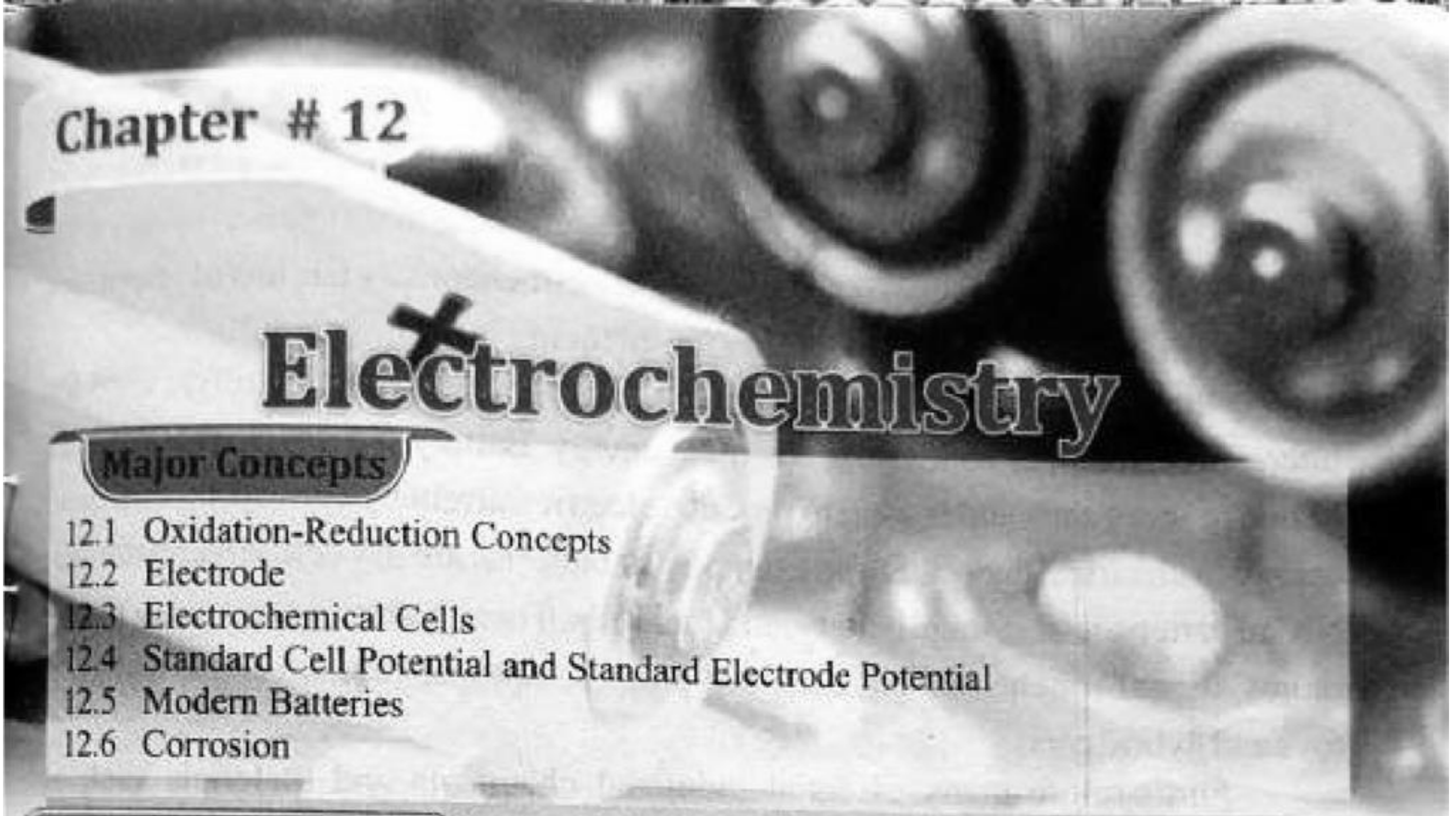

Chapter # 12

Electrochemistry

Major Concepts

12.1 Oxidation-Reduction Concepts
12.2 Electrode
12.3 Electrochemical Cells
12.4 Standard Cell Potential and Standard Electrode Potential
12.5 Modern Batteries
12.6 Corrosion

Learning Outcomes

The students will be able to:

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

Introduction

Electrochemistry is the branch of chemistry which deals with the conversion of electrical energy into chemical energy in electrolytic cells and chemical energy into electrical energy in galvanic or voltaic cells. Electrochemistry has lots of important applications but we are going to discuss few of them.

A cell consists of two electrodes that are dipped into an electrolyte used for interconversion of chemical and electrical energy. Battery is a device that consists of one or more cells and is used to produce electric current by converting chemical energy to electrical energy. Some examples of batteries are dry cell, silver batteries, NiCad battery, lead storage battery, and fuel cells. These batteries are used to power radios, digital watches, calculators, cell phones, laptops, CD players, flashlights, toys and hybrid cars.

Furthermore many essential industrial chemicals and materials such as caustic soda (NaOH), chlorine, aluminum, hydrogen, oxygen, and hydrogen peroxide are manufactured by electrolytic processes.

Electrochemical processes are not always advantageous; that is, there are some electrochemical processes that damage the materials such as corrosion of iron. The main target of electrochemistry is to prevent the corrosion to reduce the loss of materials.

12.1 Oxidation-reduction Concepts

12.1.1 Oxidation and Reduction

Oxidation and reduction can be defined in three different ways:

i) The addition of oxygen to a substance during a chemical reaction is called oxidation while the removal of oxygen from a substance during a chemical reaction is called reduction. Reduction is the reverse of oxidation.

$$PbO + C \xrightarrow{\quad\quad} Pb + CO$$

In this reaction, lead oxide is reduced to lead by losing oxygen while carbon is oxidized to carbon monoxide by gaining oxygen.

ii) The addition of hydrogen to a substance during a chemical reaction is called reduction while the removal of hydrogen from a substance during a chemical reaction is called oxidation.

$$H_2S + Cl_2 \xrightarrow{\quad\quad} S + 2HCl$$

In this example, hydrogen sulphide gas is oxidized to sulphur by losing hydrogen while chlorine is reduced to HCl by gaining hydrogen.

iii) Loss of one or more electrons by a substance is called oxidation while the gain of one or more electrons from a substance is called reduction.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

In this reaction, sodium is oxidized to sodium ion by losing electrons and chlorine is reduced to chloride ion by gaining electrons. The element that loses the electrons during the reaction is said to be oxidized. Its oxidation number increases. The element that gains electrons during the reaction is said to be reduced. Its oxidation number decreases.

12.1.2 Oxidation Numbers

The apparent charge, positive or negative, which an atom would have in a compound, is called oxidation number. It is also known as the oxidation state. It enables us to identify the elements that are oxidized or reduced. The elements that show an increase in the oxidation state are oxidized while the elements that show decrease in the oxidation state are reduced.

Rules for Assigning Oxidation Numbers

i) The oxidation number of an atom of a free element is zero. Hence, each atom in H_2^0, N_2^0, O_2^0, Br_2^0, Na^0, Mg^0, Fe^0 and Zn^0 has zero oxidation numbers.

ii) In compounds, the oxidation number of hydrogen is +1 except in metal hydrides where it is −1. Hence, the oxidation number of hydrogen is −1 in LiH, NaH, and CaH_2.

iii) The oxidation number of oxygen is −2 in all its compounds (e.g. CO_2 and CaO) except in peroxides and superoxides. In peroxides, it is −1 (e.g. H_2O_2 and Na_2O_2) and in superoxides, it is −1/2 (e.g. KO_2). The oxidation number of oxygen in oxygen difluoride, OF_2 is +2.

iv) The oxidation numbers of alkali metals, alkaline earth metals (Group IIA) and group IIIA elements are +1, +2 and +3 respectively.

v) The oxidation number of halogens (Group VIIA elements) is −1 in their binary compounds (NaCl, KBr, and $AlCl_3$). The halogens except fluorine show positive oxidation numbers when they are bonded with oxygen.

vi) The oxidation number of a monoatomic ion is equal to the charge on it. Hence, Na^+, Mg^{2+}, Al^{3+} and O^{2-} have +1, +2, +3 and −2 oxidation states respectively.

vii) In polyatomic ions such as CO_3^{-2}, SO_4^{-2} and PO_4^{-3} the sum of oxidation number of atoms of different elements is equal to the net charge on the ion. For example, in the carbonate ion (CO_3^{-2}), the oxidation number of carbon is +4 and that of oxygen is −2. Hence, the sum of oxidation numbers is $1(+4)+3(-2)=-2$.

viii) The sum of oxidation numbers of all the elements in a neutral compound is equal to zero. For example, in potassium permanganate ($KMnO_4$), the oxidation number of potassium is +1, manganese is +7 and that of oxygen is -2. Hence, the sum of the oxidation numbers is $1(+1)+1(+7)+4(-2)=0$.

ix) In any substance, the more electronegative atom has the negative oxidation number while the less electronegative atom has the positive oxidation number.

x) The same element may show different oxidation numbers in different compounds. For example, the oxidation numbers of *sulphur* in disulphur dichloride (S_2Cl_2), sulphur dioxide (SO_2), sulphuric acid (H_2SO_4), and hydrogen sulphide (H_2S) are +1, +4, +6, and −2 respectively.

Example 12.1

Calculate the oxidation number of nitrogen in HNO_3.

Solution

The oxidation number of hydrogen is +1 and that of oxygen is −2. The oxidation number of nitrogen in HNO_3 is calculated as:

$1(+1)+1(N)+3(-2) = 0$

$+1 + N - 6 = 0$

$N - 5 = 0$

Example 12.2

Find out the oxidation number of chromium in $K_2Cr_2O_7$.

Solution:

The oxidation number of potassium is +1 and that of oxygen is −2. The oxidation number of chromium in $K_2Cr_2O_7$ is calculated as:

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

$+2 + 2Cr - 14 = 0$

$2Cr - 12 = 0$

$2Cr = +12$

$Cr = +12/2$

$Cr = +6$

Example 12.3

Find out the oxidation number of nitrogen in NH_4^{+1}.

Solution:

The oxidation number of hydrogen is +1 and that of nitrogen in NH_4^{+1} is calculated as:

$$\begin{aligned} 1(N) + 4(+1) &= +1 \\ N + 4 &= +1 \\ N &= +1 - 4 \\ N &= -3 \end{aligned}$$

Example 12.4

What is the oxidation number of carbon in HCO_3^{-1}?

Solution:

The oxidation number of hydrogen is +1 and that of oxygen is –2. The oxidation number of carbon in HCO_3^{-1} is calculated as:

$$\begin{aligned} 1(+1) + 1(C) + 3(-2) &= -1 \\ +1 + C - 6 &= -1 \\ C - 5 &= -1 \\ C &= -1 + 5 \\ C &= +4 \end{aligned}$$

Practice Exercise 1:

Calculate the oxidation number of Chromium in the following species:

(i) $CrCl_3$ (ii) Cr_2O_3 (iii) $Cr_2(SO_4)_3$ (iv) CrO_4^{-2}

12.1.3 Recognizing Oxidation-Reduction Reactions

The reactions that involve oxidation and reduction are called oxidation-reduction reactions. They are also known as redox reactions. Oxidation-reduction reactions can be considered as electron transfer reactions. In the process, the electrons may either be transferred from one substance to another to form ionic bonds or shared to form covalent bonds. The process of oxidation and reduction occur simultaneously during a chemical reaction. Both of these processes occur in equivalent amounts.

Keep in mind

The number of electrons shared, gained or lost by an atom of an element is called valency whereas the apparent charge, positive or negative which an atom would have in a compound is called oxidation state.

To identify the oxidation-reduction reactions, one should know that the change in oxidation number occurs during the oxidation-reduction reaction.

Consider the reaction in which zinc metal reacts with a solution of aqueous copper sulphate containing copper ions:

$$Zn_{(s)} + CuSO_{4\,(aq)} \longrightarrow ZnSO_{4\,(aq)} + Cu_{(s)}$$

This reaction can also be shown as:

$$Zn^{0}_{(s)} + Cu^{+2}_{(aq)} + SO^{-2}_{4\,(aq)} \longrightarrow Zn^{+2}_{(aq)} + SO^{-2}_{4\,(aq)} + Cu^{0}_{(s)}$$

This is a redox reaction in which zinc metal is oxidized; that is, the zero oxidation number of zinc is converted to +2. The copper ion is reduced; that is, the +2 oxidation number of copper ion is converted to zero.

