans)

The Student should be guided to distinguish between parts and figures.

Example 12.15

A constant current was passed through a solution of $AuCl_4^-$ ions between gold electrodes. After a period of 10.0 minutes, the cathode increased in weight by 1.314 grams.

i) How much charge was passed?
ii) What was the amount of current?
iii) What volume of Cl_2 was collected at anode at 1 atm and 25°C.

Solution

The reaction at cathode is the reduction of Au (III) to Au metal

$$AuCl_4^- + 3e^- \longrightarrow Au + 4Cl^-$$

It means that for every 3 Faraday of electricity used up, 1 mole of Au is produced.

$$\text{Moles of Au} = \frac{1.314\text{g Au}}{197\text{g/mole of Au}} = 6.67\times10^{-3}$$

i)

$$\text{Charge} = 6.67\times10^{-3}\ \text{mole Au} \times \frac{3\ \text{Faraday}}{\text{mole of Au}}$$

$$= 2\times10^{-2}\ \text{Faraday}$$

$$\text{Current} = \frac{\text{Charge}}{\text{Time(s)}}$$

$$\text{Time} = 10\ \text{mins} = 10\times60 = 600\text{s}$$

$$\text{Current} = \frac{(2\times10^{-2}\text{F})(96500\text{C/F}}{600\text{s}} = 3.22\ \text{A}.$$

iii) The reaction at anode is oxidation of Cl^- ions.

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

For every 2 Faraday of electricity 1 mole of Cl_2 was produced.
For 1 Faraday of electricity = 1/2 moles of Cl_2 was produced.
For $2\text{x}10^{-2}$ Faraday of electricity = $1/2 \times 2\text{x}10^{-2}$ moles of Cl_2 was produced.
$= 1\text{x}10^{-2}$ moles of Cl_2 was produced.

Volume of Cl_2 produced can be calculate by the following formula

$$V = \frac{nRT}{P}$$

$$= \frac{1\text{x}10^{-2}\times0.08205\times298}{1}$$

$$= 0.245\text{dm}^{+3}$$

Self Check Exercise 12.10

1. Bauxite ore is used for the commercial preparation of Al. For this purpose bauxite ore is first purified to produced pure alumina, Al_2O_3. Alumina is then electrolyzed. Following reaction occurs:

$$2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$$

Calculate mass of Al, that collects at the cathode and volume of oxygen that collects at node when Al_2O_3 is electrolyzed for 10 hours with a 15 ampere current at 1 atm and 25°C.

2. Which of the following compounds will give more mass of metal, when 15 ampere current is passed through molten mass of these salts for 1 hr.

(a) NaCl (b) $CaCl_2$

Redox reactions keep the batteries in our cell phones and laptops functioning.

We have already discussed galvanic cells in section 12.2.1. Here we will discuss some important galvanic cells. Batteries are source of direct current and have become essential source of portable power in our society. Batteries provide electric power for starting internal combustion engines in automobiles, for running systems on space vehicles and for such devices as flash lights, toys, heart pacers, electronic calculators, portable radios, TVs, Tape recorders etc. A battery is a galvanic cell or a group of galvanic cell connected in series.

Batteries which can not be recharged are called primary cells e.g. dry cell, whereas batteries which can be recharged are known as secondary cells or storage batteries, e.g. Lead storage battery (automobile battery). A battery can be as tiny as a heart pacemaker implant or as large as the charge storage tanks of an electric automobile. We will discuss some of the important batteries.

1) Dry Cell

The dry cell batteries are used to power many flashlights, toys and small appliances. The anode is the zinc metal of the container and the cathode is an inert graphite rod at the center of the container in contact with a mixture of MnO_2 and carbon (charcoal) see fig 12.4. The electrolyte is a mixture of moist NH_4Cl and $ZnCl_2$. Following reactions take place in it,

At Anode

$$Zn \longrightarrow Zn^{+2} + 2\,\bar{e}$$

At Cathode

$$2NH_4^+ + 2MnO_2 + 2\bar{e} \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$$

This cell produces a potential of 1.5V. In the alkaline dry cell battery, moist paste of KOH is used as electrolyte instead of NH_4Cl and $ZnCl_2$. Following reactions take place is it.

