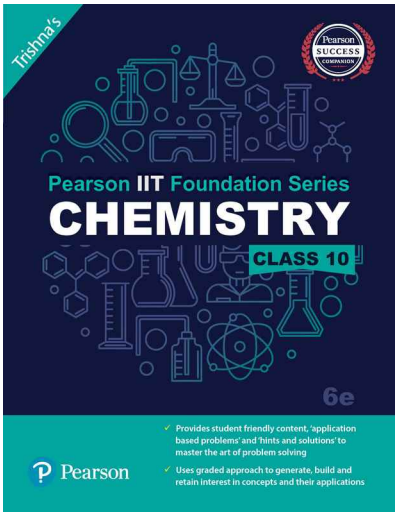
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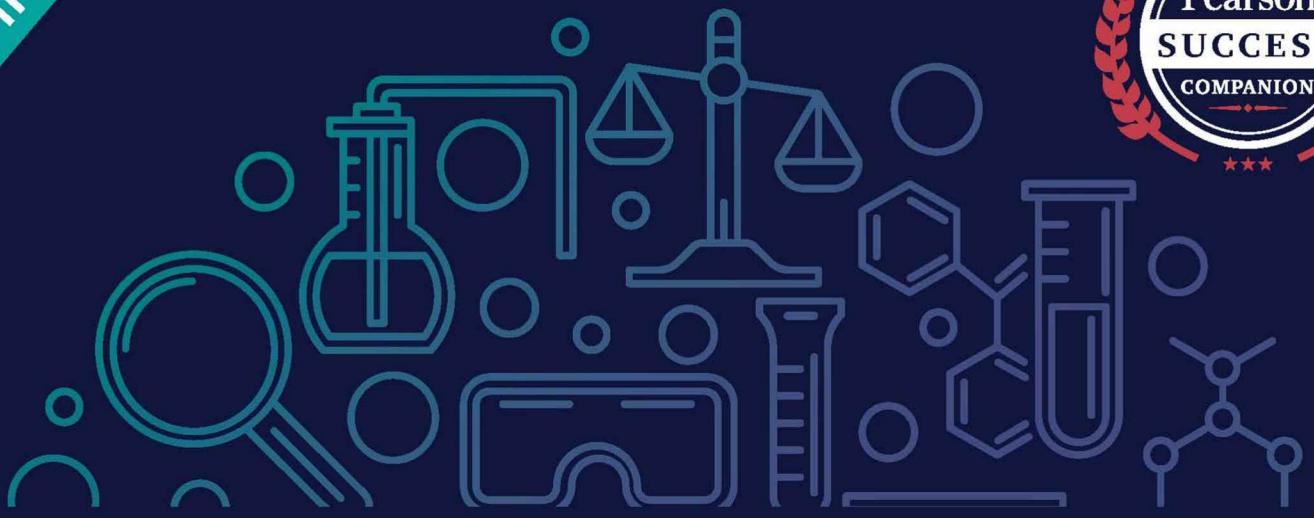

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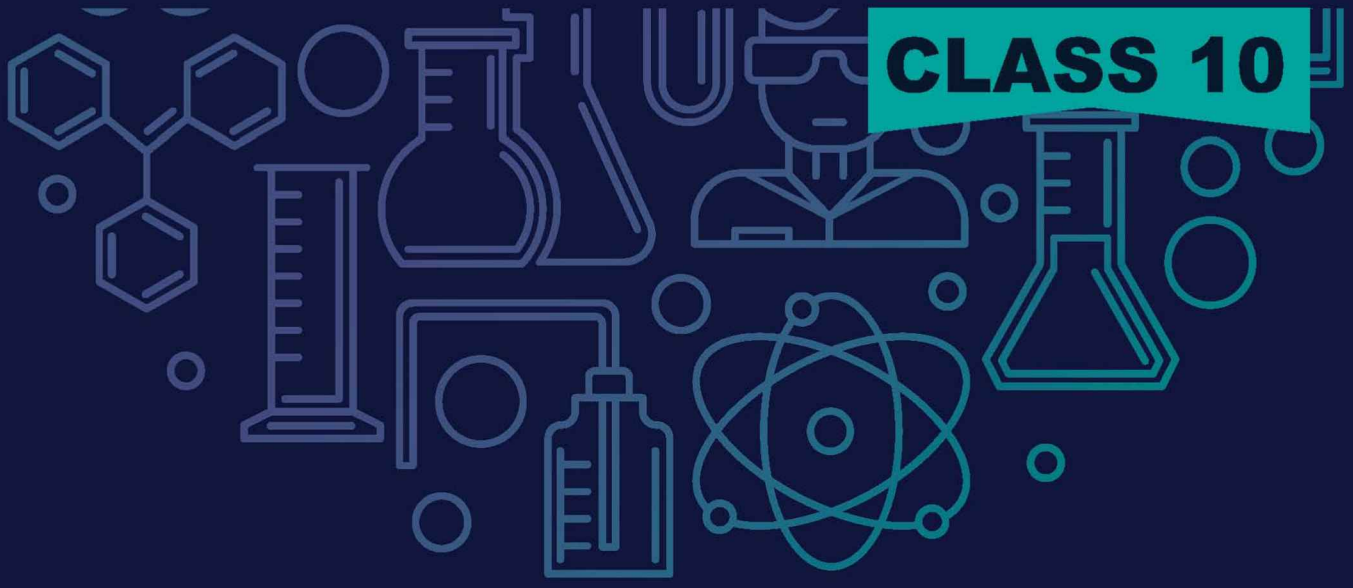

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Preface

Pearson IIT Foundation Series has developed into a trusted resource for scores of students who have aspired to be a part of the elite undergraduate institutions of India. As a result it has become one of the best selling series, providing authentic and class tested content for effective preparation.

The structure of the content is not only student friendly but is also designed in such a manner that it invigorates the students to go beyond the usual school curriculum and also act as a source of higher learning to strengthen the fundamental concepts of Physics, Chemistry, and Mathematics.

The core objective of the series is to be a one stop solution for students preparing for various competitive examinations. Irrespective of the field of study that the student may choose to take up later, it is important to understand that Mathematics and Science form the basis for most modern day activities Hence, utmost efforts have been made to develop student interest in these basic building blocks via real-life examples and application based problems. Ultimately the aim is to ingrain the art of problem-solving in the minds of the reader.

To ensure high level of accuracy and practicality this series has been authored by a team of highly qualified and experienced faculties involved in grooming the young minds. That said, we believe that there is always scope for doing things in a better manner and hence invite you to provide us with your candid feedback and suggestions on how we can make this series more superior.

Chapter Insights

Remember

Before beginning this chapter, you should be able to:

- define substance, mixture, mass, weight, etc.
- know the states of matter solid, liquid and gas
- basic properties of matter

Remember section will help them to memories and review the previous learning on a particular topics

Key points will help the students to identify the essential points in a chapter

Key Ideas

After completing this chapter, you should be able to:

- define matter, molecule, atom etc.
- know the arrangement of molecules in three different states of matter.

INTRODUCTION

The planet earth has endowed us with the basic necessities of life like air, water, food etc. Among these, air is the most vital for life and hence indispensable.

Layers of Atmosphere

Our atmosphere is divided into five layers on the basis of variations in chemical composition, density, temperature at different heights from the surface of the earth.

(i) Troposphere

(a) The layer of atmosphere which begins at the earth's surface and extends up to 20 km height is called **troposphere**.

Text: concepts are explained in a well structured and lucid manner

Note boxes are some add-on information of related topics

Note: Diluted H_2SO_4 is not used for the preparation of CO_2 because the calcium sulphate formed being insoluble in water forms a layer over marble chips and thus marble chips do not come in contact with dil H_2SO_4 further.

EXAMPLE

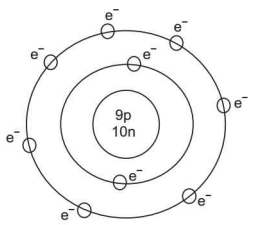
Give the electronic configuration and geometrical representation of the following elements.

(a) Flourine **(b)** Sodium **(c)** Chlorine **(d)** Carbon

SOLUTION

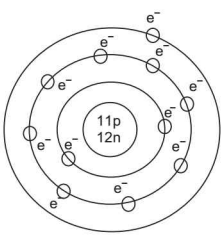
(a) Florine Z = 9

Electronic configuration = 2, 7



(b) Sodium Z = 11

Electronic configuration = 2, 8, 1



Examples given topic-wise to apply the concepts learned in a particular chapter

Illustrative examples solved in a logical and step-wise manner

TEST YOUR CONCEPTS

Very Short Answer Type Questions

***Directions for questions 1 to 10*: Fill in the blanks.**

1. In a _____ properties of the constituents are retained.
2. A mixture of alcohol and water is an example of _____ mixture.
3. A substance which is formed by the chemical combination of two or more elements is called a _____.
4. Boiling point is the temperature at which _____ is converted to _____ at one atmospheric pressure.
5. Nonmetals usually exist in _____ state.
6. _____ show the properties of metals and nonmetals.
7. With an increase in the surface area of a liquid, the rate of evaporation_____.