A redox reaction is the sum of two half- reactions; that is, an oxidation half-reaction and a reduction half-reaction.

Redox reaction = Oxidation half reaction + Reduction half reaction

An equation which shows either loss or gain of electrons is called half-reaction. A half-reaction which shows the reactant that loses electrons is called oxidation half-reaction whereas a half-reaction which shows the reactant that gains electrons is called reduction half-reaction. In oxidation half-reaction, the electrons appear on the product side of the equation whereas in reduction half-reaction, the electrons appear on the reactant side of the equation. The above reaction can be separated into two half reactions as:

Oxidation half-reaction: $Zn^{0}_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e^{-}$

Reduction half-reaction: $Cu^{+2}_{(aq)} + 2\,e^{-} \longrightarrow Cu^{0}_{(s)}$

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Applications of Redox Reactions in Daily Life

Applications of redox reactions are numerous but we are going to discuss few of them.

- The burning of wood, paper, coal, and gasoline in the presence of air is called combustion, which is rapid redox reaction.
- Many biological redox reactions provide energy that is required by living organisms to sustain life. The most familiar is the process of metabolism, which is a complex process. The oxidation of carbohydrate is an example of metabolic redox process. In this process, a carbohydrate such as glucose reacts with oxygen to produce CO_2 and water with the evolution of energy.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

- Redox process is also responsible for the operation of batteries. There is a lot of variety of batteries that are used to power many useful devices such as flashlights, radios, laptop computers, watches, and portable music players.
- Bleaching agents are oxidizing agents that are used to decolourize or lighten the colour of materials such as paper, fabrics and human hair. By redox reactions, elemental chlorine is used to bleach wood pulp to make white paper, sodium hypochlorite (NaOCl) is used to remove stains from clothes, and hydrogen peroxide is used to convert redheads into blondes of sort.
- Redox reactions are not always beneficial. The decay of metals by oxidation such as rusting of iron in the moist air is called corrosion. Corrosion is a spontaneous redox reaction and damages especially those materials which are made of iron.
- Electroplating is redox process that is used to improve the hardness, stability and appearance of metals (objects) and to protect them from corrosion.

12.1.4 Balancing Oxidation-Reduction Equations by Oxidation Number Method:

The following rules are used for balancing of redox equations by oxidation number method.

i) Write down the skeleton equation for the reaction under consideration.

ii) Write down the oxidation number of each atom above it.

iii) Identify those atoms whose oxidation numbers are changed during redox reaction.

iv) Record the oxidation numbers above the atoms whose oxidation numbers have changed.

v) Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. Arrows show the number of electrons gained or lost by single atom only.

vi) Equate (to make balance) the number of electrons gained or lost by multiplying with a suitable number.

vii) Balance rest of the equation by inspection method.

Example 12.5

Balance the following equations by oxidation number method:

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

(b) $K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + Cl_2 + H_2O$

Solution: (a)

i) Write down the skeleton equation for the reaction.

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

ii) Write down the oxidation number of each atom above it.

$$\overset{0}{Cu} + \overset{\substack{1(+1)\\+1}}{H}\;\overset{\substack{1(+5)\\+5}}{N}\;\overset{\substack{3(-2)\\-6}}{O_3} \longrightarrow \overset{\substack{1(+2)\\+2}}{Cu}(\overset{\substack{2(+5)\\+10}}{N}\;\overset{\substack{6(-2)\\-12}}{O_3})_2 + \overset{\substack{1(+4)\\+4}}{N}\;\overset{\substack{2(-2)\\-4}}{O_2} + \overset{\substack{2(+1)\\+2}}{H_2}\;\overset{\substack{1(-2)\\-2}}{O}$$

iii) Identify those atoms whose oxidation numbers have changed during the reaction.

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

In this equation, the oxidation number of copper has changed from zero to +2 and that of nitrogen has changed from +5 to +4. We should write HNO_3 twice on the left hand side because the oxidation number of nitrogen remains same (+5) in $Cu(NO_3)_2$ and changes (+4) in NO_2.

$$HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

iv) Draw arrows between the same atoms whose oxidation numbers have changed, and show the number of electrons lost, or gained by an atom.

No. of $\bar{e}$s lost (Oxidation) = 2 x 1 = 2

$$HNO_3 + \overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(NO_3)_2 + \overset{+4}{N}O_2 + H_2O$$

No. of $\bar{e}$s gained (Reduction) = 1 x 2 = 2

One copper atom lost 2 electrons and two nitrogen atoms gained 2 electrons.

v) Multiply HNO_3 and NO_2 by 2 to balance the number of electrons lost or gained during the reaction.

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

This equation can also be written as:

$$Cu + 3HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + H_2O$$

vi) Now balance rest of the equation by inspection method.

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

Solution: (b)

i) Write down the skeleton equation for the reaction.

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

ii) Write down oxidation numbers of each atom above it.

$$\overset{2(+1)}{\overset{+2}{K_2}}\ \overset{2(+6)}{\overset{+12}{Cr_2}}\ \overset{7(-2)}{\overset{-14}{O_7}} + \overset{+1}{H}\overset{-2}{Cl} \longrightarrow \overset{+1}{K}\overset{-1}{Cl} + \overset{+3}{Cr}\overset{3(-1)}{\overset{-3}{Cl_3}} + \overset{0}{K_2} + \overset{2(+1)}{\overset{+2}{K_2}}\overset{-2}{O}$$

iii) Identify those atoms whose oxidation numbers have changed during the reaction.

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

In this equation, oxidation number of chromium has changed from +6 to +3 and that of chlorine has changed from −1 to zero. The oxidation numbers of chlorine in KCl and $CrCl_3$ remain same (−1). We should, therefore, write HCl twice on the left hand side. One HCl for those chlorine atoms whose oxidation numbers have changed and one HCl for those chlorine atoms whose oxidation numbers have not changed.

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

iv) Draw arrows between the same atoms whose oxidation numbers have changed and show the number of electrons lost or gained by an atom.

No. of ēs lost (Oxidation) = 1 x 2 = 2

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

No. of ēs gained (Reduction) = 3 x 2 = 6

Here, two chlorine atoms have lost 2 electrons while two chromium atoms have gained 6 electrons.

Multiply HCl by 6, Cl_2 by 3 and $CrCl_3$ by 2 to balance the number of electrons lost or gained.

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

i) Now balance rest of the equation by inspection method.

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

Practice Exercise 2:

Balance the following equation by oxidation number method:

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

1.5 Balancing of Oxidation Reduction Equations by the Half Reaction Method:

This method of balancing the oxidation-reduction equations is also known as ion-electron method. The following rules are used for balancing of redox equations by the half reaction method:

i) Write down the skeleton equation which shows only those species that are actually involved in the reaction.

ii) Split up the equation into two half reactions i.e. oxidation and reduction half reactions.

iii) Those atoms, molecules or ions should be written which really exist. Remove all unnecessary species.

iv) Balance all atoms on either side of the equation other than hydrogen and oxygen.

v) Balance oxygen atoms by adding H_2O molecules.

vi) Balance hydrogen atoms by adding H^+ ions in acidic solution or OH^- ions in basic solution.

vii) Balance the charges by adding electrons.

viii) Balance the number of electrons lost or gained during reaction by multiplying each half reaction with a suitable number.

ix) Add both half reactions in such a way that the electrons must not appear in the final equation.

x) Cancel out substances which are present on both sides of the equation.

Example 12.6

Balance the following equation by half reaction method:

$$KMnO_4 + HCl \longrightarrow H_2O + MnCl_2 + Cl_2$$

Solution:

(i) Write down the skeleton equation.

$$KMnO_4 + HCl \longrightarrow H_2O + MnCl_2 + Cl_2$$

(ii) Now write the species which are actually involved in the reaction and remove all un-necessary species.

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

(iii) Split up the equation into two half reactions

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

$Cl^- \longrightarrow Cl_2$ (Oxidation half reaction)

(iv) Balance chlorine atoms by multiplying 2 on left hand side.

$$2Cl^- \longrightarrow Cl_2$$

(v) Balance the charge by adding 2 electrons on right hand side.

$2Cl^- \longrightarrow Cl_2 + 2e^-$ .... (A)

(vi) Balance oxygen atoms by adding $4H_2O$ molecules on R.H.S.

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

(vii) Balance hydrogen atoms by adding eight H^+ ions on L.H.S.

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

(viii) Balance the charge by adding 5 electrons on L.H.S.

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{+2} + 4\,H_2O \quad \ldots\ldots\ldots\ldots \quad (B)$$

(ix) Multiply equation (A) by 5 and equation (B) by 2 to balance the number of electrons lost or gained.

$$\left[2\,Cl^- \longrightarrow Cl_2 + 2\,e^-\right] \times 5$$

$$\left[MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{+2} + 4\,H_2O\right] \times 2$$

(x) Add both equations and cancel out the common species on both sides.

$$\begin{array}{l} 10\,Cl^- \longrightarrow 5\,Cl_2 + 10\,e^- \\ \underline{2MnO_4^- + 16\,H^+ + 10\,e^- \longrightarrow 2Mn^{+2} + 8H_2O} \\ 10Cl^- + 2MnO_4^- + 16H^+ \longrightarrow 5Cl_2 + 2Mn^{+2} + 8H_2O \end{array}$$

Practice Exercise 3:

Balance the following equation by half reaction (ion-electron) method:

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

12.1.6 Chemistry of Some Important Reducing and Oxidizing Agents

A substance that loses electrons during a chemical reaction is called reducing agent or reductant where as a substance that gains electrons during a chemical reaction is called oxidizing agent or oxidant. The oxidizing agent oxidizes other substances (increases the oxidation state of other substances) and is reduced itself. The reducing agent reduces other substances (decreases the oxidation state of other substances) and is oxidized itself. The total number of electrons gained by oxidizing agent is always equal to the total number of electrons lost by the reducing agent. Consider the following reaction in which sulphurous acid (H_2SO_3) reacts with nitric oxide (NO) to produce sulphuric acid and nitrous oxide (N_2O).

$$H_2SO_3 + 2NO \longrightarrow H_2SO_4 + N_2O$$

In this reaction, sulphurous acid is oxidizing agent because it (sulphur) loses electrons while nitric oxide is reducing agent because it gains (nitrogen) electrons. The electrons are transferred from sulphur to nitrogen.

Among elements, the metals are good reducing agents while non-metals are good oxidizing agents. In the periodic table, the alkali metals are strong reducing agents because they form positive ions readily and halogens are strong oxidizing agents because they have strong attractions for electrons and form negative ions readily.

Among compounds, the potassium dichromate ($K_2Cr_2O_7$) and potassium permanganate ($KMnO_4$) are the most important strong oxidizing agents whereas hydrogen sulphide (H_2S), sulphur dioxide (SO_2) and ferrous sulphate ($FeSO_4$) are some important reducing agents. Some of the reactions of oxidizing and reducing agents are:

i) Magnesium reacts with cold dilute nitric acid to form hydrogen gas.

$$2HNO_3 + Mg \longrightarrow Mg(NO_3)_2 + H_2$$

In this reaction, nitric acid acts as oxidizing agent and magnesium atom acts as reducing agent.

ii) Hydrogen sulphide reacts with chlorine to form hydrogen chloride and sulphur.

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

In this reaction, hydrogen sulphide acts as reducing agent and chlorine as oxidizing agent.

iii) Potassium dichromate reacts with sulphur dioxide in acidic medium to produce chromic sulphate, $Cr_2(SO_4)_3$.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

In this reaction potassium dichromate acts as an oxidizing agent while sulphur dioxide acts as a reducing agent.

iv) $KMnO_4$ reacts with concentrated HCl to produce chlorine gas.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

In this reaction, potassium permanganate acts as an oxidizing agent.

12.2 Electrode

The surfaces, in a cell, at which reactions (oxidation or reduction half-reactions) take place, are called electrodes. An electrode, in a cell, is a metal plate, wire, rod, or a piece of graphite through which the electric current enters into or leave out the electrolyte. The electrodes may or may not involve in the reactions. The electrodes that do not involve in the reactions are called inert electrodes. Electrodes are of two types; anode and cathode. The positive electrode is called anode because anions are attracted to it while negative electrode is called cathode because cations attracted to it. Oxidation takes place at anode and reduction takes place at cathode. Electrons move from anode to cathode through an external circuit.

12.3 Electrochemical Cells

A cell consisting of two electrodes dipped into an electrolyte in which a chemical reaction either produces or utilizes an electric current is called electrochemical cell.