At anode $\quad Zn + 2OH^- \longrightarrow Zn(OH)_2 + 2\bar{e}$ $\quad Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

At Cathode $\quad 2MnO_2 + H_2O + 2\bar{e} \longrightarrow Mn_2O_3 + 2OH^-$

Overall reaction:- $Zn + 2MnO_2 \longrightarrow ZnO + Mn_2O_3$

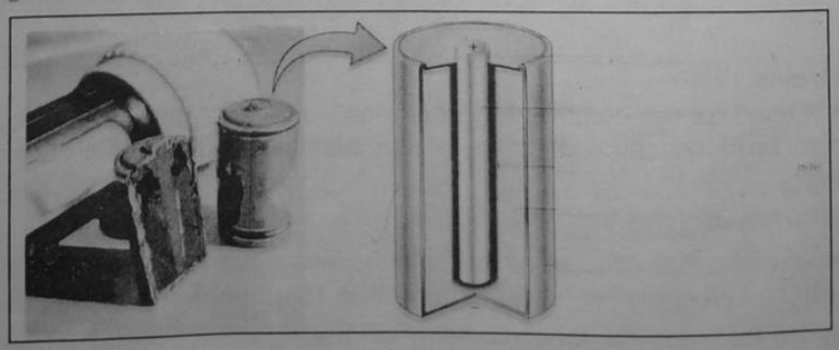


Figure 12.4: A dry celll

The student should be guided appraise significance of the information towards better understanding.

The alkaline dry cell lasts longer because the zinc anode corrodes less rapidly in basic conditions.

CAD:

An especially important type of dry cell is the nickel-cadium battery which has a Cd anode and NiO_2 as cathode. KOH is an electrolyte. Following reactions occur in it.

At anode

$$Cd_{(s)} + OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^-$$

At cathode

$$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \longrightarrow Ni\ (OH)_{2(s)} + 2OH^-_{(aq)}$$

In this cell, the products adhere to the electrodes. Thus, battery can be recharged.

Lead storage Battery:

The lead storage battery provides electrical power in automobiles. It is well suited for this use because it supplies the large current needed to drive starter motors and headlights and can be recharged easily. $2H_2SO_4 \longrightarrow 4H^+ + 2SO_4^{-2}$

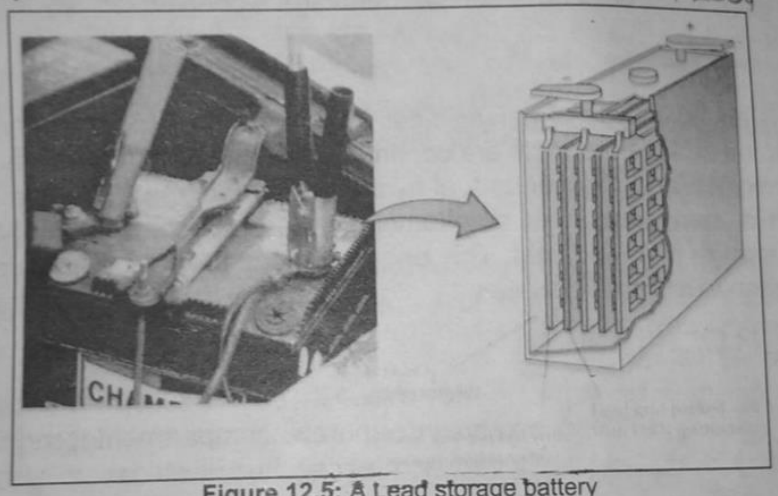


Figure 12.5: A Lead storage battery

The anode is a lead plate that becomes coated with $PbSO_4$ as the battery discharges. The cathode is lead impregnated with PbO_2 which also becomes coated with $PbSO_4$ as the battery discharges. Both electrodes are immersed in electrolyte which is 30% H_2SO_4 solution having density 1.25g cm^{-3}. The cell produces potential of two volts. Automobile batteries use three or six such cells joined in series to generate a total electrical potential of 6V or 12V respectively (see figure 12.5). Following reactions take place in it $Pb \longrightarrow Pb^{+2} + 2e^-$ (A)