16. Which among the following is an element?
    (a) Calcium oxide
    (b) Common salt
    (c) Ozone
    (d) Water
17. Evaporation is the process of conversion of
    (a) a liquid to its gaseous state below the boiling point of the substance
    (b) a liquid to its gaseous state at the boiling point of the substance
    (c) a solid to its liquid state at the melting point of the substance
    (d) a solid to its liquid state below the melting point of the substance

Different levels of questions have been included in the *Test Your Concept* as well as on *Concept Application* which will help students to develop the problem-solving skills

'Test Your Concepts' at the end of the chapter for classroom preparations

'Concept Application' section with problems divided as per complexity: Level 1; Level 2; and Level 3

CONCEPT APPLICATION

Level 1

True or false

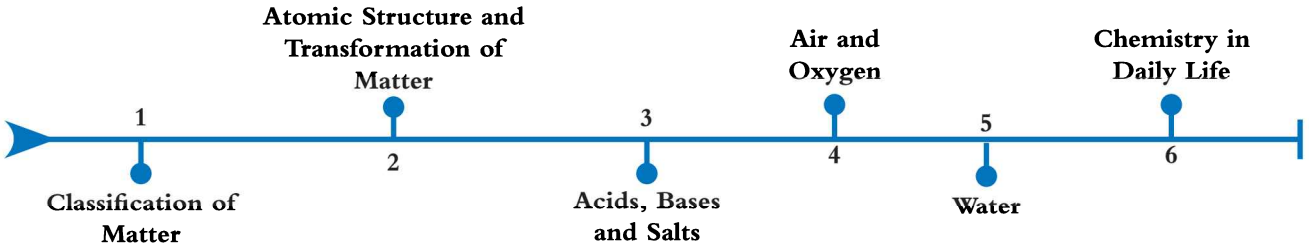
1. Gases have maximum intermolecular spaces.
2. Metals are highly ductile and malleable.
3. Evaporation takes place from the surface of a liquid and hence it is a surface phenomenon.
4. Pure substances are made up of identical molecules and hence are homogeneous in nature.
5. Tellurium is a metalloid and hence it shows properties of both metals and nonmetals.
6. Iodine is a lustrous nonmetal.
7. As the density of sodium is less than that of water it floats on water.
8. Ammonium chloride undergoes sublimation and hence it is a sublimable substance.
9. The constituents of a compound do not retain their properties and hence these cannot be separated by physical methods.
10. Sublimation is the process of the conversion of a solid to its gaseous state.

38. Carbon fibre, a recently developed allotrope of carbon is ductile and has high tensile strength.
39. Sand is insoluble in water; hence, it can be separated by filtration. Glucone-D is soluble in water; hence, it can be separated by distillation and water is collected separately.
40. Rate of evaporation is directly proportional to surface area of the liquid. This is because more number of surface molecules are exposed to atmosphere which gain kinetic energy and escape into atmosphere.
41. (i) A mixture of sawdust and water is taken in a beaker
    (ii) A filter paper is folded in the form of a cone and fitted into a funnel by moistening it with a few drops of water
    (iii) The mixture is poured gently into the filter cone and collected into another beaker which is called a filtrate.
    (iv) The solid retained on the filter paper is called a residue.

Hints and Explanation for key questions along with highlights on the common mistakes that students usually make in the examinations

Series Chapter Flow

Class 7



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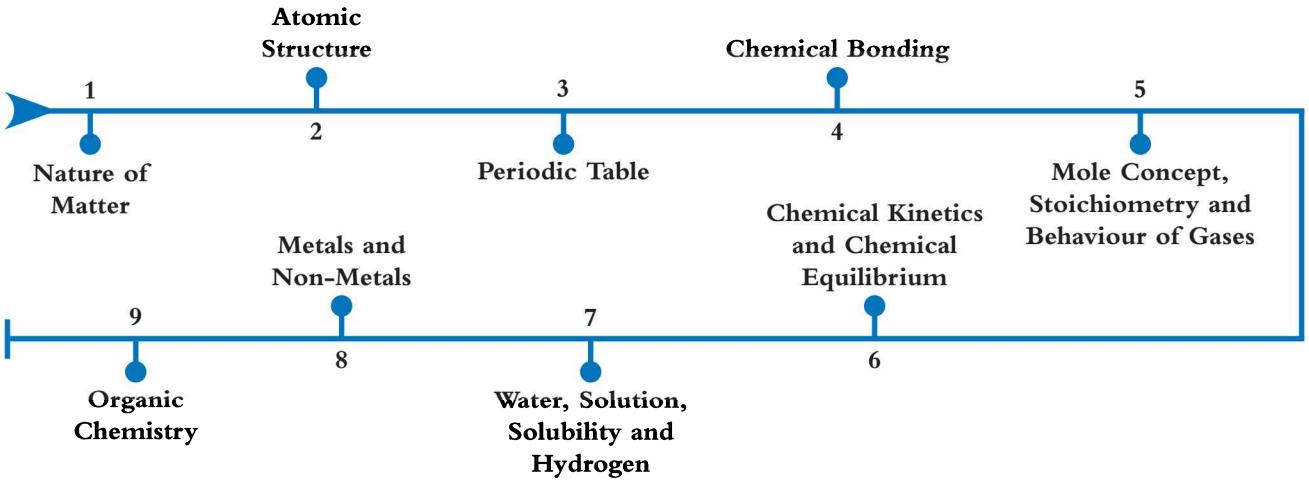

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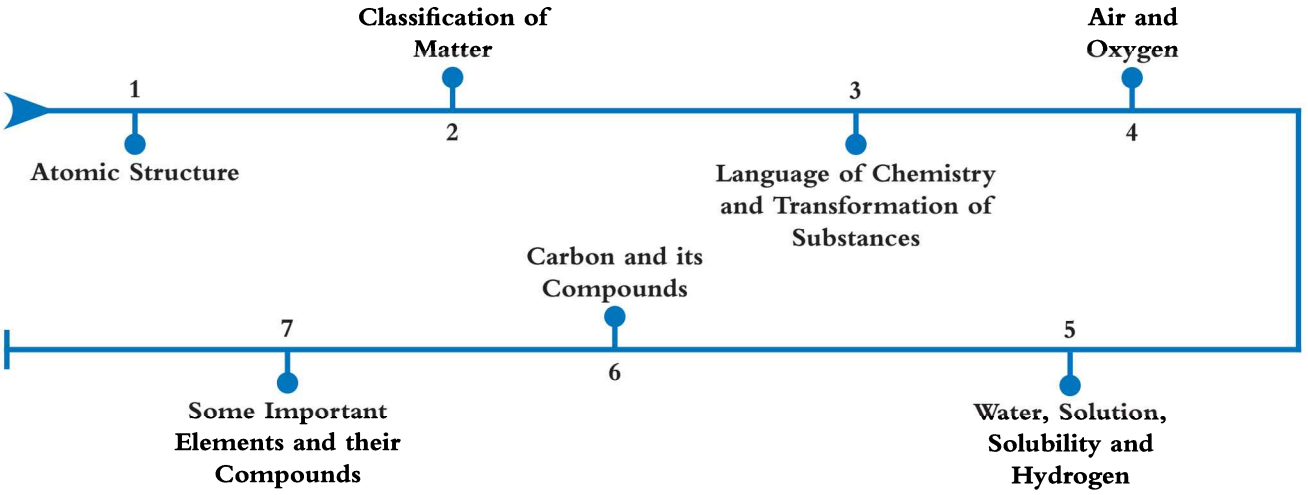

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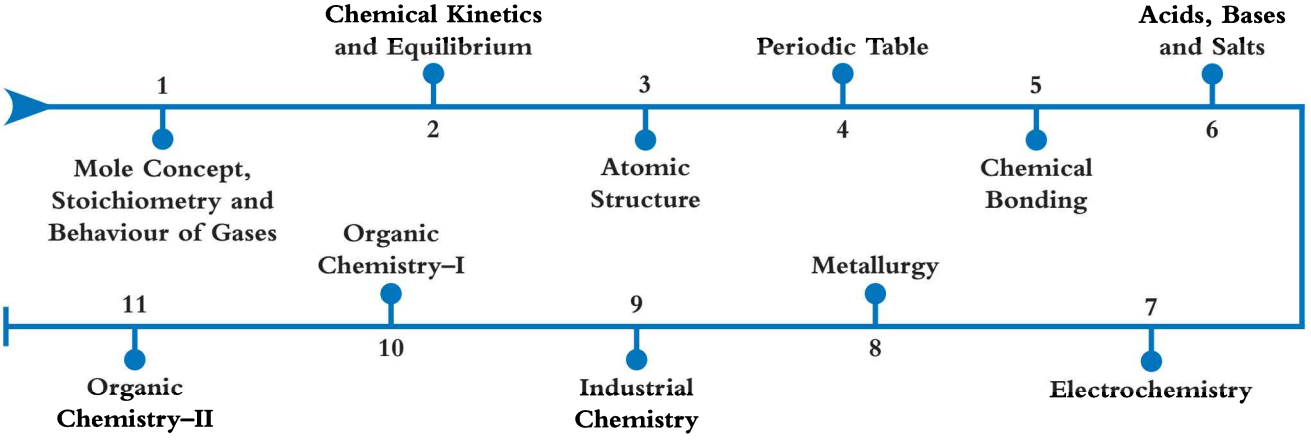


Chapter

1

Mole Concept, Stoichiometry and Behaviour of Gases

Remember

Before beginning this chapter, you should be able to:

- understand the concept of matter and atoms
- review the classification of matter and their atomic structure identify the types of chemical reactions

Key Ideas

After completing this chapter, you should be able to:

- understand the kinetic molecular theory and interrelationship among various measurable properties of gases.
- understand mole as the chemical counting unit
- derive ideal gas equation from Gas Laws and draw a comparison between ideal gas and real gas.
- study the behaviour of gases in a mixture and their relative tendency to diffuse.
- understand and to establish quantitative relationship among reactants and products and develop numerical skills with regard to calculations based on chemical equations.