Electrochemical cells are of two types:

i) Electrolytic cell
ii) Galvanic or Voltaic cell

12.3.1 Electrolytic Cells

The electrochemical cell which utilizes an electric current to produce chemical reaction is called electrolytic cell. It may also be defined as: the cell in which non-spontaneous redox reaction takes place by the passage of electricity is called electrolytic cell. Examples are Down's cell, Nelson's cell.

Working of Electrolytic Cell

Consider an electrolytic cell which is used to determine the conductivity of solution.

An electrolytic cell consists of a beaker with two electrodes which are dipped in electrolyte and connected to a direct current (DC) source. When an electric current is passed through an electrolyte, the positively charged ions (cations) move towards cathode and negative charged ions (anions) move towards anode. The solution of the ions results in the passage of a current and the bulb glows. The bulb will glow brightly in strong electrolyte and glow dimly in weak electrolytes.

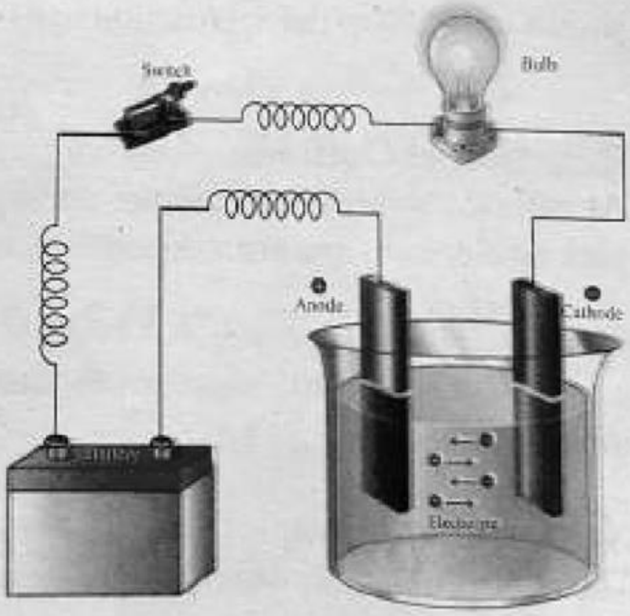


Figure 12.1: Electrolytic Cell

This movement of ionic charges through the solution due to the passage of electric current is called Electrolytic Conduction (Conduction of electricity).

12.3.2 Electrolysis of Aqueous Solution of NaCl

The electrolysis of aqueous NaCl is carried out in an electrolytic cell. This cell consists of a beaker with two electrodes which are connected to a direct current

(DC) source. When solution of concentrated NaCl is placed in the cell and the electrodes are connected to DC. As a result of this H_2 gas is produced at cathode and Cl_2 gas at anode.

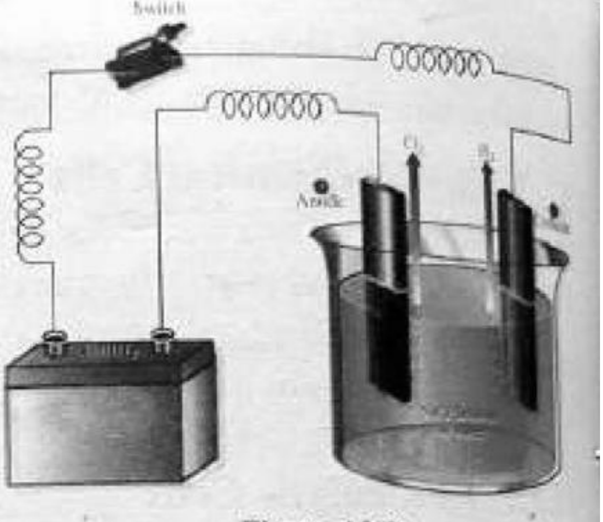


Figure 12.2:
Electrolysis of sodium chloride in water

Explanation

When NaCl is dissolved in water, it dissociates into ions as:

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

When electric current is passed through the solution, the following reactions take place at electrodes.

Reaction at Anode

At anode chloride ions (negative ions) lose electrons and are oxidized. As it shows only half of the net reaction so it is called oxidation half reaction.

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

Reaction at Cathode

At cathode sodium ions are not undergoing reduction. Actually water molecules pick up electrons and are reduced to H_2 and OH^- ions. It is reduction half reaction.

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

The H^+ ions of water act as stronger oxidizing agents as compared to Na^+ ions.

Net Cell Reaction

The net cell reaction which involves the oxidation and reduction half reactions ar called redox reactions.

$$2NaCl + H_2O \longrightarrow H_2 + Cl_2 + NaOH$$

The net cell reaction produces hydrogen gas, chlorine gas and aque solution of NaOH. Pure NaOH is then obtained by evaporation of the solution.

In the above reactions, it is clear that H_2O is more easily reduced than Na The reduction potential of water is –0.828 V while that of Na^+ is –2.714 V.

12.3.3 Difference Between Coulomb, Ampere, and Volt

The flow of electrons through an external circuit is called the electrical current. The SI unit of electric current is ampere (A) that is defined as a charge of one coulomb flowing through a conductor in one second.

$$1\ \text{Ampere} = 1\ \text{coulomb} / \text{second} \quad \text{or} \quad 1\text{A} = 1\text{C}/\text{sec}$$

The quantity of electric current is known as electric charge. The SI unit of electric charge is coulomb (C) that is defined as the product of the current in amperes (A) and time in seconds (t).

$$1\ \text{coulomb} = 1\ \text{ampere} \times 1\ \text{second} \quad \text{or} \quad 1\text{C} = 1\text{A} \times \text{sec}$$

For example, 75 coulomb current is passed in the wire when 5A current flows through a wire for 15 seconds.

$$\begin{aligned} \text{Charge in coulomb} &= \text{current in amperes} \times \text{time in seconds} \\ &= 5\text{A} \times 15\text{sec} \\ &= 75\text{C} \end{aligned}$$

An electrical potential difference is called voltage. The SI unit of potential difference (voltage) is the volt (V) that is equal to one joule (J) of energy per coulomb of charge (C).

$$1\ \text{volt} = \frac{1\ \text{joule}}{1\ \text{coulomb}} \quad \text{or} \quad 1\text{V} = \frac{1\text{J}}{\text{C}}$$

Thus, a 1.5V cell produces 1.5 Joule of energy to every 1 coulomb of charge flowing through the cell.

12.3.4 Voltaic (or Galvanic) Cells

The electrochemical cell in which electric current is produced by spontaneous redox reaction is called galvanic cell or voltaic cells. They are commonly known as batteries. The names "galvanic" and "voltaic" honor the Italian scientists Luigi Galvani (1737-1798) and Alessandro Volta (1745-1827), who assembled the first version of the cells. Examples of galvanic cells are Daniel cell, Dry cell, Ni-Cd cell, Fuel cell.

Construction of Galvanic Cell

This cell consists of two half cells (half reactions) and placed in two beakers A and B containing solution of $ZnSO_4$ and $CuSO_4$ respectively. Zn electrode is dipped in solution of beaker A and Cu electrode in solution of beaker B. Each beaker makes a half cell and two beakers together make a complete cell. These two half cells are separate from each other and connected electrically by a salt bridge.

Working of Galvanic Cell

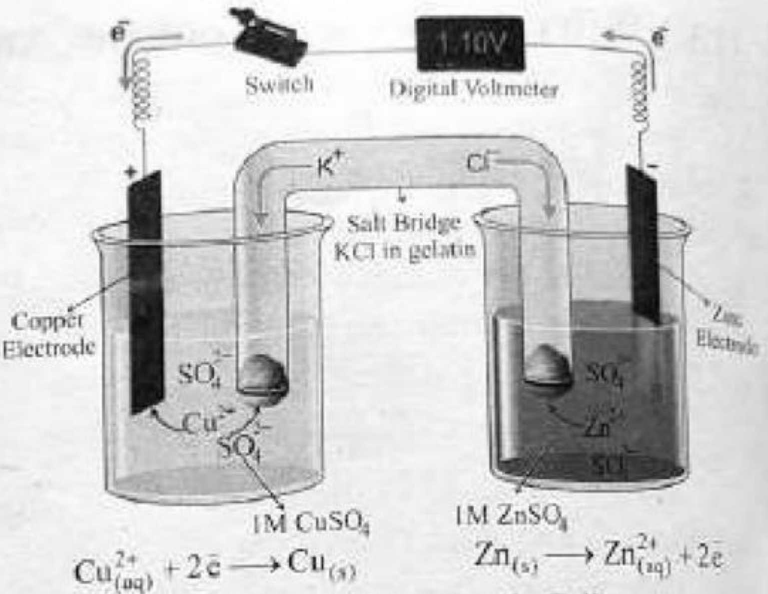


Figure 12.3: Galvanic Cell

When these two electrodes are connected externally by a wire, electrons flow from Zn-electrode to Cu-electrode. Hence Zn acts as an anode. The Cu^{2+} ions, from the solution, pick up the electrons at Cu-electrode and get reduced to copper atoms, Hence Cu acts as a cathode.

Due to flow of electrons from Zn to Cu, the cell produce an electric current and it serves as a source of electricity. Following reactions take place in the cell:

Reaction at anode: $Zn^0_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation)

Reaction at cathode: $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu^0_{(s)}$ (Reduction)

Net cell reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu^0_{(s)}$

The net cell reaction involves oxidation and reduction, hence called redox reaction. Conventionally the cell is represented as:

$$\underset{\text{anode}}{Zn^0_{(s)}/Zn^{2+}_{(aq)}\,1M} \quad \underset{\text{salt bridge}}{||} \quad \underset{\text{cathode}}{Cu^{2+}_{(aq)}\,1M/Cu^{2+}_{(aq)}}$$

'||' lines indicate salt bridge.

KNO_3, Na_2SO_4

Salt Bridge

A U-shaped tube filled with electrolyte like KCl or $NaNO_3$ in gelatin and sealed at both ends by porous glass wool is called salt bridge.

i) It connects two half cells electrically and it prevents mixing of two electrode solutions.

ii) It maintains the electrical neutrality in each half cell.

iii) It prevents charge accumulation in either solution. In the salt bridge, the ions migrate and carry the charge.

12.4 Standard Cell Potential and Standard Electrode Potential

12.4.1 Standard Cell Potential

The ability of cell to push electrons through the external circuit is expressed as potential. Electrons moves through the external circuit from anode (high pressure region) to cathode (low pressure region). The pressure of electrons at cathode is kept low by the process of reduction and the pressure of electrons at anode is kept high by the process of oxidation. The driving force that pushes the electrons from the anode and pulls them toward the cathode through the external circuit is an electrical potential, called electromotive force (emf). It is also known as cell voltage or cell potential (E).The cell potential may also be defined as the potential difference between the two electrodes in a voltaic cell. If there is no potential difference between the electrodes of the cell, then the current will not flow. The SI unit of potential difference (voltage) is the volt (V). The cell potential (or voltage) depends upon the nature of electrodes and the ions. It also depends on the concentrations of the ions and the temperature at which the cell is operated. The standard cell potential is the cell potential when both reactants and products are in their standard states. Standard cell potential is symbolized by E°. The superscript degree sign (°) indicates standard state conditions. Standard conditions include 1 M concentrations for solutions, 1 atm pressure for gases and usually 25°C temperature for the system. The liquids and solids must be present in their pure forms. The cell potential is measured by voltmeter.

12.4.2 Standard Electrode Potential

The difference of potential between an electrode and its salt solution in which the electrode is placed is called electrode potential or single electrode potential or half-cell potential. It may also be defined as:

Keep in mind

The standard oxidation potential and standard reduction potential values are always equal but opposite in signs.

The tendency of an electrode (substance) to lose or gain electrons when it is in contact with its own ions is called electrode potential. The magnitude of standard electrode potential values depends upon:

i) Nature of electrode and the ions and

ii) Concentration of the solution in which the electrode is placed.

iii) The temperature of the cell.

The potential difference between an electrode and 1M solution of its ions at 25°C (298 K) is called Standard electrode potential.

12.4.3 Standard Reduction Potential

The standard cell potential is the sum of standard oxidation potential and standard reduction potential.

$$E^{0}_{cell} = E^{0}_{ox} + E^{0}_{red}$$

The potential of an electrode at which reduction occurs is called reduction potential. It is symbolized by E^{0}_{red}. When electrode of copper is placed in a solution of copper ions, then reduction occurs.

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

Reduction potential of copper is 0.34 V and that of zinc is –0.76 V.