At anode $$Pb_{(s)} + SO^{-2}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2\bar{e}$$ $Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$ (A)

At cathode $$PbO_{2(s)} + SO^{-2}_{4(aq)} + 4H^+_{(aq)} + 2\bar{e} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

Net reaction during discharge of battery is $PbO_2 + 2e^- \longrightarrow Pb^{+2} + 2O^{-2}$

$$Pb_{(S)} + PbO_{2(S)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(S)} + 2H_2O_{(l)}$$ $2O^{-2} + 4H^+ \longrightarrow 2H_2O$

$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$

Thus during discharge H_2SO_4 is used up and its density decreases. When both the electrodes are completely covered with $PbSO_4$ the battery ceases to deliver current until it is recharged.

Recharging the Battery

Battery can be recharged by connecting its anode to the negative terminal of direct current and the cathode to the positive terminal of the direct current. Reverse chemical reactions occur at anode and cathode of the battery. Thus deposition of Pb on anode and PbO_2 on cathode take place. The reactions of recharging of battery are as follows.

At ~~cathode~~ Anode :-

$$PbSO_{4(S)} + 2\bar{e} \longrightarrow Pb_{(S)} + SO^{-2}_{4(aq)}$$

At ~~anode~~ cathode :-

$$PbSO_{4(S)} + 2H_2O_{(l)} \longrightarrow PbO_{2(S)} + SO^{-2}_{4(aq)} + 4H^{+}_{(aq)} + 2\bar{e}$$

Net reaction: $2PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(S)} + PbO_{2(S)} + 4H^{+}_{(aq)} + 2SO^{-2}_{4(aq)}$

After recharging H_2SO_4 solution is concentrated again bringing density to its initial value of 1.25 g cm^{-3}.

3) Fuel Cell

A fuel cell is a special type of galvanic cell in which reactants are continuously supplied as they are consumed and the products are continuously removed. A fuel cell is based upon the reaction between oxygen and a gaseous fuel hydrogen or methane. We have learnt in section 11.1.3 that when hydrogen burns in air, an exothermic reaction occurs. A lot of chemical energy is released in the form of heat and light. This energy is used for cutting and welding metals. In this reaction hydrogen is oxidized to water.

$$H_{2(g)} + O_{2(g)}\, H_2O_{(g)} + \text{heat}$$

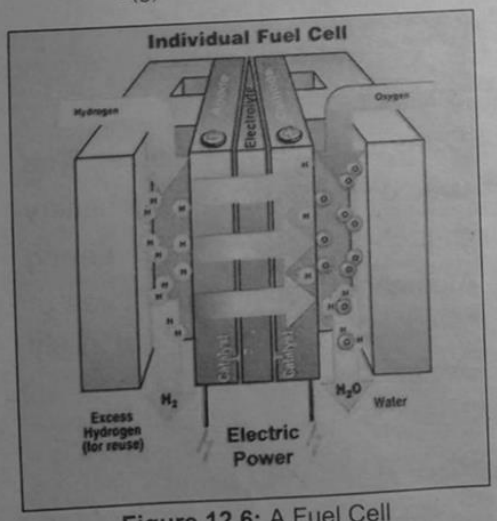


Figure 12.6: A Fuel Cell

However, if this oxidation-reduction reaction is carried in separate compartments connected in series. Electrons released in the oxidation of hydrogen in one compartment begin to flow through the external circuit towards the other compartments. There these electrons bring about reduction of oxygen. Thus electricity begins to flow in the circuit. The energy released from the reaction of hydrogen with oxygen to form water is converted to electrical energy. A hydrogen-oxygen fuel cell has three compartments separated from one another by porous carbon electrodes (see figure 12.6). These electrodes contain platinum as catalyst. The middle compartment contains a hot aqueous solution of KOH. Hydrogen gas is passed through the anode compartment and oxygen is passed through the cathode compartment.