INTRODUCTION

Chemistry is the branch of science which deals with the study of matter in different perceptions. Matter can be basically classified on the basis of molecular composition as elements, compounds and mixtures. The various elements are given names and symbols and the names and formulae of various compounds have been derived based on certain rules. The study of naming these compounds and derivation of formulae for these is the prerequisite for representing chemical reactions in the form of chemical equations. Therefore, the language of chemistry which involves the study of symbols, formulae and chemical equations with respect to the above aspects is of utmost significance.

SYMBOL

All elements are represented by means of their symbols. A symbol represents the atom of an element which may consist of a single letter or a combination of letters derived either from its English name or from its Latin name.
A symbol is the short hand notation which represents a single atom of an element.

Example

H ⇒ Hydrogen

Hg ⇒ Hydrarg yrum (Latin name for mercury)

He ⇒ Helium

FORMULAE

A molecule of an element or a compound is represented by means of a formula. Formula is written with the help of symbols of the respective constituent element(s) along with the actual number of atoms of the respective elements.
A formula is the short hand notation which represents a single molecule of an element or compound.

Example

Cl ⇒ one molecule of chlorine consists of two atoms.

$CaCO_3$ ⇒ one calcium atom, one carbon atom and three oxygen atoms

Derivation of Formulae of Compounds

A molecule is formed by the combination of a positive radical and a negative radical, but by itself is electrically neutral. Hence the number of positive and negative radicals which form a molecule of the compound depends on the charge(s) on the respective radicals.

Positive Radicals	Negative Radicals	Formulas	Explanation
Na^+	Cl^-	NaCl	One Na^+ neutralizes one Cl^- since both of them are unipositive
H^+	SO_4^{-2}	H_2SO_4	Two H^+ are required to neutralize one SO_4^{-2}
Al^{+3}	CO_3^{-2}	$Al_2(CO_3)_3$	Two Al^{+3} are required to neutralize three CO_3^{-2}
Ca^{+2}	PO_4^{-3}	$Ca_3(PO_4)_2$	Three Ca^{+2} are required to neutralize two PO_4^{-3}

Naming of Inorganic Compounds

Inorganic compounds are classified into three categories, namely, acids, bases and salts. Naming of the respective categories follows certain rules, which we now discuss.

Naming of Acids

Acids usually contain hydrogen ion (H^+) as the positive radical. Hence the name of the acid depends on the constituent(s) of its negative radical.

Types of Acid	Types of Negative Radical	Suffixes
1. Binary acids	Negative radical consists of a single nonmetal Examples: HCl, HBr, etc.	"ic" (prefix hydro) Hydrochloric acid Hydrobromic acid
2. Oxyacid	Negative radical consists of a nonmetal and oxygen. The name of the oxyacid depends on the percentage of the oxygen associated with a specific nonmetal.	
	Acids with comparatively less percentage of oxygen. Examples: H_2SO_3, HNO_3, H_3PO_3, etc.	"ous" Sulphurous acid, nitrous acid, phosphorous acid, etc.
	Acids with comparatively more percentage of oxygen. Examples: H_2SO_4, HNO_3, H_3PO_4, etc.	"ic" Sulphuric acid, nitric acid, phosphoric acid, etc.

If the acid contains lesser number of oxygen atoms than the corresponding "ous" acid, "hypo" prefix is given to the negative radical, whereas "per" prefix is given to the negative radical when the acid contains greater number of oxygen atoms than the corresponding "ic" acid.

Examples

Hypochlorous	acid	$HClO$
Chlorous	acid	$HClO_2$
Chloric	acid	$HClO_3$
Perchloric	acid	$HClO_4$

Naming of Bases

Bases generally contain hydroxyl radical (OH^-) as the negative radical and a metal ion as its positive radical. While writing the name of the base, the name of the metal is written first followed by hydroxide.

Examples

$Ca(OH)_2$	Calcium hydroxide
$Mg(OH)_2$	Magnesium hydroxide
$NaOH$	Sodium hydroxide
$Al(OH)_3$	Aluminium hydroxide

Naming of Salts

The positive radical present in the salt comes from the corresponding base and the negative radical comes from the corresponding acid.

Name of the salts starts with the name of the metal present as a positive radical which is followed by the name of a negative radical. Name of the negative radical depends on the name of the acid from which the salt is produced.

Acids from which the salt is produced	Suffixes and names of the salt
1. "ous" acid Examples: Sulphurous acid (H_2SO_3) Nitrous acid (HNO_2) Phosphorous acid (H_3PO_3)	"ite" $CaSO_3$ → Calcium sulphite $Zn(NO_2)$ → Zinc nitrite $Mg(PO_3)_2$ → Magnesium phosphite
2. "ic" acid Examples: Sulphuric acid (H_2SO_4) Nitric acid (HNO_3) Phosphoric acid (H_3PO_4)	"ate" $ZnSO_4$ → Zinc sulphate $NaNO_3$ → Sodium nitrate $AlPO_4$ → Aluminium phosphate

If NH_4^+ is present as the positive radical in the base or in the salt, ammonium is written in place of the name of the metal.

EXAMPLE

Ammonium hydroxide (base) → NH_4OH

The formula of a metal phosphide is M_3P_2. Identify formulae of the

(a) metal oxide **(b)** metal nitrite **(c)** metal bicarbonate

SOLUTION

Initial condition **Final condition**

Since the formula of metal phosphide is M_3P_2, metal ion is M^{+2}

(a) Formula of metal oxide is $M^{+2}O^{-2} \Rightarrow MO$

(b) Formula of metal nitrite is $M^{+2}NO_2^{-1} \Rightarrow M(NO_2)_2$

(c) Formula of metal bicarbonate is $M^{+2}\ HCO_3^{-1} \Rightarrow M(HCO_3)_2$

EXAMPLE

Ammonium phosphate (salt) → $(NH_4)_3PO_4$

Metal M forms two oxides A and B in which the ratios of number of oxygen atoms to the total number of atoms present in the molecule are 3 : 5 and 1 : 2 respectively. Determine the formulae of A and B.

SOLUTION

Metal ions present in A and B are M^{+a} and M^{+b} respectively,

$\therefore$ Formula of A is $M^{+a}O^{-2} \Rightarrow M_2O_a$

$\therefore$ Ratio $= \dfrac{a}{2+a} = \dfrac{3}{5}$

$\Rightarrow 5a = 6 + 3a \Rightarrow 2a = 6 \Rightarrow a = 3$

$\therefore$ metal oxide A is $M^{+3}O^{-2} \Rightarrow M_2O_3$

Formula of B is $M^{+b}O^{-2} \Rightarrow M_2O_b$

$\therefore$ Ratio $= \dfrac{b}{2+b} = \dfrac{1}{2}$

$\Rightarrow 2b = 2 + b \Rightarrow b = 2$

$\therefore$ metal oxide B is $M^{+2}, O^{-2} \Rightarrow MO$

Another aspect of the study of matter involves the different physical states of matter, i.e., solids, liquids and gases. Existence of matter in three distinct states entirely depends on the arrangement of molecules.

Molecules are closely packed in solids, comparatively loosely packed in liquids but very loosely packed in gases. This type of molecular arrangement, gives the gas molecules maximum freedom of movement which results in the various unique properties that gases exhibit. The gases neither have a definite shape nor a definite volume due to the random movement of the gas molecules. The unique characteristics of gases can be explained with the help of **kinetic molecular theory**.

KINETIC THEORY OF GASES

(i) All gases are made up of tiny particles known as molecules.

(ii) The huge intermolecular spaces make the forces of attraction between the gas molecules negligible.

(iii) The molecules are in constant random motion. During motion, the molecules collide with each other and also with the walls of the container. These collisions are perfectly elastic. The pressure exerted by a gas is due to the collisions of the molecules with the walls of the container.

(iv) The average kinetic energy of gas molecules is proportional to the absolute temperature of the gas.

Characteristics of Gases

Gases are highly compressible and diffusible. They neither have a definite shape nor definite volume. The gases occupy the entire volume available to them. Therefore, the volume of a gas is taken as the volume of the container.

The study of gases is much simpler than that of solids and liquids because the physical properties of all the gases are found to be identical. For example, the compressibility or thermal expansion of all the gases are the same, but this is not so in case of solids and liquids. The properties of solids and liquids differ widely from substance to substance, but the gases generally obey some common rules known as the **gas laws**.

Gas Laws

Gas laws give the interrelationship among the measurable properties of a gas which have been experimentally established.