The potential of an electrode at which oxidation occurs is called oxidation potential. It is symbolized by E^{0}_{ox}. When electrode of zinc is placed in a solution of zinc ion, then oxidation occurs.

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

Oxidation potential of zinc is 0.76 V and that of copper is –0.34 V.

Keep In mind

Note that the standard oxidation potential and standard reduction potential values are always equal but opposite in signs.

The reduction potential at their standard states is called standard reduction potential and the oxidation potential at their standard states is called standard oxidation potential.

12.4.4 Measurement of Electrode Potential

There is no method to measure the potential for a single electrode; only the cell potentials can be measured. However it can be measured with reference to some standard electrode such as Standard Hydrogen Electrode (SHE). Standard electrode potential of hydrogen is taken as zero at all temperatures.

Standard Hydrogen Electrode (SHE)

It consists of platinum foil which is coated with finely divided black platinum and encased with a glass sleeve. It is dipped in 1M HCl solution. Pure hydrogen gas at 1 atm pressure is bubbled into 1M HCl solution. The hydrogen gas is absorbed on the platinum foil. The platinum acts as a conductor and facilitates the establishment of equilibrium between hydrogen gas and its ions in solution.

$$H_2 \rightleftharpoons 2H^+ + 2e^- \text{ [Oxidation (SHE acts as anode)]}$$

$$2H^+ + 2e^- \rightleftharpoons H_2 \text{ [Reduction (SHE acts as cathode)]}$$

The double arrows show only that the reaction is reversible, but not that there is true equilibrium.

The potential of this electrode is arbitrarily taken as zero at all temperatures. By convention this half-cell is written as oxidation and all other half cell reactions as reductions.

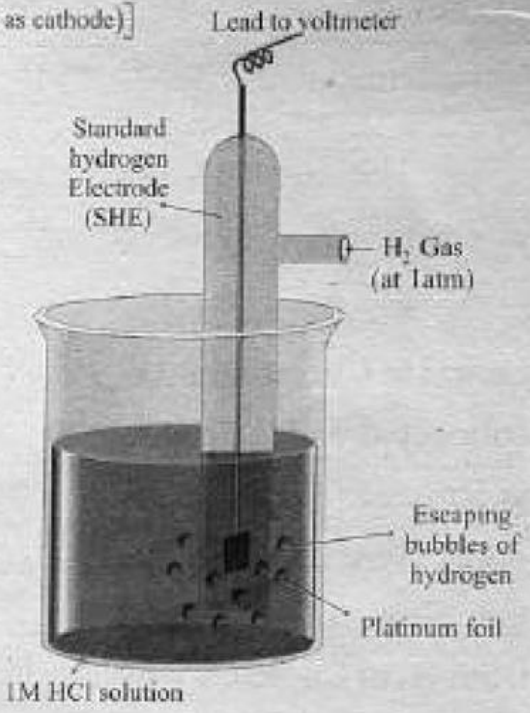


Figure 12.4: Standard Hydrogen Electrode (SHE)

Working with SHE

The electrode whose electrode potential is to be determined is connected with SHE and a galvanic cell is established. The two solutions are separated by a salt bridge. As the potential of SHE is zero, therefore, the voltmeter reading gives electrode potential of the electrode under test. The SHE may act as the anode or cathode depending upon the nature of electrode coupled with it.

To measure the electrode potential of zinc, a galvanic cell is established between zinc electrode dipped in 1M solution of its ions and SHE at 25°C. Zn acts as anode and hydrogen cathode act as inert electrode on which hydrogen gas is bubbled at 1 atmosphere. The electrode potential (E°) value of Zn is – 0.76 volts as shown by voltmeter. The cell reactions are:

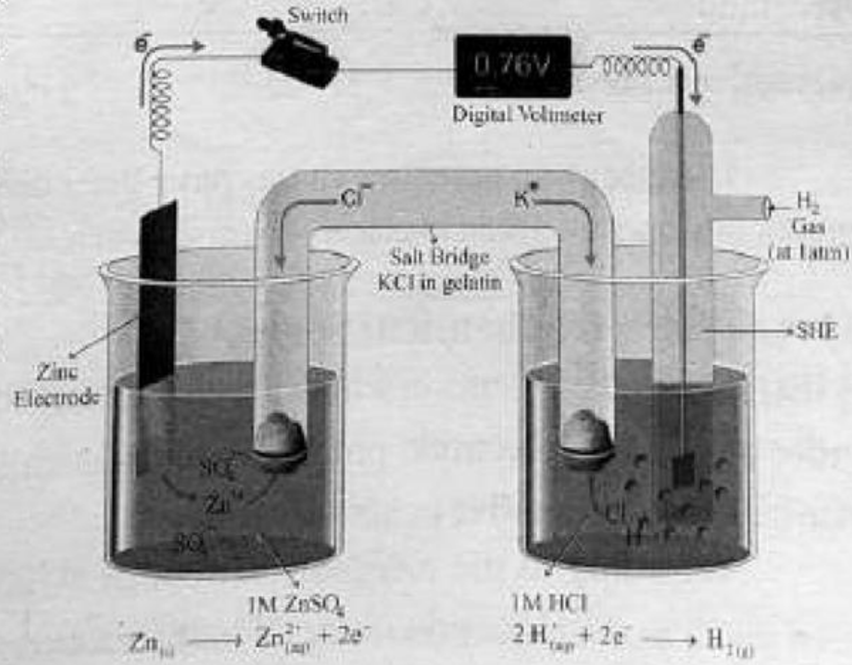


Figure 12.5: Galvanic Cell for measuring the electrode potential of zinc.

At anode: $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation)
At cathode: $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$ (Reduction)
Net cell reaction: $Zn^0_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$ (Redox Reaction)

The elements which have negative value of E° have tendency to lose electrons (not to gain electrons).

Similarly when Cu in 1M Cu^{2+} solution is connected with *SHE*, the voltmeter reads 0.34 volts. Here meter shows the flow of electrons from H_2 to Cu, so Cu acts as a cathode. The cell reactions are:

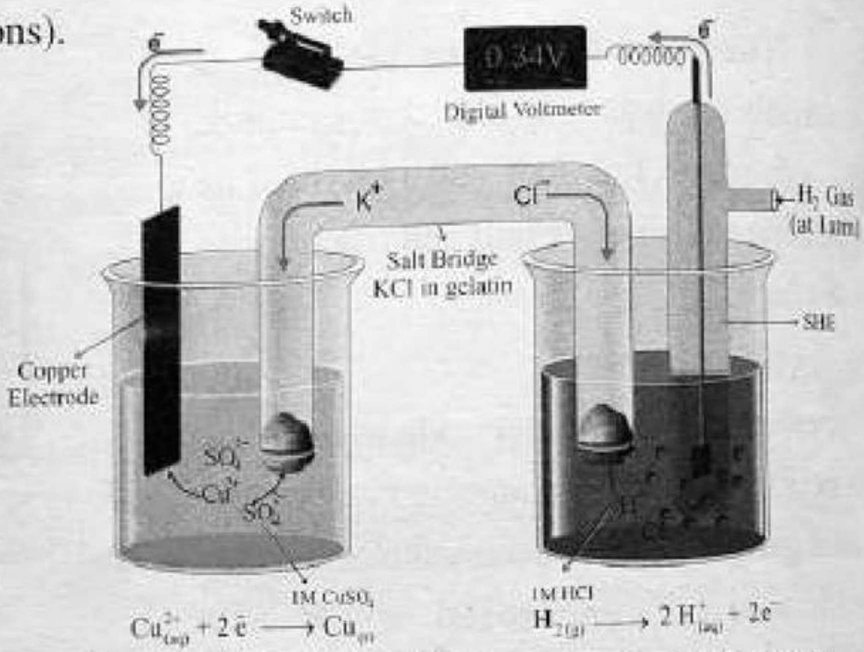


Figure 12.6: Galvanic Cell for measuring the electrode potential of copper.

At anode: $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$ (Oxidation)
At cathode: $Cu^{2+}_{(aq)} + 2\bar{e} \longrightarrow Cu_{(s)}$ (Reduction)
Net cell reaction: $H_{2(g)} + Cu^{2+}_{(aq)} \longrightarrow 2H^+_{(aq)} + Cu^0_{(s)}$ (Redox reaction)

The electrode potential values have been determined for all of the elements practically and are given in electrochemical series.

12.4.5 Electrochemical Series

A list (series) of elements in which they are arranged in the increasing or decreasing order of standard electrode potential values is called electrochemical series. It is also called electromotive or activity series.

According to the recommendation of IUPAC, the electrode potential has been given in the reduction mode. If half -reactions are written in oxidation mode, their potentials are oxidation potentials. By changing mode, magnitude of the potential does not change, only signs are reversed.

order is reversed here!!

Table 12.1: Standard Reduction Potentials in Water at 25°C

Reduction Half Reaction	E°(V)	Reduction Half Reaction	E°(V)
$F_{2(g)} + 2\bar{e} \rightleftharpoons 2F^-_{(aq)}$	+2.87	$Sn^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Sn_{(s)}$	-0.14
$O_{3(g)} + 2H^+_{(aq)} + 2\bar{e} \rightleftharpoons O_{2(g)} + H_2O$	+2.07	$Ni^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Ni_{(s)}$	-0.25
$Co^{3+}_{(aq)} + \bar{e} \rightleftharpoons Co^{2+}_{(aq)}$	+1.82	$Co^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Co_{(s)}$	-0.28
$Ce^{4+}_{(aq)} + \bar{e} \rightleftharpoons Ce^{3+}_{(aq)}$	+1.61	$Cd^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Cd_{(s)}$	-0.40
$Au^{3+}_{(aq)} + 3\bar{e} \rightleftharpoons Au_{(s)}$	+1.50	$Fe^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Fe_{(s)}$	-0.44
$Cl_{2(g)} + 2\bar{e} \rightleftharpoons 2Cl^-_{(aq)}$	+1.36	$Cr^{3+}_{(aq)} + 3\bar{e} \rightleftharpoons Cr_{(s)}$	0.74
$O_{2(g)} + 4H^+_{(aq)} + 4\bar{e} \rightleftharpoons 2H_2O$	+1.23	$Zn^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Zn_{(s)}$	-0.76
$Br_{2(l)} + 2\bar{e} \rightleftharpoons 2Br^-_{(aq)}$	+1.07	$2H_2O + 2\bar{e} \rightleftharpoons H_{2(g)} + 2\bar{O}H_{(aq)}$	-0.83
$2Hg^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Hg^{2+}_{2(aq)}$	+0.92	$Mn^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Mn_{(s)}$	-1.18
$Hg^{2+}_{2(aq)} + 2\bar{e} \rightleftharpoons 2Hg_{(l)}$	+0.85	$Al^{3+}_{(aq)} + 3\bar{e} \rightleftharpoons Al_{(s)}$	-1.66
$Ag^+_{(aq)} + \bar{e} \rightleftharpoons Ag_{(s)}$	+0.80	$Be^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Be_{(s)}$	-1.85
$Fe^{3+}_{(aq)} + \bar{e} \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77	$Mg^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Mg_{(s)}$	-2.37
$O_{2(g)} + 2H^+_{(aq)} + 2\bar{e} \rightleftharpoons H_2O_{2(aq)}$	+0.68	$Na^{2+}_{(aq)} + \bar{e} \rightleftharpoons Na_{(s)}$	-2.71
$I_{2(s)} + 2\bar{e} \rightleftharpoons 2I^-_{(aq)}$	+0.53	$Ca^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Ca_{(s)}$	-2.87
$O_{2(g)} + 2H_2O_{2(aq)} + 4\bar{e} \rightleftharpoons 4OH^-$	+0.40	$Sr^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Sr_{(s)}$	-2.89
$Cu^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Cu_{(s)}$	+0.34	$Ba^{2+}_{(aq)} + 2\bar{e} \rightleftharpoons Ba_{(s)}$	-2.90
$Cu^{2+}_{(aq)} + \bar{e} \rightleftharpoons Cu^+_{(aq)}$	+0.15	$K^+_{(aq)} + \bar{e} \rightleftharpoons K_{(s)}$	-2.93
$Sn^{4+}_{(aq)} + 2\bar{e} \rightleftharpoons Sn^{2+}_{(aq)}$	+1.03	$Li^+_{(aq)} + \bar{e} \rightleftharpoons Li_{(s)}$	-3.05
$2H^+_{(aq)} + 2\bar{e} \rightleftharpoons H_{2(g)}$	0.00		
$Pb^{2+} + 2\bar{e} \rightleftharpoons Pb_{(s)}$	-0.13		

Increasing strength as reducing agent
Increasing ease of oxidation

Increasing strength as oxidizing agent
Increasing ease of reduction

Increasing strength as reducing agent
Increasing ease of oxidation

Increasing strength as oxidizing agent
Increasing ease of reduction

Applications of Electrochemical Series

i) Calculation of the Voltage of Cells

From the series we can calculate the cell voltage (cell potential). The sum of the oxidation potential and reduction potential is called cell voltage.