At anode hydrogen is oxidized to water and at cathode oxygen is reduced to hydroxide ions.

Anode reaction = $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$

Cathode reaction = $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Net cell reaction $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

This is clearly the equation for the burning of hydrogen in oxygen but in a fuel cell it is burning without flame. Thus the electrons released in the oxidation of hydrogen flow through the circuit towards the cathode. A hydrogen-oxygen cell delivers 0.9 V. The fuel cell operates at high temperature so the water formed evaporates and may be condensed. The water removed in spacecraft is consumed by the astronauts. The fuel cells of this kind have been used by American space program.

4. Solar Cell

Devices that convert solar energy directly into electric energy are called solar cells. A semiconductor material is used in these cells. This material generates voltage output with light input. A basic solar cell consists of two layer of different types of semi-conductive materials. These materials are joined together to form a junction. When one layer is exposed to light, many electrons acquire enough energy and break away from their parent atoms. Such electrons cross the junction. This means that negative ions are formed on one side of the junction and positive ions are on the other side. Thus a potential difference is developed which causes electrons to flow. Semiconductor made of silicon gives an output of 0.5 V per cell. Research is continuing to get more output with other semi-conductor material. In future solar cells will serve as a cheap source of energy.

12.3 Corrosion and its Prevention

You have learned definition of corrosion and rusting of iron as an example in your grade IX X. Here we will discuss electrochemical cause of corrosion. We will use e.m.f data to understand corrosion and its prevention.

Corrosion is a natural process, which converts, refined metals to their more stable metal oxides. The oxidizing agent in corrosion chemistry is atmospheric oxygen. It is most familiar in the form of the rusting of iron. Rusting is an electrochemical process. One of the half reaction in rusting is

$$Fe^{+2} + 2\bar{e} \longrightarrow Fe \qquad E^0 = -0.44V$$

Reverse of this reaction

$$\text{i.e. } Fe \longrightarrow Fe^{+2} + 2\bar{e}$$

is driven by the presence of oxygen. Iron (II) is oxidized further to iron (III) and various insoluble hydrated oxides of iron (III) are deposited as the red-brown precipitate known as rust. These oxides are porous, flake off and expose metal to further corrosion. The process of corrosion occurs when metal is in contact with water. The water layer present on the surface of iron or a water droplet on its surface dissolves O_2 and CO_2. In certain industrial areas where SO_2 or other acidic vapours are present also dissolve. Thus metal comes in contact with the electrolyte. The reduction half reaction is:

The student should be guided to discriminate between the concepts.

$$O_{2(g)} + 4H^{+}_{(aq)} + 4\bar{e} \longrightarrow 2H_2O_{(l)} \qquad E^0 = +1.23V$$

is is more positive than Fe^{+2} - Fe couple, so it can drive the following reaction:

$$Fe \longrightarrow Fe^{+2} + e^{-} \qquad \text{(oxidation reaction)}$$

The E^0 cell of the combined half-reactions is

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

$$E^0_{cell} = +1.23 - (-0.44)$$

$$E^0_{cell} = +1.67V$$

Therefore, there is a strong tendency towards oxidation. Oxidation of iron occurs in an erior region of the droplet whereas reduction of O_2 occurs near the air-droplet interface. (See 12.7)