Boyle's Law

The volume of a given mass of a gas is inversely proportional to the pressure exerted by the gas at constant temperature.

$$V \propto \frac{1}{P} \text{ (T = constant)}$$

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

$$PV = K \text{ (constant)}$$

The product of pressure and volume of a given mass of a gas is constant at constant temperature.

If at constant temperature, a gas occupies a volume V_1 at a pressure P_1 and a volume V_2 at a pressure P_2, then $\mathbf{P_1V_1 = P_2V_2}$ **(T = constant).**

Graphical Representation of Boyle's Law

(i) Volume (V) vs Pressure (P)

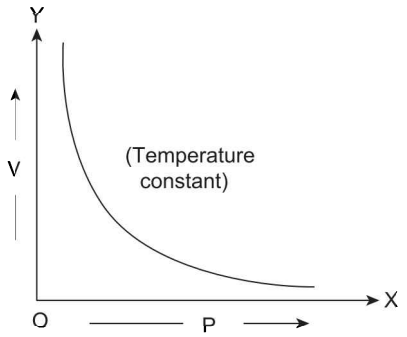


Figure 1.1 Boyle's law graph I

(ii) Volume (V) vs $\frac{1}{\text{Pressure (P)}}$

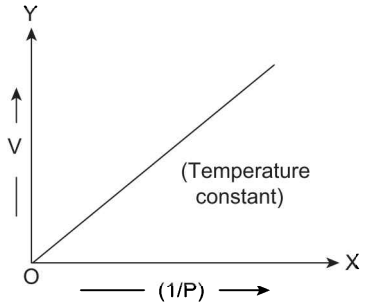


Figure 1.2 Boyle's law graph II

(iii) The product of pressure and volume (PV) vs pressure (P)

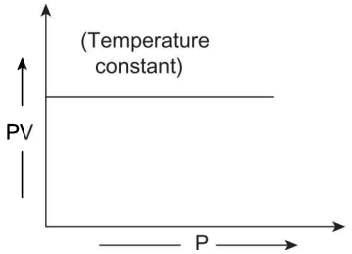


Figure 1.3 Boyle's law graph III

NUMERICAL PROBLEM

1. 5 ℓ of methane gas at 2 atm pressure is compressed to 1.6 ℓ at constant temperature. Calculate the final pressure.

SOLUTION

Initial condition	Final condition
$V_1 = 5\ell$	$V_2 = 1.6\ell$
$P_1 = 2\,\text{atm}$	$P_2 = ?$

According to Boyle's law, PV = PV

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{5 \times 2}{1.6} = 6.25\,\text{atm}$$

Final pressure = 6.25 atm

2. The pressure of a certain volume of gas is reduced to half of its initial pressure at constant temperature. Calculate its new volume.

SOLUTION

Initial condition	**Final condition**
$V_1 = V$	$V_2 = ?$
$P_1 = P\ P_2 = ½\,P$	

According to Boyle's law,

$$P_1V_1 = P_2V_2$$

$$\Rightarrow V_2 = \frac{V \times P}{\frac{1}{2}P} 2V$$

Final volume = 2V

Charle's Law

At constant pressure, the volume of a given mass of a gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C increase or decrease in temperature respectively. If V_0 is the volume of gas at 0°C and V_t is the volume of gas at t°C, (P = constant)

$$V_t = V_0\left[1 + \frac{t}{273}\right]$$

$$V_t = V_0\left[\frac{273 + t}{273}\right]$$

$$V_t = V_0\left[\frac{T}{273}\right]; T = \text{absolute temperature}$$

$$\frac{V_0}{273} = \text{Constant}$$

$\therefore \quad V \propto T$

If V_1 and V_2 are the volumes occupied by a given mass of gas at temperatures T_1 and T_2

$$\frac{\mathbf{V_1}}{\mathbf{T_1}} = \frac{\mathbf{V_2}}{\mathbf{T_2}} \ (\mathbf{P = constant})$$

Charle's law can otherwise be stated as the volume occupied by a given mass of a gas is directly proportional to the absolute temperature of the gas at constant pressure.

Graphical representation of Charle's Law

(i) Volume (V) vs absolute temperature (T)

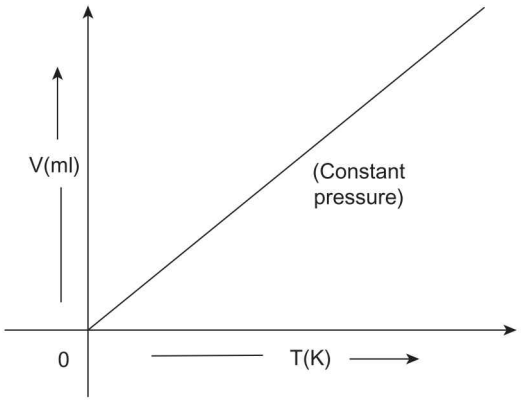


Figure 1.4 Charle's law graph-I

(ii) Volume (V) vs temperature (t) in celsius scale

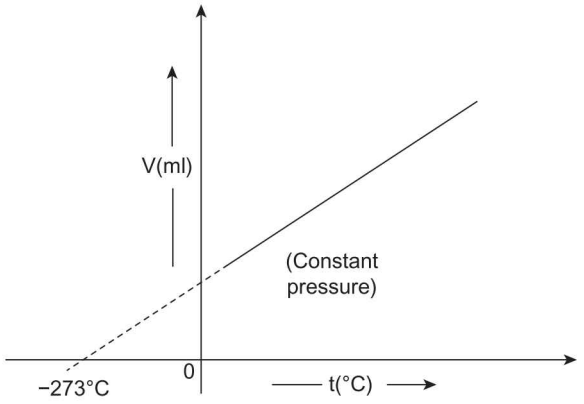


Figure 1.5 Charle's law graph-II

A straight line which intersects the *x*-axis at −273°C is obtained as V = 0 when t = −273°C

Mathematically, volume at –273°C, $V_t = V_0 + \frac{V_0}{273}(-273)$,

$$\therefore\ V_t = V_0\left[\frac{273-273}{273}\right] = 0$$

Absolute Zero

From the graph (ii) V vs t, the straight line intersects the temperature axis at –273°C showing that the gas occupies zero volume at this temperature. That means it is the lowest temperature that can be attained theoretically. Therefore it is called **absolute zero**.

NUMERICAL PROBLEM

1. At a certain pressure, the volume occupied by a given mass of a gas is 10 ℓ at 0°C, calculate the volume occupied by the gas at 91°C at the same pressure.

SOLUTION

Initial condition	**Final condition**
$V_1 = 10\,\ell$	$V_2 = ?$
$T_1 = 273\,K$	$T_2 = (273 + 91)K = 364K$

According to Charle's law, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\Rightarrow \frac{10}{273} = \frac{V_2}{364} \Rightarrow V_2 = \frac{10 \times 364}{273} = 13.33\,\ell$$

2. Calculate the temperature at which the volume of a given mass of gas gets reduced to 3/5th of original volume at 10°C without any change in pressure.

Initial condition	**Final condition**
$V_1 = V$	$V_2 = 3/5V$
$T_1 = (273 + 10)K = 283K$	$T_2 = ?$

According to Charle's law, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$T_2 = V_2 \times \frac{T_1}{V_1}$$

$$\Rightarrow T_2 = \frac{3V}{5} \times \frac{283}{V}$$

$$\Rightarrow T_2 = 169.8K \Rightarrow T_2 = -103.2°C$$

The volume of a given mass of gas depends on its temperature and the pressure imposed. Hence in order to define the volume of a gas a **standard temperature and pressure** has been accepted all over the world.

Standard Temperature and Pressure (STP)

The conditions of standard temperature and pressure are given below.

Standard temperature = 0°C = 273 K
Standard pressure = 760 mm of Hg (mercury)
= 76 cm of Hg = 1 atm

Gay-Lussac's law of combining volumes of gases: Gay-Lussac proposed a law pertaining to gaseous reactions which ultimately led to another gas law the Avogadro's law.

Gay-Lussac's law states that when gases chemically react, they do so in volumes which bear a simple whole number ratio to each other and to the volumes of the products, provided the products are also in gaseous state under similar conditions of temperature and pressure.

Explanation

In the reaction of carbon monoxide with oxygen, two volumes of carbon monoxide react with one volume of oxygen to give two volumes of carbon dioxide under similar conditions of temperature and pressure.

$$\underset{2\text{vol}}{CO} + \underset{1\text{vol}}{CO} + O_2 \rightarrow \underset{2\text{vol}}{CO_2} + CO_2$$

The volume ratio of carbon monoxide, oxygen and carbon dioxide is 2 : 1 : 2.

Amedo Avogadro, in 1811, gave his hypothesis to explain Gay-Lussac's law. It was experimentally confirmed later and was established as Avogadro's law.

Avogadro's Law

Avogadro's law states that equal volumes of all gases contain equal number of molecules under similar conditions of temperature and pressure.

If n is the number of molecules present in volume V of any gas at temperature T and pressure P, then $V \propto n$ when T and P are constant.

Example: 1 ℓ of hydrogen, helium and hydrogen chloride contain equal number of molecules in them provided their volumes are measured at the same temperature and pressure.