Mathematically,

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

Let us find out cell voltage of Cu - Zn (Daniel) cell.

At anode (Oxidation): $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ $\quad E^\circ_{ox} = +0.76V$

At cathode (Reduction): $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ $\quad E^\circ_{red} = +0.34V$

The voltage of the cell (E°_{cell}) is calculated as:

$$E^{o}_{cell} = E^{o}_{ox} + E^{o}_{red}$$
$$E^{o}_{cell} = 0.76 + 0.34$$
$$= 1.10V$$

ii) Prediction of the Feasibility of a Chemical Reaction:

From the electrochemical series, we can determine whether the reaction is possible or not. We sum up the voltages of two half reactions, if voltage of the cell is positive, the reaction is possible and if negative, the reaction is not possible. Let us see the reactions:

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

From the electrochemical series, we have

$$\begin{array}{llr} Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-} & & E^{o}_{ox} = +0.76V \\ Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)} & & E^{o}_{red} = +0.34V \\ \hline Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)} & & E^{o}_{cell} = +1.10V \end{array}$$

The voltage is positive, hence the reaction is feasible (possible).

Consider another example:

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

From the electrochemical series, we have:

$$\begin{array}{llr} Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow Zn_{(s)} & & E^{o}_{red} = -0.76V \\ Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^{-} & & E^{o}_{ox} = -0.34V \\ \hline Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)} & & E^{o}_{cell} = -1.10V \end{array}$$

The sum of E° values of the two half-cell reactions is negative, hence the reaction is not feasible (possible).

iii) Comparison of Relative Tendency of Metals and Non-Metals to get Oxidized or Reduced:

Greater the value of standard reduction potential (E^{o}_{red}) of a given specie, greater is its tendency to accept electrons to undergo reduction and hence to act as an oxidizing agent. For example, the ions such as Cu^{2+}, Ag^{+}, Hg^{++} and non-metals like F_2, Cl_2, and Br_2 act as oxidizing agents. On the other hand, the species having lower value of standard reduction potential (E^{o}_{red}) show greater tendency to lose electrons. They undergo oxidation and hence act as reducing agents. For example, metals lying below SHE such as Zn, Mg, and Li readily lose electrons and act as reducing agents.

iv) Reaction of Metals with Dilute Acids

Greater the value of E°_{red} of metal, lesser is its tendency to lose electrons to form metal cations and so weaker is its tendency to displace H_2. For example, metals like Cu, Ag and Au which have sufficiently high positive values of E°_{red} do not liberate hydrogen from acids. While metals like Zn, Mg and Ca having low E°_{red}, liberate hydrogen gas when they react with acids.

$$Au + HCl \longrightarrow \text{No Reaction}$$

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

v) Displacement of One Metal by another from its Solution

From electrochemical series, we can determine whether a given metal will be displaced by another metal or not. A metal will displace another metal from the aqueous solution of its salt that lies below it in the series. For example, Zn will displace Cu.

$$Zn^0_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu^0_{(s)}$$

12.5 Modern Batteries

The cells which are used to produce electric current by chemical change are called batteries.

Batteries are of two types:

Primary and secondary batteries

12.5.1 Primary Batteries

The galvanic cells which cannot be recharged are called *primary cells*. For example, dry cell batteries.

Dry Cell Batteries

Dry cell batteries are used in torch lights, portable radios, toys, calculators, electronic watches etc. They are called dry cells because they do not have a liquid electrolyte. Some important types of dry cells are:

i) Leclanche dry cell
ii) Alkaline battery
iii) Nickel - Cadmium (NiCd) cell

I) Leclanché Dry Cell

The first dry cell was invented by Georges Leclanché (1839 - 1882) in

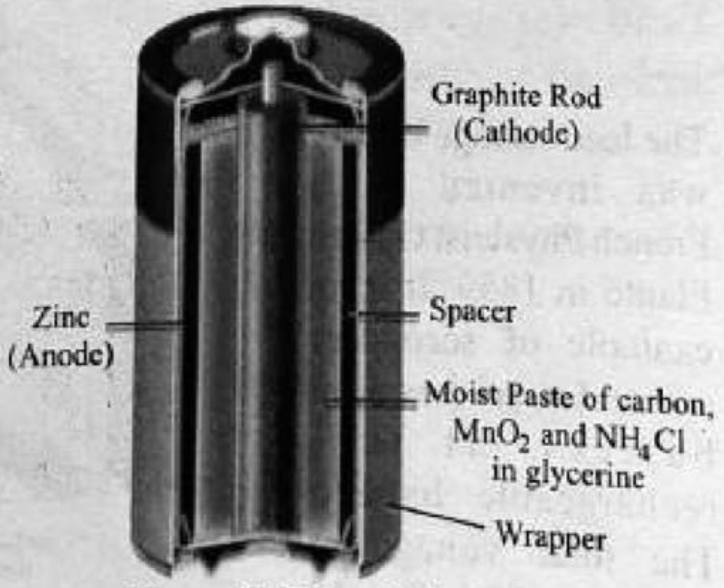


Figure 12.7: Dry Cell

1866. This dry cell battery has a zinc container which acts as anode and a moist paste of carbon powder, solid MnO_2 and solid NH_4Cl in glycerin around a carbon (graphite) rod which acts as cathode. When both electrodes (zinc container and carbon rod) are connected, electrons are released from zinc and current is produced. The reactions are:

At anode: $Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation)

At cathode: $2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$ (Reduction)

This cell produces a potential of about 1.5 volts.

ii) Alkaline Battery

Batteries with alkaline electrolyte were first invented by Waldemar Jungner in 1899. This is a type of dry cell. In this cell, zinc acts as anode and MnO_2 acts as cathode. KOH (or NaOH) is used as an electrolyte because of which it is known as alkaline battery. The battery is enclosed in a steel container. The zinc anode is slightly porous giving it a larger effective area. This cell delivers more current and has longer life than a common zinc cell.

The following reactions take place in this cell:

At Anode: $Zn_{(S)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(S)} + 2e^-$ (Oxidation)

At Cathode: $2MnO_{2(s)} + H_2O_{(l)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$ (Reduction)

Net Reaction: $Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \longrightarrow Zn(OH)_{2(s)} + Mn_2O_{3(s)}$

The voltage of this cell is 1.5 volt.

12.5.2 Secondary Batteries

The galvanic cells which can be recharged are called *secondary cells*. Examples are lead storage battery and NiCad battery.

Lead Storage Battery or Lead Accumulator

The lead storage battery was invented by a French Physicist Gaston Planté in 1859. It is an example of secondary cell and is used as a car battery. It is a rechargeable battery. The total voltage of battery is either 6 or 12

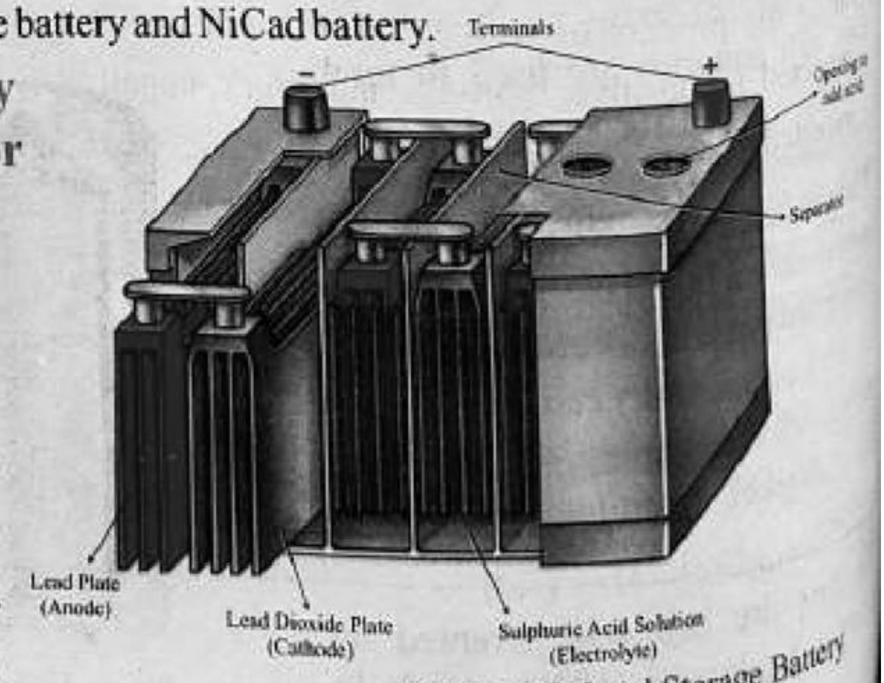


Figure 12.8: Lead Storage Battery

volts depending upon the number of cells used in its construction. The voltage of each cell is 2 volt. In the lead storage battery, the anodes are made up of lead metal (Pb) and cathodes are made up of lead dioxide (PbO_2). These electrodes are dipped in 30% H_2SO_4 solution (density = $1.25gcm^{-3}$).

Discharging

At anode, lead atoms lose two electrons each to form Pb^{2+} ions which combine with SO_4^{2-} ions present in the solution to give solid $PbSO_4$. $PbSO_4$ deposits on anode.

$$\begin{array}{ll} \text{At anode:} & Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2e^- \\ \text{(Oxidation)} & Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} \\ \hline & Pb_{(s)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} + 2\bar{e} \end{array}$$

The electrons released in the reaction pass round an external circuit as an electric current. This electric current is used for starting the engine of vehicle and for lighting up of car lights and so on.

At cathode, the electrons from the anode are accepted by PbO_2 and H^+ ions to produce lead ions and water as:

$$\begin{array}{ll} \text{At cathode:} & PbO_{2(s)} + 4H^+_{(aq)} + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O_{(l)} \\ \text{Reduction:} & Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \longrightarrow PbSO_{4(s)} \\ \hline & PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2\bar{e} \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)} \end{array}$$

When both the electrodes are covered with $PbSO_4$ deposits, then the cell is unable to produce any more current until it is recharged.

Recharging

During the process of recharging, the red positive (+) lead of the charger is connected to positive terminal and black negative (–) lead of the charger is connected to negative terminal of the battery. So, the reverse reaction takes place and cell starts recharging. The reactions which occur at electrodes are:

$$\begin{array}{ll} \text{At anode:} & PbSO_{4(s)} \longrightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \\ & Pb^{2+}_{(aq)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^+_{(aq)} + 2\bar{e} \\ \text{At cathode:} & PbSO_{4(s)} \longrightarrow Pb^{2+}_{(aq)} + SO^{2-}_{4(aq)} \\ & Pb^{2+}_{(aq)} + 2e^- \longrightarrow Pb_{(s)} \\ \hline \text{Net reaction:} & PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO^{2-}_{4(aq)} \end{array}$$

During discharging the density of acid (30% H_2SO_4) falls to 1.15g cm^{-3}. After recharging, the H^+ and SO_4^{2-} ions go back in solution and increase the density of acid again up to 1.25gcm^{-3}. The voltage of each cell returns to around 2 volts. Now this battery is used again.

Nickel Cadmium Cell (Rechargeable)

Nickel cadmium battery was invented by Waldemar Jungner in 1899 of Sweden. Nickel cadmium (or NiCd) cell is an important type of dry cell. It has acquired wide spread use in recent years. In this cell cadmium acts as anode. It undergoes oxidation in an alkaline (basic) electrolyte. The NiO_2 acts as cathode which undergoes reduction.

The reactions are:

At anode: $Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2\bar{e}$ (Oxidation)

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

Net reaction: $Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(l)}$

It is a rechargeable battery and is used in mobile phones, electronic calculators, electrical shutters, portable computers etc. It is more expensive than lead storage battery.

12.5.3 Fuel Cells

It is voltaic cell in which gaseous fuel (chemical energy) is converted into electrical energy (electricity).