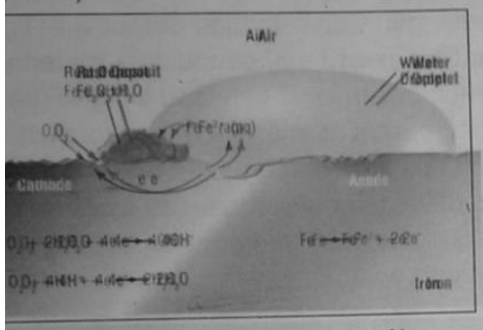


Figure 12.7: Corrosion process of iron

Corrosion cannot be eliminated, but sealing the surface from attacks can slow it down. The corrosion of a metal can be prevented by painting the metal so that it does not come in contact with oxygen and moisture and other harmful agents. Painting also provides visual appeal. That is why bridges, trains, cars etc are painted. A metal surface can also be protected by coating it with a thin layer of a second metal that is less electropositive than the first. This can be done by galvanization or electroplating.

alvanization

Objects made of iron are dipped in molten zinc and dried. This process is known as **alvanization**. If a scratch penetrates the zinc layer, iron is still protected because Zn oxidizes referentially. This is because Zn is more active metal than iron, as the potentials for reduction how. Any oxidation that occurs dissolves Zn rather than Fe. Thus Zn acts as sacrificial coating n Fe. This is also known as sacrificial corrosion.

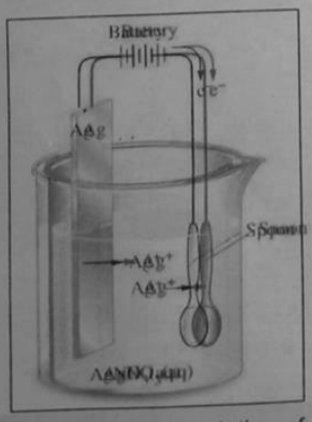


Figure 12.8: Electroplating of sliver

$$Fe^{+2} + 2\bar{e} \rightleftharpoons Fe \qquad E^0 = -0.44V$$

$$Zn^{+2} + 2\bar{e} \rightleftharpoons Zn \qquad E^0 = -0.76\ V$$

Electroplating

Electrolysis can be used to deposit one metal on another. A layer of silver or gold is often plated on jewelry and tableware made from inexpensive metals such as iron. The article to be plated is used as cathode. The metal, which is to be deposited on the article, is used as anode. Water-soluble salt of anode metal is used as electrolyte. When electrical potential is applied, electrons are ejected from anode and move into the cathode (article). Metal ions of anode in solution

The student should be guided to evaluate the different ideas to discover new facts.

apture the electrons and adhere to the article (cathode). For example, in silver plating, silver od is used as anode and sodium cyanide is used as electrolyte. Cynaide ions form a complex ith silver ions (see figure 12.8).

$$Ag^{+}_{(aq)} + 2CN^{-}_{(aq)} \rightleftharpoons [Ag(CN)_2]^{-}_{(aq)}$$

Anode reaction

$$Ag_{(s)} \longrightarrow Ag^{+}_{(aq)} + e^{-}$$

Cathode reaction

$$[Ag(CN)_2]^{-}_{(aq)} + e^{-} \longrightarrow Ag_{(s)} + 2CN^{-}_{(aq)}$$

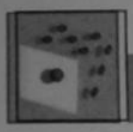
Steel objects are often protected from corrosion by electroplating with Aluminum or Chromium. These metals form a thin protective coating of oxide which inhibits further corrosion. The potential of the passive oxide coating is much like a noble metal.