In chemistry, the mass of any substance irrespective of its state is measured in terms of gram molecular weight or gram molecule and gram atomic weight or gram atom. Atomic weight of a substance expressed in grams is called its **gram atomic weight or gram atom**. Molecular weight of a substance expressed in grams is called its **gram molecular weight or gram molecule**.

Gram Molecular Volume (GMV)

One gram molecule of any dry gas at STP occupies the same volume, i.e., 22.4 ℓ or 22.4 dm^3. This is called gram molar volume or GMV.

Example: 1 gram molecule of dry chlorine gas occupies 22.4 ℓ of volume at STP.

Since GMW of chlorine is 71 g, 71 g of chlorine gas occupies 22.4 l of volume at STP.

Vapour Density

Vapour density (VD) of a gas or vapour is the ratio of the mass of a certain volume of gas or vapour to the mass of the same volume of hydrogen gas when their volumes are measured under similar conditions of temperature and pressure.

Relation Between Molecular Weight or Relative Molecular Mass vand Vapour Density

VD of a gas or vapour at a certain temperature and pressure

$$= \frac{\text{Mass of the certain volume of gas or vapour}}{\text{Mass of the same volume of } H_2 \text{ gas}}$$

[Volume of both the gases are measured at that particular temperature and pressure]

$$= \frac{\text{mass of n molecules of the gas or vapour}}{\text{mass of n molecules of } H_2 \text{ gas}}$$

[By applying Avogadro s law]

$$= \frac{\text{mass of 1 molecule of the gas or vapour}}{\text{mass of 1 molecule of } H_2 \text{ gas}} = \frac{1}{2} \times \frac{\text{mass of 1 molecule of the gas or vapour}}{\text{mass of 1 atom of hydrogen gas}}$$

$= \frac{1}{2} \times$ relative molecular mass (Molecular weight)

$\therefore$ Molecular weight or relative molecular mass = 2 × VD

i.e., relative molecular mass is twice the vapour density of the gas or vapour.

EXAMPLE

Gas laws are universally applicable for all gases whereas such universal laws could not be established for solids and liquids. Comment on this statement.

SOLUTION

Gases differ from solids and liquids in the extent of intermolecular forces of attraction. Since gases are characterized by negligible forces of attraction, the molecules behave independent of the neighbouring molecules. Due to large intermolecular spaces, the coefficient of volume expansion is same for all gases. Moreover, in case of gases the molecules are considered as point masses and hence the volume occupied by the molecules is negligible in comparison to the total volume. Therefore, the physical behaviour of all gases being similar, certain laws could be established which are universally applicable. In case of liquids and solids, the molecules are considered as rigid spheres and the coefficient of volume expansion is not uniform for all substances, such universal laws can not be established.

EXAMPLE

Boyle's law says that pressure and volume are inversely proportional to each other. However, when a balloon is blown, both volume and pressure increase continuously. Justify

SOLUTION

When a balloon is blown continuously, more and more air is forced into the balloon which increases the volume as well as the number of collisions of air molecules on the walls of the balloon that is pressure. Boyle's law is applicable for a given mass of a gas. Hence it is not valid in the above case.

EXAMPLE

Why is Kelvin temperature always positive?

SOLUTION

Absolute zero which is equal to −273°C is the minimum possible temperature for a gas. Any centigrade temperature greater than −273°C will become positive when converted to absolute scale. Since centigrade temperature less than −273°C is not possible, Kelvin temperature cannot have a negative value

EXAMPLE

A certain mass of a gas taken in 1 litre cylinder exerts a pressure of 500 mm Hg at a certain temperature. If the gas is transferred to another cylinder where it exerts 20% more pressure, calculate the volume of the cylinder at the same temperature.

SOLUTION

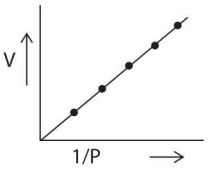
$V_1 = 1000$ cc, $P_1 = 500$ mm of Hg,

$$P_2 = P_1 + \frac{20P_1}{100} = 500 + \left(\frac{20 \times 500}{100}\right) = 600 \text{ mm of Hg}$$

$$P_2V_2 = P_1V_1,\ V_2 = \frac{P_1V_1}{P_2} = \frac{1000 \times 500}{600} = 833 \text{ cc}$$

EXAMPLE

The slope of a given straight line graph with constant temperature is found to be 0.2 ℓ atm at 5 atmospheric pressure. Calculate the volume of gas at that pressure.



SOLUTION

Slope = 0.2 ℓ atm, P = 5 atm.

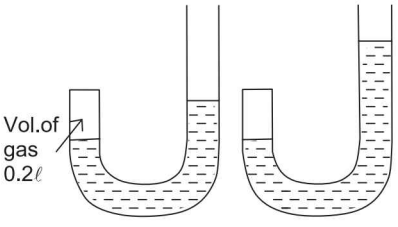
According to Boyle's law,

$$P \propto \frac{1}{V},\ P = \text{constant} \times \frac{1}{V} = \text{slope} \times \frac{1}{V};\ 0.2 \times \frac{1}{V} = 5 \Rightarrow V = \frac{0.2}{5}$$

$= 0.04$ ℓ

EXAMPLE

J-shaped tube closed at one end was used by Boyle to study the relationship between the pressure of the trapped gas and its volume. Such a set up is given here. Initially some amount of gas is taken in the tube and mercury is poured in it. The volume of gas is 0.2 ℓ and the difference in the height of the mercury column is 760 mm of Hg. Now some more amount of mercury is poured and the difference in the height of the mercury column is found to be 1140 mm of Hg. Calculate the new volume of gas considering the temperature constant.



SOLUTION

$V_1 = 0.2$ ℓ $V_2 = ?$

$P_1 = 760$ mm + 760 mm $P_2 = 1140$ mm + 760 mm

According to Boyle's law $P_1V_1 = P_2V_2$

$$1520 \times 0.2 = 1900 \times V_2 \Rightarrow V_2 = \frac{1520 \times 0.2}{1900} = 0.16\,\ell$$

EXAMPLE

A cylinder was filled with a gas at 2 atm pressure at 27°C and can withstand a pressure of 12 atm. At what temperature the cyliner bursts when the building catches fire?

SOLUTION

$P_1 = 2$ atm, $P_2 = 12$ atm

$T_1 = 27 + 273 = 300$ K, $T_2 = ?$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow T_2 = \frac{T_1 P_2}{P_1} \Rightarrow T_2 = \frac{12 \times 300}{2} = 1800 \text{ K} = 1527^\circ \text{ C}$$

$\therefore$ Cylinder bursts at or above 1527°C

EXAMPLE

After usage for a certain period, a cooking gas cylinder was considered to be empty as no gas was coming out of it. Is the cylinder empty in its true sense? Explain what happens if the cylinder is kept in hot water or shaken vigorously. Explain by applying kinetic molecular theory.

SOLUTION

No. It is not empty in its true sense. In a cooking gas cylinder, the gas was initially at a high pressure. As the gas was drawn out from the cylinder, the amount of gas in the cylinder decreases thereby reducing the pressure inside the cylinder. The gas will come out of the cylinder as long as the pressure of the gas inside the cylinder is more than the atmospheric pressure. When it is kept in hot water or shaken vigorously, kinetic energy of gas molecules increases and number of collisions increases. Thus pressure increases and gas comes out of the cylinder.

Avogadro Number and Mole Concept

Avogadro Number

Scientists experimentally determined that the number of atoms present in 12 g of carbon i.e., 1 g atom of carbon 12 isotope is 6.023×10^{23}.

Different experiments showed that 1 g atom or 1 g molecule of any substance contains the same number (6.023×10^{23}) of elementary particles or chemical units (atoms, molecules or ions). This constant number is called the Avogadro number which is denoted by N_A or L. It also represents the number of molecules present in 1 g molar volume.

The Avogadro number, i.e., 6.023×10^{23} is taken as the unit to measure the amount of substances and is called **mole**.

Mole

A mole is defined as the quantity of substance which contains the same number of elementary particles or chemical units as the number of atoms present in 12 g of C-12 isotope.

Hence, 1 mole of any substance contains the Avogadro number of elementary particles or units. The elementary particles can be atoms, molecules, ions, etc.

Therefore, it can be concluded that

(i) 1 g atom of any substance is equivalent to one mole of atoms of that substance and contains the Avogadro number of atoms.

(ii) 1 g molecule of any substance is equivalent to one mole of molecules of that substance and contains the Avogadro number of molecules.

Examples

1. One mole of hydrogen atoms	6.023×10^{23} hydrogen atoms 1 g atom of hydrogen or 1 g hydrogen
2. One mole of carbon atoms	6.023×10^{23} carbon atoms 1 g atom of carbon or 12 g of carbon
3. One mole of NaCl	6.023×10^{23} Na^+ ions and 6.023×10^{23} Cl^- ions
4. One mole of ammonia gas	1 g molecule of sodium chloride or 58.5 g of NaCl 6.023×10^{23} NH_3 molecules 1 g molecule of ammonia or 17 g of NH_3

Examples

(i) Calculate the number of moles of sodium (Na) atoms present in 11.5 g of sodium.

$$\text{Number of moles of sodium atoms} = \frac{\text{mass of sodium}}{\text{GAW}} = \frac{11.5}{23} = 0.5$$

i.e., 0.5 moles of Na atoms are there in the given 11.5 g sample

(ii) Calculate the number of moles of water (H_2O) present in 4.5 g of water.

$$\text{Number of moles of water molecules} = \frac{\text{mass of water molecules}}{\text{GMW}} = \frac{4.5}{18} = 0.25$$

i.e., 0.25 moles of H_2O are there in 4.5g of water.