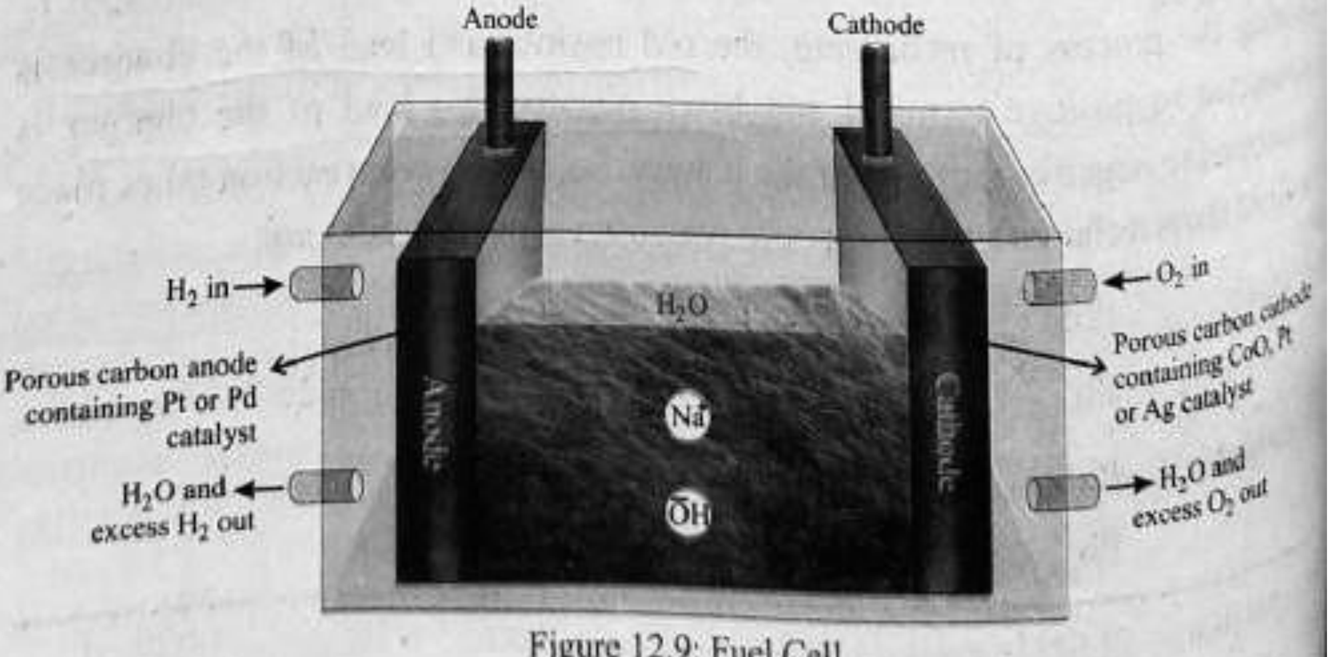


Figure 12.9: Fuel Cell

In this cell, gaseous fuels such as hydrogen and oxygen are allowed to undergo redox reactions. As a result of this electrical energy is produced.

This cell consists of three compartments separated from each other by porous electrodes. The electrodes are hollow tubes made of porous compressed carbon filled by platinum or palladium catalysts at the anode and cobalt oxide, platinum, or silver catalyst at the cathode.

An electrolyte such as KOH or NaOH is placed in the central compartment. Hydrogen is passed through anode and oxygen through the cathode. These gases diffuse slowly through the electrodes and react with electrolyte at 150°C and at high pressure. Hydrogen is oxidized to water at anode and oxygen is reduced to hydroxide ions at cathode.

The reactions are:

At anode: $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4\bar{e}$ (Oxidation)

At cathode: $O_{2(g)} + 2H_2O_{(l)} + 4\bar{e} \longrightarrow 4OH^-_{(aq)}$ (Reduction)

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

Such cells run continuously as long as reactants are supplied.

A number of cells are connected together to obtain several kilowatts of power.

Advantages of Fuel Cells

i) The fuel cells are very efficient. They convert 75% fuel (i.e. chemical energy) into electricity. The ordinary electricity generator using oil or natural gas has an efficiency of 35-40%, whereas a diesel engine has an efficiency of 25-30%. Rest of the energy is lost as heat.

ii) The fuel cells are free from (noise and thermal) pollution.

iii) The water formed as an end product can be used for drinking purpose for an astronaut in space vehicles.

iv) Oxygen and hydrogen can be continuously supplied to the cell and there is no need for replacement of any electrical energy.

Society, Technology and Science

Solar Cells as the Source of Energy in Future:

Solar cells (also called photovoltaic cells) are electronic devices that convert the solar energy into electricity. Solar energy is the energy obtained from the sun's radiation (sunlight) that is used to generate electricity, to heat or cool homes, or cause chemical reactions. The solar cells are connected together to form a panel. Solar panels can be linked to a rechargeable battery that collects energy in the day to be used at any time, even at night when there is no sun. Solar energy is a type of renewable energy; it will never run out. Solar energy is clean and pollution free. Solar panels are extremely reliable, need little maintenance and have a long life. Solar energy can be used in remote areas to generate electricity where it is too difficult to provide much needed electricity by using traditional methods.

If we compare these characteristics to those of fossil fuels such as coal, oil, gas and nuclear power, then we will able to decide which source is better for us. Solar energy is a rapidly growing way to generate electricity.

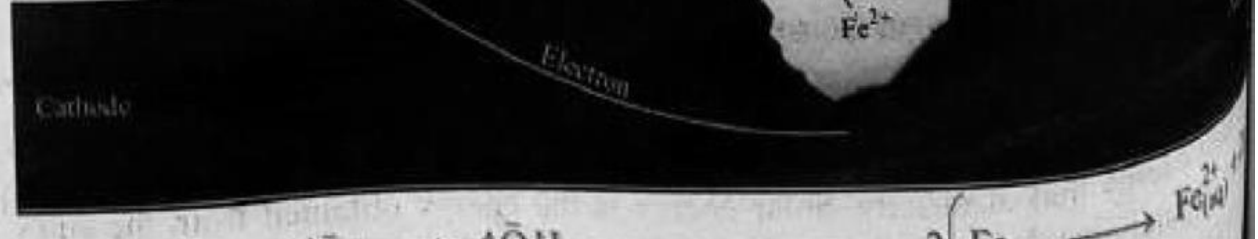
12.6 Corrosion

The process of chemical decay of metals by an electrochemical process is usually known as corrosion. Corrosion is a spontaneous redox reaction that occurs when metal comes in contact with oxygen in the presence of moisture. The metal is oxidized and converted to an unwanted compound; that is, to an oxide. This is the most common form of corrosion. The corrosion is generally a surface phenomenon.

Corrosion of Iron (Rusting)

The most familiar example of corrosion is the rusting of iron. Rusting of iron needs both oxygen gas and moisture. It does not occur in moisture free air (dry air) and air free water (oxygen-free water). Iron which is a silver white metal is converted to red-brown mass (rust) when comes in contact with moist air. The rust is hydrated iron (III) oxide ($Fe_2O_3.x\ H_2O$ where x varies from 2 to 4, it is not fixed). The iron corrodes (rusts) rapidly when comes in contact with less active metal such as copper and corrodes slowly when comes in contact with a more active metal such as zinc.

When iron comes in contact with moist air, a galvanic cell is produced where one part of iron acts as cathode and other part of iron acts as anode.



$2H_2O_{(l)}+O_{2(g)}+4\bar{e} \longrightarrow 4\bar{O}H_{(aq)}$

$2\left(Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)}\right.$

Figure 12.10: Rusting of Iron

The electrons flow from anode to cathode. The following reactions occur:

At anode: $2Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

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

Net cell reaction: $2Fe_{(s)} + O_{2(g)} + 2H_2O_{(l)} \longrightarrow 2Fe^{2+}_{(aq)} + 4OH^-_{(aq)}$

The iron (II) ions are further oxidized by oxygen and forms iron (III) ions that react with hydroxide ions to form rust.

$$2Fe^{2+}_{(aq)} + 4OH^-_{(aq)} + \tfrac{1}{2}O_{2(g)} \longrightarrow \underset{\text{(Rust)}}{Fe_2O_3.\,2H_2O_{(s)}}$$

The overall reaction can also be written as:

$$2Fe_{(s)} + \tfrac{3}{2}O_{2(g)} + x\,H_2O_{(l)} \longrightarrow Fe_2O_3.\,x\,H_2O_{(s)}$$

Interesting information:

Corrosion of iron forms oxide layer on the surface which protects the iron from further corrosion. The oxide layer on the surface of aluminum also protects it from corrosion. The aluminum has low reduction potential value and is therefore, more reactive than iron and we expect to be corrode readily. But in actual practice, it corrodes slowly. The exceptional stability of aluminum is due to the formation of compact layer of oxide (Al_2O_3), which protects the metal from further corrosion. On the other hand, the oxide layer of iron is permeable and allows oxygen and moisture to penetrate further into the metal and promotes corrosion.

Prevention of Corrosion

The methods that are used to prevent the metal from corrosion are listed below:

Alloying

The corrosion of metal can be prevented or minimized by lowering its reactivity through alloying. For example, stainless steel which is an alloy of iron, chromium, silicon, and nickel is resistant to corrosion. Stainless steel is used for making knives, spoons, forks, utensils, scissors, and surgical instruments.

Oil or Grease Coating

The corrosion of metal can be prevented or minimized by covering the surface of metal with grease or oil. For example, the nuts, bolts, tools, parts of machinery, and parts of engines are coated with grease or oil to protect them from rusting.

Paint Coating

The corrosion of metal can be prevented or minimized by covering the surface of metal with paint. For example, the iron bridges, windows, doors, gates, and the bodies of rickshaws, cars, buses, and trucks are coated with paints to protect them from corrosion (rusting).

Galvanizing

The process in which sheets of metals (iron) are coated with thin layer of zinc to prevent corrosion is called galvanizing. It is also known as zinc coating or anode coating. This process can be done by dipping a clean sheet of iron into a bath of molten zinc. If zinc coating is damaged by a scratch or a dent, corrosion starts. The standard reduction potential value of zinc is less than iron, so zinc is more easily oxidized and the iron is therefore protected. This method is used to protect underground storage tanks, pipes, oil rigs and ships from rusting. This method is also used to protect dust-bins, drums, and buckets from corrosion (rusting). The metals most frequently used for this purpose are aluminum and magnesium, because these metals are much more reactive than iron and form a compact layer which minimizes their own corrosion.

Electroplating

The process in which a thin layer of one metal is deposited on another metal (object) by means of electrolysis to prevent corrosion is called electroplating.

Electroplating is carried out by using the metal (object) to be plated as a cathode and the metal to be deposited as an anode. The electrolyte is an aqueous solution of salt of the metal being deposited. The electrodes are connected with a battery. When electric current is passed through the solution, the metal to be deposited (anode) is oxidized to its cations and enters into the solution. These cations are reduced and deposited onto the object to be plated (cathode). In this process, a thin layer of metal is deposited onto the object which is then pulled out from the solution. The process of electroplating is used to improve the hardness, stability and appearance of objects and to protect them from corrosion. Some examples of electroplating are tin-plating, chromium-plating, silver-plating, and gold-plating.

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Tin is non-poisonous and is used for plating tiffin-boxes. Chromium is often plated onto a bicycle handle, bars and car bumpers made of iron and steel to protect them from corrosion and give them a shiny appearance. The jewelries, trophies, and medals are commonly silver-plated. Some other common examples of silver-plating are cups, dishes, spoons, and objects made of steel. Silver is a stable metal and does not react with oxygen and vapours of water present in the atmosphere. The silver-plated objects lose luster (chamak) and turn black when kept for a long time in the air due to formation of a thin layer of silver sulphide (Ag_2S) by the action of hydrogen sulphide (H_2S) gas present in the air. Gold is a very stable metal and do not react with water vapours, and gases that are present in the atmosphere. Gold is used for decorative plating. The gold-plated objects do not lose luster and look new for several years.