SUMMARY OF KEY TERMS

1. Redox reactions i.e., oxidation and reduction reactions involve the transfer of electrons or change in oxidation numbers.
2. Redox equations can be balanced by using oxidation number method and ion electron method.
3. The driving force behind the spontaneous redox reaction is called the cell potential.
4. The magnitude of cell potential depends upon the conditions under which the measurement is made. Under standard conditions, all solutions have 1M concentration; all gases have partial pressure of 1 atm. The standard potential for the reduction of H^{+} to hydrogen gas is arbitrarily taken as zero volts.
5. In a galvanic cell, oxidation and reduction reactions take place at separate electrodes and electron flow through the external circuit. These separate parts of the galvanic cell are half cells. The reactions which occur at these half cells are the half-cell reactions. A salt bridge allows the ions to flow between the half cells.
6. In a galvanic cell, the oxidation occurs at node and reduction occurs at cathode and the electrons flow in the external circuit from anode to cathode.
7. Voltaic cells use a spontaneous redox reaction to drive an electric current through a wire. Whereas, the electrolytic cells use an electric current to drive a redox reaction.
8. The quantity of electricity carried by 1mole of electron is called a faraday. It is equal to 96,500 coulombs.
9. In electrolysis electric current from an external source drives a non-spontaneous chemical reaction. The amount of chemical reaction that takes place in electrolysis is directly proportional to quantity of charge transferred at the electrode.
10. A battery is a galvanic cell or a group of galvanic cells connected in series. Some of the well-known batteries are the dry cell, the nickel-cadmium battery, lead-storage battery used in automobiles, fuel cells etc.
11. The corrosion of metals is an electrochemical phenomenon.

References for further learning:

- Bodener and Pardue, chemistry an experimental science 2/e
- Steven s. Zumdahl, chemistry
- Zumdahl, introductory chemistry third edition
- Olmsted and Williams, chemistry, the molecular science
- Silberberg, chemistry, the molecular nature of matter and change



Exercise

1: Choose the Correct Answer

i. The electrode through which the electron enter the electrolytic solution is
(a) Anode (b) Cathode (c) Salt bridge (d) Electrolyte.

ii. Oxidation number of S in $Na_2S_2O_3$ is
(a) +1 (b) +2 (c) +3 (d) +4

iii. In the electrolysis of molten $ZnCl_2$, the cathode reaction is $Zn^{+2} + 2e^- \rightarrow Zn$ what quantity of electricity is used up for the production of half mole of Zn
(a) 2 Coulombs (b) 1F (c) 2F (d) 2 ampere

iv. 4. How many moles of Cr will be produced by 1.5 Faradays of electricity by the following reaction $Cr^{+3} + 3e^- \longrightarrow Cr$
(a) 0.1 (b) 0.2 (c) 0.03 (d) 1.5 (e) 0.5

v. $E^0_{Sn} = -0.14V$, $E^0_{Pb} = -0.13V$
(a) Sn^{+2} can oxidize Pb (b) Pb^{+2} can oxidize Sn
(c) Both can oxidize each other (d) Both can reduce each other.

vi. A fuel call operates at _____ temperature
(a) Low (b) Medium (c) Room (d) High

vii. The oxidation number of Cl in $HClO_4$ is
(a) –1 (b) +1 (c) +5 (d) +7

viii. In which of the following compounds oxidation number of N is +5
(a) NO_2 (b) N_2O_4 (c) N_2O_3 (d) N_2O_5

ix. The Passage of current through an electrolyte is due to the movement of
(a) Electrons (b) Anions (c) Cations (d) Ions

x. Oxidation number of an element in Free State is
(a) Negative (b) Positive (c) Zero (d) ± 1

xi. Which of these is not true of an electrolyte.
(a) It can conduct electricity in molten state
(b) It can conduct electricity in the form of aqueous solution.
(c) It can conduct electricity in the solid form.
(d) It can be an acid, a base or a salt.

xii. Corrosion is an electrochemical process which requires
(a) Oxygen (b) Water
(c) Acidic vapours (d) Basic vapours

12. a
13. a,b
14. a, b, c
15. a, b, c, d

xiii. A fuel cell is based upon the reaction between
(a) Oxygen (b) Gaseous fuel (c) KOH (d) Pt

1. a
2. a,b
3. a, b, c
4. a, b, c, d

Explain, why?

(a) Reduction of 1 mole of each Zn^{+2} and Ag^{+} require different Faradays of electricity. Due to ion difference

(b) It is not possible to measure the potential of an isolated half-cell. to complete the circuit.

(c) The life of a dry cell is shorter than that of an alkaline dry cell.

Write the spontaneous reaction for the following sets of half-reactions.