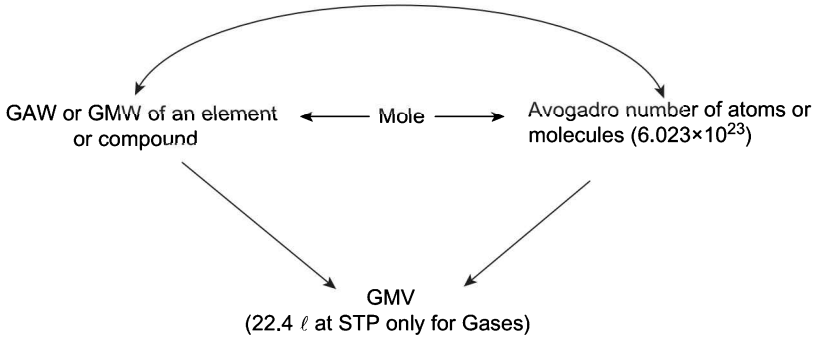
Relation Between GMV, Mole and Avogadro Number

1 g mole of any dry gas occupies 22.4 ℓ volume at STP. Hence 22.4 ℓ of a dry gas at STP contains 6.023×10^{23} molecules, i.e., Avogadro number of molecules.

Example: 32 g or 1 mole of dry oxygen gas occupies 22.4 ℓ volume at STP and contains 6.023×10^{23} molecules of oxygen.

Example: 4 g or 1 mole of dry helium gas occupies 22.4 litres at STP and contains 6.023×10^{23} atoms because helium is a monoatomic gas.

Schematic Representation of Different Relationships for Mole



NUMERICAL PROBLEM

1. Calculate the number of molecules present in 16.8 ℓ of gas "X" at STP. Also determine its gram molecular weight if the above sample weighs 26.625 g.

SOLUTION

Volume of the given gas = 16.8 ℓ at STP

Number of moles present in that volume = 16.8/22.4 = 0.75 mole

Number of molecules in 0.75 moles = $0.75 \times 6.023 \times 10^{23} = 4.52 \times 10^{23}$

Weight of 0.75 moles of the gas X = 26.625 g

Gram molecular weight of "X" = Weight/No. of moles = 26.625/0.75

= 35.5 g

2. Calculate the volume occupied by 200 g of SO_3 gas at STP and the number of molecules present in it.

Weight of SO_3 taken = 200 g

$$\text{Number of moles of } SO_3 = \frac{200}{\text{GMW of } SO_3} = \frac{200}{80} = 2.5 \text{ moles}$$

Volume occupied by 1 mole of gas is 22.4 ℓ, at STP

Volume occupied by the given amount of gas = $2.5 \times 22.4 = 56$ ℓ.

Number of molecules present in 1 mole of gas = 6.023×10^{23}

Number of molecules present in the given amount of gas = $2.5 \times 6.023 \times 10^{23} = 15.05 \times 10^{23}$ molecules

3. What is the volume occupied by 30.1×10^{23} molecules of carbon dioxide gas at STP? Calculate the mass of this gas.

Number of molecules = 30.1×10^{23}

$$\text{Number of moles of gas} = \frac{30.1 \times 10^{23}}{6.023 \times 10^{23}} = 5 \text{ moles}$$

Volume occupied by 5 moles of gas = $22.4 \times 5 = 112$ ℓ.

Mass of the given gas = Number of moles × GMW = $5 \times 44 = 220$ g

Ideal Gas Equation

The behaviour of gases can be described by three laws.

According to Boyle's law, for a given mass of gas, $V \propto \frac{1}{P}$ [T is constant]

According to Charles's law, for a given mass of gas, $V \propto T$ [P is constant]

According to Avogadro's law, $V \propto n$ [P and T are constant]

Combining the three gas laws,

$V \propto \frac{nT}{P}$ [when all the functions vary independently] or $PV \propto nT$

or $PV = nRT$ [R is a constant]

A hypothetical gas called ideal gas obeys the equation under all conditions of temperature and pressure. Hence this equation is called an **ideal gas equation** and R is called universal gas constant.

However, no gas is perfectly ideal. All gases show nearly ideal behaviour under the conditions of low pressure and high temperature and are called real gases.

When one mole of a gas is considered, the equation becomes

PV = RT ($\because$ n =1 mole). The value of "R" depends upon the units in which pressure and volume are taken.

EXAMPLE

Volume occupied by 16 g of oxygen is same as that occupied by 1 gram of hydrogen under similar conditions of temperature and pressure. Explain.

SOLUTION

Both 16 g of oxygen and 1 g of hydrogen corresponds to 0.5 moles of molecules and hence occupy same volume under similar conditions of temperature and pressure.

EXAMPLE

'X' grams each of nitrogen and carbon monoxide are considered. Draw a comparison with respect to number of moles.

SOLUTION

Nitrogen and carbon monoxide possess equal gram molecular mass. Therefore, equal masses of these two gases possess equal number of moles.

NUMERICAL PROBLEM

1. A gas at a pressure of 2.0 atm is heated from 0°C to 273°C and the volume compressed to 1/4th of its original volume. Find the final pressure.

SOLUTION

Initial condition	**Final condition**
$V_1 = V$	$V_2 = \frac{1}{4}V$
$T_1 = 0°C$ or $273\,K$	$T_2 = 273°C$ (or) $546\,K$
$P_1 = 2\,atm$	$P_2 = ?$

According to gas equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} = \frac{2 \times V}{273} \times \frac{546}{V} \times 4,\ P_2 = 16\,atm$$

2. If a gas occupies 30 ℓ at 27°C and 1 atm, what volume would it occupy at 227°C and 5 atm?

Initial condition	**Final condition**
$V_1 = 30l$	$V_2 = ?$
$P_1 = 1$ atm	$P_2 = 5$ atm
$T_1 = 27°C = 300\,K$	$T_2 = 227°C = 500\,K$

According to gas equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\ V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2} = \frac{30 \times 1}{300} \times \frac{500}{5} = 10\ell$

3. What is the volume occupied by 30 g of neon gas at 67°C and 750 mm of Hg?

According to the ideal gas equation

$$PV = nRT \quad (1)$$

n = number of moles = weight/molecular weight = 30/20

Pressure = (750/760) atm [1 atm = 760 mm of Hg]

$$T = (273 + 67)\ K = 340\ K$$

From equation (1),

$$V = nRT/P$$

$$V = \frac{30}{20} \times \frac{0.0821 \times 340}{(750/760)} \left(\frac{g \times \ell .atm / k.mol \times K}{g / mol \times atm} \right) = 42.43\,\ell$$

Dalton's law of partial pressures

The ideal gas equation establishes the relationship among the pressure exerted by a certain number of moles of a gas, its temperature and the volume occupied by it. But the pressure exerted by a mixture of gases present in a container was studied by Dalton. Dalton's law states that "the total pressure exerted by a mixture of non-reacting gases taken in a container at a given temperature is the sum of the practical pressures of the individual gases that each gas would exert if it were taken alone in that container. This statement is known as **Dalton's law of partial pressure**.

Partial pressure is the pressure exerted by each constituent of the gaseous mixture when they are kept individually in the same container.

If the partial pressures of the constituents of the gaseous mixture are p_1, p_2, p_3..... and so on, then according to Dalton's law of partial pressures, the total pressure $p = p_1, p_2, p_3$ .....

If n_1 is the number of moles of a constituent of the gaseous mixture take in a container of volume V and p_1 is the pressure exerted by it at temperature T, then

$$P_1 = n_1 \times \frac{RT}{V} \qquad (1) \text{ (from the ideal gas equation)}$$

Similarly, if P is the total pressure exerted by the gaseous mixture at temperature T, and n is the total number of moles take in the container of volume V, then RT

$$P = n\frac{RT}{V} \quad (2)$$

Dividing equation (1) by equation (2), we obtain

$$\frac{p_1}{p} = \frac{n_1}{n}$$

$$\therefore \quad p_1 = \frac{n_1}{n} \times P$$

$\therefore$ Partial pressure (p_1) = Mole fraction (n_1/n) × total pressure of the gas (P)

Mole fraction is the ratio of number of moles of an individual gas to the total number of moles of all gases in a mixture.

Dalton's law of partial pressure is not applicable to gaseous mixture in which the component gases react with each other chemically.

Example: It is not applicable to a mixture of carbon monoxide and oxygen which react with each other to form carbon dioxide at ordinary temperature:

$$2CO + O_2 \rightarrow 2CO_2$$

NUMERICAL PROBLEM

A 2 ℓ flask contains 22 g of carbon dioxide and 1 g of helium at 20°C. Calculate the partial pressure exerted by CO_2 and He if the total pressure is 3 atm.