Summary of Facts and Concepts

- Electrochemistry is the branch of chemistry in which we study about the interconversion of chemical and electrical energy.
- The reactions in which electrons are transferred from one reactant to another are called oxidation-reduction (or redox) reactions.
- Oxidation is the loss of electrons and reduction is the gain of electrons. Oxidation occurs at anode and reduction occurs at cathode. The electrons flow from anode to cathode.
- Oxidation state (or oxidation number) is defined as the apparent charge, positive or negative, which an atom would have in a compound. An atom may have different oxidation states in different compounds.
- Oxidizing agent is a substance that oxidizes other substances and gets reduced itself in a chemical reaction. Examples of oxidizing agents are non-metals.
- Reducing agent is a substance that reduces other substances and gets oxidized itself in a chemical reaction. Examples of reducing agents are metals.
- The flow of electrons is called electric current or electricity.
- A substance through which electric current can pass is called conductor while a substance through which an electric current cannot pass is called non-conductor or insulator. Metals are conductors while non-metals are insulators.
- Redox reaction is the sum of oxidation-half reaction and reduction-half reaction. Oxidation-half reaction is a half reaction in which a substance loses electrons whereas the reduction-half reaction is a half reaction in which a substance gains electrons.
- Redox potential is a combined term involving oxidation potential and reduction potential. Oxidation potential is the potential of an electrode at which oxidation occurs while reduction potential is the potential of an electrode at which reduction occurs.
- Electrode potential is the difference of potential between an electrode and its salt solution in which the electrode is placed. The potential difference between an electrode and 1M solution of its ions at 25°C is called standard electrode potential.
- Electromotive force is a force that moves the electrons from the anode to the cathode through the external circuit (wire). It is abbreviated by emf.
- The emf of a galvanic cell is called cell potential or cell voltage and is measured in volts. The cell potential under standard conditions is called standard cell potential.
- Electrochemical cells are of two types: galvanic and electrolytic. Chemical energy is converted to electrical energy in galvanic cell while electrical energy

is converted to chemical energy in electrolytic cell.

- Galvanic (or voltaic) cell is a cell in which electric current is produced by spontaneous redox reaction. Electrolytic cell is a cell in which non-spontaneous redox reaction occurs by the passage of electricity.
- A battery is a galvanic cell or a group of cells connected in a series.
- Corrosion is the process of chemical decay of metals due to action of surrounding medium. The most common example of corrosion is the rusting of iron.
- The corrosions of metals can be reduced or prevented by number of methods but the most important is electroplating.
- Electroplating is an electrolytic process in which a thin layer of one metal is deposited on another metal.

Questions and Problems

Q.1. Four answers are given for each question. Select the correct one:

i) The cell in which electrical energy is converted into chemical energy is:

(a) Electrolytic cell (b) galvanic cell

(c) NiCd cell (d) fuel cell

ii) Which one of the following reactions is **NOT** a redox reaction:

(a) $C + O_2 \longrightarrow CO_2$

(b) $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$

(c) $ZnSO_4 + Cu \longrightarrow CuSO_4 + Zn$

(d) $2Na + Cl_2 \longrightarrow 2NaCl$

iii) The oxidation state of manganese is +3 in:

(a) MnO (b) MnO_2 (c) Mn_2O_3 (d) Mn_2O_7

iv) In the following reaction, the substance that undergoes reduction is:

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

(a) H_2O (b) CO_2 (c) $C_6H_{12}O_6$ (d) O_2

v) Which one of the following is the strongest oxidizing agent?

(a) Oxygen (b) chlorine (c) fluorine (d) nitrogen

vi) Which one of the following substances is oxidized in the reaction given below:

$Mg + 2HCl \longrightarrow MgCl_2 + H_2$

(a) Mg (b) HCl (c) $MgCl_2$ (d) H_2

vii) Which statement is *correct* about the Daniel cell (Zn-Cu cell)?

(a) The Daniel cell is an example of an electrolytic cell.

(b) The spontaneous cell reaction involves the oxidation of Cu by Zn^{2+}

(c) The spontaneous cell reaction involves the reduction of Zn^{2+} to Zn

(d) The spontaneous cell reaction involves the reduction of Cu^{2+} to Cu

viii) The reaction that occurs at cathode is known as:

(a) Redox (b) oxidation

(c) reduction (d) decomposition

ix) Which of the following statement is **NOT** correct for a galvanic cell:

a) Oxidation occurs at anode

b) reduction occurs at cathode

c) both '*a*' and '*b*'

d) electrons flow from cathode to anode

x) Galvanizing is a process in which sheets of metals are coated with thin layer of .... to prevent corrosion:

(a) Tin (b) zinc (c) copper (d) silver

Q.2. Fill in the blanks with suitable words given in the brackets:

i) A substance through which electric current _________ pass is called conductor. (can/cannot)

ii) The _________ electrode is called anode. (positive/negative)

iii) Spontaneous chemical reactions take place in _________ cell. (electrolytic/galvanic)

iv) Ionic compounds conduct electricity in _________ state. (solid/molten)

v) Oxidation occurs during chemical reaction by _________ of electrons. (gain/loss)

vi) The tendency of an electrode to gain electrons is called reduction potential. (gain/lose)

vii) The cells that can be recharged are called _________ cells. (primary/secondary)

viii) The oxidation number of chlorine in $KClO_4$ is ________. (-1/+7)

ix) The method of electroplating is used to protect ________ from corrosion. (metal/non-metal)

x) Aluminum is ________ reactive than iron. (less/more)

Q.3. Label the following statments as True or False:

i) Oxidation takes place at anode.

ii) The reduction potential of zinc is 0.34 V.

iii) Oxidizing agent oxidizes other substances.

iv) Fluorine is the strongest oxidizing agent.

v) Half-cell of an active metal acts as cathode.

vi) The element is reduced when its oxidation number is increased.

vii) Fuel cell is the example of voltaic cell.

viii) The moist air is necessary for rusting of iron.

ix) The SI unit of voltage is coulomb.

x) Corrosion is a spontaneous redox reaction.

Q.4: What is electrochemistry? Give its important applications.

Q.5: Is electrochemical process always advantageous?

Q.6: What are redox reactions? Give applications of redox reactions in daily life.

Q.7: Define oxidation number and describe the rules for assigning the oxidation numbers.

Q.8: Calculate the oxidation number of 'S' in the following species:

(i) H_2S (ii) SO_2 (iii) SO_3 (iv) $Na_2S_2O_3$

Q.9: How can you recognize oxidation reduction reactions? Explain briefly.

Q.10: Write down the rules, which are used for balancing of redox equations by oxidation number method and by the half reaction method.

Q.11: Balance the following equations by oxidation number method:

a) $Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

b) $HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$

c) $MnO_2 + HCl \longrightarrow MnCl_2 + Cl_2 + H_2O$

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

Q.12: Balance the following equations by half reaction (ion-electron) method:

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

b) $HNO_3 + HI \longrightarrow NO + H_2O + I_2$

c) $Cu + NO_3^{-1} \longrightarrow Cu^{+2} + 2NO_2$

Q.13: What is meant by the terms oxidizing and reducing agents? Give some important reactions of oxidizing and reducing agents.

Q.14: Define the terms anode and cathode with reference to a specific voltaic cell.

Q.15: What are electrochemical cells? What is the difference between galvanic cell and electrolytic cell?

Q.16: Describe the construction and working of galvanic cell.

Q.17: Describe the electrolysis of aqueous solution of NaCl.

Q.18: Distinguish between electrical terms coulomb, ampere, and volt.

Q.19: Define salt bridge. What is the function of salt bridge?

Q.20: Explain briefly:

a) Standard cell potential.

b) Standard electrode potential.

c) Standard reduction potential.

Q.21: Describe the construction and working of standard hydrogen electrode.

Q.22: What is electrochemical series? Give its important applications.

Q.23: What are dry cells? What are the important types of dry cells? Explain.

Q.24: Write a short note on lead storage battery.

Q.25: What are fuel cells? What are the advantages of fuel cells?

.26: Define and explain corrosion. What do you know about the corrosion (rusting) of iron? What are the methods to prevent the metal from corrosion?

.27: Answer the following questions briefly:

a) Why is it necessary to use a salt bridge in a galvanic cell?

b) Why is the cathode of a galvanic cell considered to be the positive electrode?

c) Why sodium ion (Na^+) acts as an oxidizing agent whereas sodium atom (Na) acts as a reducing agent?

d) SHE acts as cathode when connected with zinc electrode but acts as anode when connected with copper electrode, why?

e) Zinc displaces hydrogen from acids but copper cannot, why?

f) Why iron doors and bodies of cars are painted routinely?

g) Why damp air is necessary for rusting of iron?

h) Why the bracelets and rings made of gold look new even after several years of use?

Answers to the Selected Practice Exercises

Chapter No.1

(1) 157.9g (2) 0.1mol

(3) 111g (4) 91mol

(5) 1.505×10^{24} molecules

(6) 6.69×10^{24} molecules

(7) $50.43dm^3$ (8) $25.47dm^3$

(9) 182.5g (10) 7.5mol

(11) 130.37g (12) $700.44dm^3$

(13) % of N in NH_3 = 82.35%, % of N in HNO_3 = 22.22%

(14) e (15) 90.79%

Chapter No.4

(1) (a) 0.355atm (b) 360mbar
(c) 5.22psi

(2) $17.5dm^3$ (3) $26.77cm^3$

(4) 56000mL (5) 44.89atm

(6) 3.99kg (7) $1.89gdm^{-3}$

(8) 101.59atm (9) 1.46

Chapter No.7

(2) 24.24 (3) 0.0024M

(4) $9.33\times10^{-10}M$ (5) 4.56×10^{-8}

Chapter No.8

(1) Acidic, $[H^+] > 10^{-7}M$

(2) Basic, pH > 7

(3) (a) 2.5×10^6 (b) 1.99×10^8

(4) 7.37 (5) 8.4×10^{-6}

Chapter No.9

(1)(a) Rate = $K[NO]^2[O_2]^1$ Third Order
(b) $K = 215mol^{-2}dm^6S^{-1}$

Chapter No.10

(1) 15% (2) 1.5%

(3) 5% (4) 2M

(6) 2m

(7) $X_{C_2H_6O_2} = 0.162$, $X_{H_2O}=0.838$

(8) 0.004ppm = 4ppb = 4000ppt

(9) $\Delta T_b = 1.65℃$
b.p of aq. Solution = 101.65℃

(10) $152gmol^{-1}$ (11) $92gmol^{-1}$

(12) $\Delta T_f = 3.19℃$
freezing point depression of antifreeze = −3.19℃

Chapter No.11

(1) $\Delta H_n = 1087.8kJmol^{-1}$

(2) $-688.2kJmol^{-1}$

Chapter No.12

(1) (i) +3 (ii) +3

Answers to the Selected Problems

Chapter No.1

(14) 55.8g

(15) (b) 14g of O_2 is required
(c) 49g of CaO is produced

(16) (a) 1.375mol (b) 1.375mol

(17) 240g (18) 56L

(19) 31.25mol (20) 3.97mol

(25) $CO_3^{-2} = 1.505\times10^{24}$ particles
$C_9H_8O_4 = 1.204\times10^{27}$ particles

(26) $V_{SO_2} = 28.02dm^3$
$V_{Ar} = 11.207dm^3$

(28) (i) 50% (ii) 53.33%
(iii) 26.67% (iv) 66.67%
(v) 53.33%

(29) Br_2 is limiting reactant and Mass of HBr 16.02g

(30) 56.16g

(31) Carbon is limiting reactant and mass of SiC is 13.2g

(32) Mass of N_2O = 124.85g
Mass of H_2O = 102.15g

(33) (a) Theoretical yield of Cu = 5.28g
(b) Percentage yield of Cu = 94.7%

(34) 83.34%

Chapter No.2

(41) $E=4.05\times10^{-19}J$

(42) $\nu=5.26\times10^{14}Hz$
$E=3.49\times10^{-19}J$
$=1.75\times10^{6}m^{-1}$

(44) $\Delta E=1.635\times10^{-18}J$

(45) $\nu=4.57\times10^{14}Hz$,
$\lambda = 656nm$

Chapter No.3

(50) Percent ionic character of HF =41.36%
HF is more ionic than HCl

(51) 6.08D (52) $1.80\times10^{-20}C$

Chapter No.4

(28) 1.47 psi and 101.325mbar

(29) 110.92 atm (30) 15.2mmHg

(31) $8.15dm^{3}$ (32) 2.83mL

(33) 579.16K (35) $682.56dm^{3}$

(36) $28dm^{3}$ (37) $61.64dm^{3}$

(38) $56.73m^{3}$ (39) 221.47K

(40) 1.81mol (41) $17gmol^{-1}$

(42) $128.81gmol^{-1}$ (44) 760mmHg

(45) 4 psi

(46) $P_{H_2}=0.744atm$
$P_{Ne}=0.149atm$
$P_{Kr}=0.107\ atm$

(47) 2.65

(48) $M_x=44gmol^{-1}$
The unknown gas is CO_2

(49) $15.9gmol^{-1}$

Chapter No.7

(5) 2.118×10^{20}

(26) $2.08\times10^{-3}M$ (25) 4.99

(28) $1.304\times10^{-5}M$ (27) $6.87\times10^{-3}M$

(30) 3.73 (29) 6.91×10^{-9}

Chapter No.8

(17) (a) $[H^+]=1.58M$
$[OH^-]=6.33\times10^{-15}M$
(b) $[OH]=2.236\times10^{9}M$
$[H^+]=4.47\times10^{-24}M$