$Au^{+3}_{(aq)} + 3e \longrightarrow Au_{(s)} \qquad E^0 = 1.5\ V$

$NO^{-}_{3(aq)} + 4H^{+}_{(aq)} + 3e^{-} \longrightarrow NO_{(g)} + 2H_2O_{(l)} \qquad E^0 = 0.096\ V$

$Au^{+3} + 3e \longrightarrow Au$

$NO + 2H_2O \longrightarrow NO_3^- + 4H^+ + 3e^-$

$Au^{+3} + NO + 2H_2O \rightarrow Au + NO_3^- + 4H^+$

Explain the following with reasons.

(a) The oxidation potential of Zn is +0.76V and its reduction potential is –0.76V

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

(c) Na and K can displace hydrogen from acids but Cu and Pt cannot.

(d) Lead stroage battery is rechargeable battery. reverse the process.

(e) Zn plating saves Fe from corrosion.

What kind of reaction occurs at the negative terminal of the galvanic cell? Anode (oxidation)

Corrosion is often accelerated where the coating on the body of a car has begun to crack, interpret it.

How many hours would electroplating have to be continued at the rate of 5 amperes if 75g of copper is to be deposited from $CuSO_4$ Solution? Moles = Mass / M.Mass = 1.18 moles

Differentiate between the following

(a) A galvanic and electrolytic cell

(b) Oxidation half-reaction and reduction half-reaction

9. Sketch the galvanic cell based on the following overall reaction. Show direction of electron flow and identify the anode, write balanced reaction. Assume all concentrations are 1.0 M

(a) $Cr^{+3}_{(aq)} + Cl_{2(aq)} \longrightarrow Cr_2O^{-2}_{7(aq)} + Cl^{-}_{(aq)}$ $2Cr^{+3} + 7H_2O \rightarrow Cr_2O_7 + 6e^- + 14H^+$ (oxi) Anode

(b) $Cu^{+2}_{(aq)} + Mg_{(s)} \longrightarrow Mg^{+2}_{(aq)} + Cu_{(s)}$ $3Cl_2 + 6e^- \rightarrow 6Cl^-$ (Red) cathode

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

10: Calculate E^0 for the following cells, which reactions are spontaneous as written under standard conditions.

(a) $2Ag^{+}_{(aq)} + Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2Ag_{(s)}$ (a) $2Ag^+ + 2e^- \rightarrow Ag$ (Red) $E^\circ_{cell} = +0.46V$ spontaneous

(a) $Cu \rightarrow Cu^{+2} + 2e^-$ (oxi)

(b) $Zn^{+2}_{(aq)} + Ni_{(s)} \longrightarrow Ni^{+2}_{(aq)} + Zn_{(s)}$

(c) $Al_{(s)} + 3H^{+}_{(aq)} \longrightarrow Al^{+3}_{(aq)} + H_{2(g)}$

11: An electroplating apparatus in used to coat jewelry with gold. What mass of gold can be deposited from a solution that contains $\{Au(CN)_4\}^{-1}$ ion if a current of 5.0 amperes flows for 30 minutes, following half-reaction occurs.

$$\{Au(CN)_4\}^{-1}_{(aq)} + 3e^- \longrightarrow Au_{(s)} + 4CN^-_{(aq)}$$

12: Determine oxidation number of all the atoms in the following

(a) K_2CO_3 (b) P_4 (c) XeF_4 (d) F_2O

(e) PCl_5 (f) NH_3 (g) Fe_3O_4

13: Balance the following half-reactions

(a) $Cu^{+} \longrightarrow CuO$ (b) $I \longrightarrow IO^{-1}_3$ $3H_2O + I^\circ \rightarrow \overset{+5\ -6\ =\ -1}{IO_3} + 5e^- + 6H^+$