SOLUTION

$$\text{Number of moles of } CO_2 = \frac{\text{Weight of } Co_2}{\text{Molecular Weight of } Co_2} = \frac{22}{44} = 0.5.$$

$$\text{Number of moles of He} = \frac{1}{4} = 0.25$$

Partial pressure = Mole fraction × total pressure

$$Pco_2 = \frac{0.5}{0.5+0.25} \times 3 = 2$$

$$p_{He} = \frac{0.25}{0.75} \times 3 = 1 \text{ atm.}$$

Diffusion is one of the significant properties of gases. The process of spreading out of gas molecules spontaneously is called diffusion. As a result of this, gas molecules uniformly occupy the space available.

The number of gas molecules that pass through a unit area in unit time at a given temperature and pressure is called its **rate of diffusion**. In other words, the volume of the gas that diffuses in unit time at specific temperature and pressure is called its **rate of diffusion**. Rate of diffusion of a gas increases with the increase of temperature while it decreases with the increase of pressure.

Thomas Graham observed that the rate of diffusion of different gases depends on their respective densities provided they are under similar conditions of temperature and pressure. He established a quantitative relationship between the rate of diffusion of gases and their densities.

Graham's Law of Diffusion

Under similar conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square root of their densities.

i.e., $r \alpha \frac{1}{\sqrt{d}}$ [T and P are constant]

or $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$ (where r_1 and r_2 are the rate of diffusion of two gases having densities d_1 and d_2, respectively).

Rates of diffusion of gases are also inversely proportional to their molecular weights because equal volume of all gases contains equal number of molecules if the temperature and pressure are kept constant.

$\therefore \quad \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$ where r_1 and r_2 are the rates of diffusion of two gases and their molecular weights are M_1 and M_2, respectively.

NUMERICAL PROBLEM

1. What is the ratio of the rate of diffusion of helium gas to that of oxygen under identical conditions?

SOLUTION

According to Graham's law of diffusion,

$$\frac{r_{He}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_e}}} = \sqrt{\frac{32}{4}}$$

$$\left(\frac{r_{H_e}}{r_{O_2}}\right) = 2\sqrt{2} : 1$$

2. Rate of diffusion of a saturated hydrocarbon is about 1/6th of that of hydrogen under similar conditions of temperature and pressure. What is the molecular formula of that hydrocarbon?

SOLUTION

Let the molecular weight of the hydrocarbon be M_x and its rate of diffusion be r_x

$$\frac{r_{H_2}}{r_x} = \sqrt{\frac{M_x}{M_{H_2}}}, \quad r_x = 1/6 \; r_{H_2}$$

$$\therefore \frac{r_{H_2}}{r_x} = 6 = \sqrt{\frac{M_x}{2}}$$

$$\Rightarrow 36 \times 2 = M_x$$

$$\Rightarrow M_x = 72$$

Molecular weight of the hydrocarbon is 72.

Let the number of carbon atoms present in one molecule of the hydrocarbon be m.

$\because$ the hydrocarbon is saturated, the number of hydrogen atoms present in that hydrocarbon molecule is 2m + 2

$\therefore$ (12 × m) + 2m + 2 = 72

$\Rightarrow$ 14m + 2 = 72 $\Rightarrow$ m = 5

$\therefore$ Molecular formula of the hydrocarbon is C_5H_{12}.

EXAMPLE

A certain amount of oxygen is prepared by the thermal decomposition of potassium chlorate and is collected by downward displacement of water. The pressure of the gas collected is measured with the help of a manometer. The pressure recorded is found to be more than the pressure recorded for the same volume of oxygen cylinder containing same amount of oxygen under the same conditions. How do you account for this deviation?

SOLUTION

When oxygen is prepared, it is collected over water. Since water is in equilibrium with water vapour, the oxygen gas collected is not dry oxygen gas and it is mixed with some amount of water vapour. The total pressure exerted by this moist oxygen gas is the sum of the partial pressures of

oxygen and water vapour. The pressure recorded for the same volume of pure and dry oxygen gas is obviously less than the previous case. The pressure of water vapour in the collected gas is called aqueous tension.

Expressing Concentrations of Solutions Using Mole Concept

A solution is a homogenous mixture of two or more components. The solution that contains only two components is called a binary solution. The component which is present in minor proportions is called the solute and the component which is present in major proportions is called the solvent.

The concentration of a solution refers to the relative proportions of solute and solvent present in the solution. The concentrations of solutions can be expressed in various ways by applying the concept of mole.

Molarity

It is the most convenient and commonly used unit for expressing the concentration of a solution.

Molarity can be defined as the number of moles of a solute present in 1 ℓ of a solution. It is denoted by "M."

If n = number of moles of the solute present in the solution

W = Weight of the solute in grams

GMW = Gram molecular weight (mass) of the solute

V = Volume of the solution, then

$$M = \frac{n}{V} = \frac{W}{GMW} \times \frac{1}{V \text{ in} \ell} \text{ or } M = \frac{W}{GMW} \times \frac{1000}{V \text{ in ml}}$$

Example: 0.4 M sodium carbonate solutions means 0.4 moles of sodium carbonate is present in 1000 ml of the solution.

Mole Fraction

Mole fraction of a component in a solution can be defined as the ratio of the number of moles of that component to the total number of moles of all the components of the solution. If "x" represents mole fraction, then

$$x_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}}, \text{ where n represents number of moles}$$

$$x_{solvent} = \frac{n_{solvent}}{n_{solute} + n_{solvent}}$$

The sum of mole fractions of all components in a solution is equal to unity.

$$x_{solute} + x_{solvent} = 1$$

The concentration of the solution can also be expressed in terms of weight percentage, volume percentage and weight volume percentage.

Weight Percentage (w/w)

The mass of a solute expressed in grams present in 100 g of a solution is called the weight percentage of the solute in the solution.

$$\textbf{Weight percentage of the solute} = \frac{\textbf{Weight of the solute}}{\textbf{Weight of the solution}} \times 100$$

Example

10% (w/w) sodium hydroxide solution

10 g of sodium hydroxide is present in 100 g of the solution.

Weight/volume of percentage (w/v)

The mass of a solute expressed in grams present in 100 ml of a solution is called the weight/volume percentage of the solute in the solution.

$$\textbf{Weight/volume percentage of the solute} = \frac{\textbf{Mass of the solute (g)}}{\textbf{Total volume of the solution (ml)}} \times 100$$

Example

10% (w/v) Na_2CO_3 solution

10 g of Na_2CO_3 present in 100 ml of the solution.

Volume Percentage (v/V)

The volume of the liquid in millilitre present in a 100 ml solution is called the volume percentage of the solute in the solution.

$$\textbf{Volume percentage of the solute} = \frac{\textbf{Volume of the solute}}{\textbf{Volume of the solution}} \times 100$$

Example

70% (v/v) isopropyl alcohol solution

70 ml isopropyl alcohol is present in 100 ml of the solution.

NUMERICAL PROBLEM

1. What is the molarity of a solution containing 15 g of NaOH dissolved in 500 ml of solution?

SOLUTION

$$\text{Molarity} = \frac{\text{Weight}}{\text{G.M.W}} \times \frac{1000}{\text{V}} = \frac{15}{40} \times \frac{1000}{500} = 0.75\,\text{M}$$

2. A solution is prepared by dissolving 9.8 g of H_2SO_4 in 54 g of water. What is the mole fraction of H_2SO_4?

SOLUTION

Weight of H_2SO_4 = 9.8 g

GMW of H_2SO_4 = 98

Number of moles of H_2SO_4 present in the solution = 9.8/98 = 0.1

Number of moles of H_2O = 54/18 = 3

Mole fraction of H_2SO_4 = 0.1/(0.1+3) = 0.032

3. What is the percentage by weight of sulphuric acid, if 13 g of H_2SO_4 is dissolved to make 78 g of solution?

Weight of H_2SO_4 = 13 g

Weight of solution = 78

$$\left(\frac{\text{w}}{\text{w}}\right)\% \text{ of } H_2SO_4 = \frac{13}{78} \times 100 = 16.6\%$$

4. If 40 g of ethyl alcohol is dissolved in 50 ml of water, then calculate the weight/volume percentage of ethyl alcohol present in the solution. [density of ethyl alcohol = 0.8 g/ml]

Amount of ethyl alcohol = 40 g

Volume of ethyl alcohol $= \frac{40}{0.8} = 50$ ml

Volume of water = 50 ml

Total volume of the solution is 100 ml

$$\left(\frac{w}{v}\right)\% \text{ ethyl alcohol is } \frac{40}{100} \times 100 = 40\%$$

5. What is the molarity of 25% $\left(\frac{w}{v}\right)$ solution of HCl?

25% $\left(\frac{w}{v}\right)$ solution of HCl corresponds to 25g of HCl present in 100 ml of solution.

Amount of HCl present in 1000 ml of solution = 250 g

$$\text{Molarity} = \frac{250}{36.5} \times \frac{1000}{1000} = 6.85\,\text{M}\,[\text{GMW of HCl} = 36.5]$$

EXAMPLE

Specific gravity of 84% (w / W) pure HNO_3 is 1.54. What volume of HNO_3 is required to prepare one litre of 0.5M HNO_3 solution?