(18) $[H^+]=4.0\times10^{-15}M$

(20) pOH = 12.2, the solution is acidic

(21) pH = 10.3

(22) $[H^+]=3.16\times10^{-5}$
$[OH^-]=3.16\times10^{-10}$

(28) pH = 3.385 (29) $K_a=2.401\times10^{-10}$

Chapter No.9

(10) (a) Reaction order for CO = First Order
Reaction order for Cl_2 = First Order
Over all order for reaction = Second Order
$Rate=K[CO]^{1}[Cl_2]^{1}$
(b) $K=1.6710^{-6}mol^{-1}dm^{3}S^{-1}$

Chapter No.10

(40) 22.22% (41) 11%

(42) 5% (43) 0.02m

(45) 0.5M

(46) (a) 0.4m (b) 2.5m

(47) (a) 3M (b) 0.5M

(48) $X_{C_7H_8}=0.17$ (50) 78.667 ℃

(51) $74.56gmol^{-1}$ (52) −1.86 ℃

Chapter No.11

(22) $\Delta H_n=133.9KJmol^{-1}$

(23) $-1016KJmol^{-1}$

Chapter No.12

(8) (i) S = −2 (ii) S = +4
(iii) S = +6 (iv) S = +2

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Table of Metric Units

Quantity	Unit	Symbol
Energy	Calorie	cal
Pressure	Millimeter of mercury	mm Hg
Specific heat	Joule per kilogram degree Celsius	J/kg.°C
Temperature	Degree Celsius	°C
Volume	Litre	L

Table of SI Base Units

Quantity	Unit	Symbol
Length	Metre or Meter	m
Mass	Kilogram	Kg
Time	Second	s
Electric current	Ampere	A
Temperature	Kelvin	K
mount of substance	Mole	mol
uminous intensity	Candela	cd

Table of some Important Derived Units

Quantity	Unit	Symbol
rea	Square metre	m^2
orce	Newton	N
lume	Cubic metre	m^3
ensity	Kilogram per cubic metre	kg/m^3
ergy or heat	Joule	J
essure	Pascal	Pa
ectric potential	Volt	V
ectric charge	Coulomb	C
ecific heat	Joule per kilogram-kelvin	J/kg.K
quency	Hertz	Hz

Table of SI Prefixes

ix	Symbol	Meaning	Multiplier	Prefix	Symbol	Meaning	Multiplier
	E	Quintillion	10^{18}	deci	d	Tenth	10^{-1}
	P	Quadrillion	10^{15}	centi	c	Hundredth	10^{-2}
	T	Trillion	10^{12}	milli	m	Thousandth	10^{-3}
	G	Billion	10^{9}	micro	µ	Millionth	10^{-6}
	M	Million	10^{6}	nano	n	Billionth	10^{-9}
	k	Thousand	10^{3}	pico	p	Trillionth	10^{-12}
	h	Hundred	10^{2}	femto	f	Quadrillionth	10^{-15}
	da	Ten	10^{1}	atto	a	Quintillionth	10^{-18}

Table of Physical Constants

Quantity	Symbol	Value
Acceleration due to gravity	g	$9.80665\ m/s^2$
Atomic mass unit	amu	$1.660539 \times 10^{-24} g$ $1.660539 \times 10^{-27} kg$
Avogadro's number	N_A	6.0221367×10^{23} particles/mol
Bohr radius	a_o	$5.291772949 \times 10^{-11} m$
Charge-to-mass ratio of electron	e/m	$1.75881962 \times 10^{11} C/kg$
Electron or proton charge	e	$1.602176 \times 10^{-19} C$
Faraday's constant	F	9.6485309×10^{4} C/mol
General gas constant	R	8.3145 J/(mol.K) $0.082058\ dm^3$. atm/(mol.K)
Mass of electron	m_e	5.485799×10^{-4} amu $9.109382 \times 10^{-31} kg$
Mass of neutron	m_n	1.008665 amu $1.674927 \times 10^{-27} kg$
Mass of proton	m_p	1.007276 amu $1.672622 \times 10^{-27} kg$
Molar volume	V_m	$22.414 \times 10^{-3} m^3/mol$ $22.414\ dm^3/mol$
Pi	π	3.1415926536
Planck's constant	h	6.626069×10^{-34} J.s
Rydberg constant	R_∞	$3.28984 \times 10^{15} Hz$ $1.09737315685 \times 10^{-7} m^{-1}$ $1.09737315685 \times 10^{-2} nm^{-1}$
Speed of light (m vacuum)	c	$2.99792 \times 10^{8} ms^{-1}$
Vacuum permittivity	ε	$8.85419 \times 10^{-12} J^{-1}C^{2}m^{-1}$

Table of important Conversion Factors

Length (SI unit = meter)

1 kilometer (km) = 1000 m
= 0.62137 mile (mi)
1 meter (m) = 1.0936 yards
= 39.37 inch (in.)
= 100 centimeters (cm)
= 1000 millimeters (mm)
1 inch = 2.54 centimeters (cm)
1 mile = 1.609 km = 5280 feet (ft)

1 foot = 12 in.
= 30.48 cm
1 yard (yd) = 36 in.
= 0.9144 m

Mass (SI unit = kilogram)

1 kilogram (kg) = 1000 grams (g)
= 2.2046 pounds (lb)
1 pound = 0.45359 kg
= 453.59 g
= 16 ounces
1 gram = 1000 milligrams (mg)
= 6.02×10^{23} amu
1 ton = 2000 lb
= 907.185 kg
1 metric ton = 1000 kg
= 1.103 tons
= 2204.62 lb
1 ounce (oz) = 28.3 g

Volume (SI unit = cubic meter)

1 liter (L) = 1 decimeter cube (dm^3)
= 1000 milliliters (mL)
= 10^{-3} cubic meter (m^3)
= 1.0567 quarts (qt)
1 gallon (gal) = 4 qt
= 8 pints (pt)
= 3.785 L
= 128 fluid ounces (liq. oz)
1 quart (qt) = 2 pt
= 0.946 L
= 32 liq. oz
1 fluid ounce = 29.6 mL
1 milliliter = 1 centimeter cube (cm^3)
= 10^{-3} L

Pressure (SI unit = pascal)

1 pascal (Pa) = N/m^2
= 1 kg/ms^2
1 atmosphere = 760 millimeter of mercury (mmHg)

= 760 torr
= 76 centimeter of mercury (cmHg)

= 101325 Pa
= 101.325 kilopascals (kPa)
= 14.7 pound per square inch (lb/in^2)

1 bar = 100000 Pa
= 0.98692 atmospheres (atm)
1 torr = 1 mm Hg

Energy (SI unit = joule)

1 joule (J) = 1 Newton meter (Nm)

= 1 kg m^2/s^2
= 0.23901 calorie
= coulomb volt (CV)
= 10^7 erg
1 calorie (cal) = 4.184 J
1 electron volt (eV) = 96.485 kJ/mol
= 1.60218×10^{-19} J
1 kilowatt hour (kWh) = 3600 kJ

Temperature (SI unit : Kevin)

0 kelvin (K) = -273.15°C
= -459.67°F

$$K = {}^{\circ}C + 273.15$$

$$^{\circ}C = K - 273.15$$

$$^{\circ}C = \frac{(^{\circ}F - 32)}{1.8}$$

$$^{\circ}F = 1.8 \times {}^{\circ}C + 32$$

Time (SI unit = second)

1 minute (min) = 60 seconds (s)
1 hour (hr) = 60 minutes
= 3600 seconds
1 day (d) = 24 h
= 1440 min
= 86400 s
1 year (yr) = 365.25 d
= 8766 hr

Names, Formulas and Valencies of Some Common Ions

Monovalent positive ions (cations)		Monovalent negative ions (anions)	
Ammonium	NH_4^+	Acetate	$C_2H_3O_2^-$ or CH_3COO^-
Cesium	Cs^+	Bisulphate or Hydrogen sulphate	HSO_4^-
Cuprous or Copper (I)	Cu^+	Bisulphite or Hydrogen sulphite	HSO_3^-
Hydrogen	H^+	Bicarbonate or Hydrogen carbonate	HCO_3^-
Lithium	Li^+	Bromate	BrO_3^-
Silver	Ag^+	Bromide	Br^-
Sodium	Na^+	Chlorate	ClO_3^-
Divalent positive ions		Chloride	Cl^-
Barium	Ba^{2+}	Chlorite	ClO_2^-
Cadmium	Cd^{2+}	Cyanide	CN^-
Calcium	Ca^{2+}	Fluoride	F^-
Chromous or Chromium (II)	Cr^{2+}	Hydride	H^-
Cobaltous or Cobalt (II)	Co^{2+}	Hydroxide	OH^-
Cupric or Copper (II)	Cu^{2+}	Hypochlorite	ClO^-
Cuprous or Copper (I)	Cu_2^{2+}	Iodate	IO_3^-
Ferrous or Iron (II)	Fe^{2+}	Iodide	I^-
Magnesium	Mg^{2+}	Nitrate	NO_3^-
Manganous or Manganese (II)	Mn^{2+}	Nitrite	NO_2^-
Mercuric or Mercury (II)	Hg^{2+}	Perchlorate	ClO_4^-
Mercurous or Mercury (I)	Hg_2^{2+}	Permanganate	MnO_4^-
Plumbous or Lead (II)	Pb^{2+}	Thiocyanate	SCN^-
Strontium	Sr^{2+}	**Divalent negative ions**	
Nickel (II)	Ni^{2+}	Carbonate	CO_3^{2-}
Stannous or Tin (II)	Sn^{2+}	Chromate	CrO_4^{2-}
Zinc	Zn^{2+}	Dichromate	$Cr_2O_7^{2-}$
Trivalent positive ions		Oxalate	$C_2O_4^{2-}$
Aluminum	Al^{3+}	Oxide	O^{2-}
Antimony (III)	Sb^{3+}	Peroxide	O_2^{2-}

Arsenic (III)	As^{3+}	Silicate	SiO_3^{2-}
Bismuth (III)	Bi^{3+}	Sulphide	S^{2-}
Chromic or Chromium (III)	Cr^{3+}	Sulphate	SO_4^{2-}
Ferric or Iron (III)	Fe^{3+}	Sulphite	SO_3^{2-}
Titanous or Titanium	Ti^{3+}	Thiosulphate	$S_2O_3^{2-}$
Tetravalent positive ions		**Trivalent negative ions**	
Manganic or Manganese (IV)	Mn^{4+}	Arsenate	AsO_4^{3-}
Plumbic or Lead (IV)	Pb^{4+}	Borate	BO_3^{3-}
Stannic or Tin (IV)	Sn^{4+}	Phosphate	PO_4^{3-}
Titanic or Titanium (IV)	Ti^{4+}	Phosphide	P^{3-}
Pentavalent positive ions		Phosphite	PO_3^{3-}
Antimony (V)	Sb^{5+}	**Tetravalent negative ions**	
Arsenic (V)	As^{5+}	Carbide	C^{4-}

Formulas and Molecular Masses of some Common Substances

Substances	Formulas	Molecular Masses (amu)	Substances	Formulas	Molecular Masses (amu)
Chlorine	Cl_2	71	Hydrogen	H_2	2
Bromine	Br_2	160	Oxygen	O_2	32
Iodine	I_2	254	Nitrogen	N_2	28
Hydrogen monoxide	H_2O	18	Sodium chloride	$NaCl$	58.5
Ammonia	NH_3	17	Sulphuric acid	H_2SO_4	98
Methane	CH_4	16	Sodium hydroxide	$NaOH$	40
Carbon dioxide	CO_2	44	Magnesium sulphate	$MgSO_4$	120
Carbon monoxide	CO	28	Magnesium carbonate	$MgCO_3$	84
Glucose	$C_6H_{12}O_6$	180	Hydrogen peroxide	H_2O_2	34
Benzene	C_6H_6	78	Potassium iodate	KIO_3	214
Acetylene	C_2H_2	26	Potassium permanganate	$KMnO_4$	158
Potassium iodide	KI	166	Manganese dioxide	MnO_2	87
Cholestrol	$C_{27}H_{46}O$	386	Magnesium sulphide	MgS	56.4
Caffeine	$C_8H_{10}O_2N_4$	194	Copper sulphate	$CuSO_4$	159.6