(c) $S \longrightarrow H_2S$ (d) $SO^{-2}_4 \longrightarrow SO_2$

14: Balance the following reactions by ion electron method

(a) $SO_2 + MnO^-_4 \longrightarrow Mn^{+2} + HSO^-_4$

(b) $BrO^{-2}_3 + SO_2 \longrightarrow HSO^-_4 + Br^-$

(c) $2N_2O_4 \longrightarrow NO^-_3 + NO$

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

(e) $H_2O_2 + MnO^-_4 \longrightarrow Mn^{+2} + O_2$

(f) $Cr_2O^{-2}_7 + Cl^{-1} \longrightarrow Cr^{+3} + Cl_2$

(g) $IO^{-1}_3 + AsO^{-3}_3 \longrightarrow I^{-1} + AsO^{-3}_4$

(h) $H_3AsO_3 + Cr_2O^{-2}_7 \longrightarrow H_3AsO_4 + Cr^{+3}$

Balance the following equations by oxidation number method

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

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

(iii) $Ag + H_2S + O_2 \longrightarrow Ag_2S + H_2O$

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

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

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

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

(viii) $NaClO_2 + Cl_2 \longrightarrow NaCl + ClO_2$

(ix) $Na + H_2O \longrightarrow NaOH + H_2$

6. A dead lead storage battery has 5g of $PbSO_4$ deposited on each of its anodes.It is connected to a charger that supplies 0.12 ampere of current at a voltage of 13V. To which electrode, Pb or PbO_2 should the anode of charger be connected? Write the half reaction occuring at this electrode during charging?

7. Calculate the mass of Cu and O_2 produced by the electrolysis of $CuSO_4$ solution on passing 5.0 amperes of current for 2 hrs. What would be the volume of O_2 at S.T.P.

Following reactions occurs at the electrodes.

At Anode $2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

At Cathode $Cu^{+2}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Ans: 11.184g,4.18dm^3)

Ifa chromium steel bicycle handlebar is scratched, exposing steel, will chromium or steel corrode? Chromium will corrode first.

Use the activity series of metals to predict the products of following single replacement reactions. Give reason.

i) $Cu_{(s)} + HCl_{(aq)} \longrightarrow$ No reaction

ii) $Cu_{(s)} + HCl_{(aq)} \longrightarrow$ No reaction

iii) $3\,Mg_{(s)} + 2CrCl_{3(s)} \longrightarrow 3MgCl_2 + 2Cr$

iv) $NiO_{(s)} + H_{2(g)} \longrightarrow$ No reaction

v) $Cd_{(s)} + CuSO_{4(aq)} \longrightarrow CdSO_4 + Cu$

Justify that photosynthesis in plants is a redox reaction.

$$6\overset{-2}{CO_2} + 6H_2O \xrightarrow{\text{chlorophyll}} C_6H_{12}O_6 + 6\overset{0}{O_2}$$

(oxidation)

21. Metal A can displace metal B from its aqueous solution, metal B can displace metal D from its aqueous solution, but it cannot displace metal C from its aqueous solution. Metal C can displace metal A from its aqueous solution. Metals B and D can be displaced from their aqueous solution by hydrogen. Arrange these metals and hydrogen in order of decreasing activity.

C A H B D

22. Differences in the standard potentials of electrodes A and B, B and C are 1.5V and 3.0V respectively.

A-B=1.5V

B-C=3.0V

a) Calculate the cell potential of the working cell between A and C.

b) Identify cathode in this cell.

23. Standard electorde potentials of three electrodes are in the following order,

$$E^0_A > E^0_B < E^0_c$$

4 2A

Choose anode in the working cell, when (a) Electrodes A and C are joined in series. (b) Electrodes B and C are joined in series (c) Electrodes A and B are joined in series.

3A 2A 4 3A

24. Evaluate the importance of standard reduction potentials.

22. A-B=1.5V

A=1.5+B

B-C=3.0V

C=B-3.0

A-C

1.5+B-B+3 ⇒ 4.5V

OR

8.5 7

E°_{cell} A-B ⇒ 1.5V

E°_{cell} B-C -

E°_{cell} A-C