SOLUTION

specific gravity of HNO_3 = 1.54

$$M = \frac{w}{GMM} \times \frac{1000}{V} \Rightarrow 0.5 = \frac{x}{63} \times \frac{1000}{1000} \Rightarrow x = 31.5 \text{ g}$$

31.5 g of HNO_3 is present in 1 ℓ of solution.

84 g is present in 100 g of solution

31.5 g is present in ? g of solution

$$= \frac{31.5 \times 100}{84} = 37.5\,\text{g}$$

$$\text{Density} = {}^{\text{weight}}/_{\text{volume}} \Rightarrow 1.54 = {}^{37.5}/_{\text{volume}} \Rightarrow V = {}^{37.5}/_{1.54} = 24.35 \text{ m ℓ}$$

$V_1 M_1 = V_2 M_2$ 24.35ml of given HNO_3 is required.

Stoichiometry

The word stoichiometry is derived from the Greek word "stoicheion" meaning element and "metron" meaning measurement. It is the area of study where we learn about the quantity of the reactants(s) required to get specific quantity of product(s).

In order to understand the quantitative relation between the reactants and products, knowledge of the composition of the reactants and the products is required. This composition also helps us to determine the formulae of the molecules of the reactants and products.

Percentage Composition of a Compound

Percentage composition is the mass of each constituent element present in 100 g of a compound.

$$\text{Percentage of an element present in a compound} = \frac{\text{Weight of the element in one mole of the compound}}{\text{GMW of the compound}} \times 100$$

Example

Calculation of percentage composition of calcium carbonate.

$$\text{GMW of } CaCO_3 = 100 \text{ g}$$

$$\text{Percentage of calcium in calcium carbonate} = \frac{40}{100} \times 100 = 40\%$$

$$\text{Percentage of carbon in } CaCO_3 = \frac{12}{100} \times 100 = 12\%$$

$$\text{Percentage of oxygen in } CaCO_3 = \frac{48}{100} \times 100 = 48\%$$

Molecular and Empirical Formula of a Compound

A compound can be represented by two types of formulae, i.e., empirical formula and molecular formula. Empirical formula gives the simplest integral ratio of the number of atoms of different constituent elements present in one molecule of the compound. Molecular formula represents the exact number of atoms of different elements present in one molecule of the compound.

Example

Molecular formula of glucose $\rightarrow C_6H_{12}O_6$

Empirical formula of glucose$\rightarrow CH_2O$

The ratio of the number of atom of carbon, hydrogen and oxygen in glucose is 1 : 2 : 1

Determination of Empirical Formula of a Compound From its Percentage Composition

Example: Percentage compositions of various elements in a compound are as follows—carbon 20.04%, hydrogen 6.6%, nitrogen 46.03% and oxygen 26.67%. What is the empirical formula of the compound?

Elements	Percentages of Element	Atomic Ratios	Simplest Ratios
C	20.04	$\frac{20.04}{12} = 1.67$	$\frac{1.67}{1.66} = 1$
H	6.66	$\frac{6.66}{1} = 6.66$	$\frac{6.66}{1.66} = 4$
O	26.67	$\frac{26.67}{16} = 1.66$	$\frac{6.66}{1.66} = 4$
N	46.03	$\frac{46.03}{14} = 3.28$	$\frac{3.28}{1.66} = 2$

Empirical formula of the compound = $CH_4O_4N_2$

The empirical formula of a compound is CH_2O. If its vapour density is 90, find out the molecular formula of the compound.

Solution

Empirical formula = CH_2O

Empirical formula weight = 12 + (1× 2) + 16 = 30

Vapour density = 90

Molecular weight = VD × 2 = 180

Molecular formula = $(\text{empirical formula})_n$

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{180}{30} = 6$$

Thus, molecular formula = $(CH_2O)_6 = C_6H_{12}O_6$

In stoichiometry, we find out the quantitative relationship between the reactants and the products on the basis of balanced chemical equation.

EXAMPLE

What is meant by 22 carrat gold in terms of percentage purity?

SOLUTION

24 carrat gold is considered to have 999.99 parts of gold per 1000 g. Therefore one carrat is taken as one part of 24. That means 22 carrat gold is 22 parts per 24 parts. Accordingly, parts of gold in 1000 g of 22 carrat gold can be calculated. From this, percentage can be found out.

Amount of gold in 1000 g of 22 carrat gold = $\frac{22}{24} \times 1000 = 916.3$ g

Percentage of gold = 91.6%

Balanced Chemical Equation

A balanced chemical equation is the one in which the number of atoms of each element are equal in its reactants and products.

Examples:

$$2H_2 + O_2 \rightarrow 2H_2O$$

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

The information that can be obtained from a balanced chemical equation include the following:

(i) The nature and chemical composition of the reactants and the products in a chemical reaction.

(ii) The number of moles of various reactants and products involved in a chemical reaction.

The balanced chemical equation is called the stoichiometric equation.

The quantitative relationship between the various reactants and products can be established based on either the weight of the substances or the volume of the substances in case of gases.

Calculations Based on Chemical Equations

Three types of relationships can be established between the chemical substances involved in the chemical reaction.

(i) Weight–weight relationship of the reactants and products.

(ii) Weight–volume relationship in reactions involving at least one gaseous substance.

(iii) Volume–volume relationship in case of reactions involving all gaseous substances.

Calculation Based on Weight–Weight Relationship

Example: Calculate the weight of zinc required for the liberation of 10 g of hydrogen gas on reaction with H_2SO_4.

Solution

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$
$$1 \text{ mole} \qquad 1 \text{ mole}$$

Atomic weight of zinc is 65.5

1 mole of hydrogen = 2 g of hydrogen

10 g of hydrogen $= \frac{10}{2} = 5$ moles

1 mole of H_2 gas is produced from 1 mole of zinc

5 moles of H_2 gas are produced from 5 moles of zinc.

1 mole of zinc = 65.5 g

5 mole of zinc = 65.5 × 5 = 327.5 g

Calculations Based on Weight–Volume Relationship

Example: Calculate the weight of sodium bicarbonate to be dissociated to give 0.56 ℓ of CO_2 gas.

Solution

$$2NaHCO_3 \rightarrow NaCO + HO + CO$$
$$2 \text{ moles} \qquad 1 \text{ mole}$$

GMW of $NaHCO_3$ = 84 g

1 mole of CO_2 occupies 22.4 ℓ

22.4 ℓ of CO_2 is produced from 2 × 84 g of $NaHCO_3$

0.56 ℓ of CO_2 is produced from $\frac{0.56 \times 2 \times 84}{22.4} \times 4.2\,g$

Calculations Based on Volume–Volume Relationship

Example: Calculate the volume of carbon monoxide gas required to react with oxygen to give 11.2 ℓ of CO_2 gas.

Solution

$$2CO + O_2 \rightarrow 2CO_2$$
$$2 \text{ moles} \qquad 2 \text{ moles}$$

2 × 22.4 ℓ CO_2 gas is produced from 2 × 22.4 ℓ CO gas.

11.2 ℓ CO_2 gas is produced from 11.2 ℓ CO gas.

Calculations Involving Percentage Purity of Compounds

Percentage purity of a chemical compound is the actual amount of pure substance present in a sample of compound when it contains certain amount of impurities. For example, a sample of 90% pure limestone contains 90% calcium carbonate and 10 g of impurities for every 100 g of limestone.

Example: Calculate the weight of 80% pure limestone required to produce 11 g of CO_2 gas.

Solution

$$CaCO_3 \rightarrow CaO + CO_2$$
$$1\text{mole} \qquad 1 \text{ mole}$$

44 g of CO_2 is produced from 100 g of $CaCO_3$

$\therefore$ 11 g of CO_2 is produced from $\frac{100}{44} \times 11 = 25\,\text{g}$ of $CaCO_3$

As the limestone is 80% pure, the weight of impure limestone required $= \frac{100}{80} \times 25\text{ g} = 31.2\,\text{g}.$

Calculations Involving Limiting Reagent

The reactant which decides the amount of products formed in a reaction is called the limiting reagent.

NUMERICAL PROBLEM

Calculate the amount of sodium oxide formed when 2.3 g of sodium reacts with 3.2 g of oxygen.

SOLUTION

$$4Na + O_2 \rightarrow 2Na_2O$$
$$4 \text{ moles} \quad 1 \text{ mole} \quad 2 \text{ moles}$$

4×23 g of sodium reacts with 32 g of O_2

2.3 g of sodium reacts with $= \frac{2.3 \times 32}{4 \times 23} = 0.8\,\text{g}$

As the amount of oxygen present is 3.2 g, all the oxygen is not utilized for formation of sodium oxide. The amount of sodium oxide formed is determined by sodium. 4×23 g of sodium produces 2×62 g of sodium oxide.

$$2.3\text{ g of sodium produces} = \frac{2.3 \times 2 \times 62}{4 \times 23} = 3.1\,\text{g}$$

Amount of sodium oxide formed = 3.1 g

EXAMPLE

A mixture of sodium carbonate and sodium bicarbonate was subjected to heating. Some loss in weight was found. How does this information help us to find out the composition of mixture?

SOLUTION

Between sodium carbonate and sodium bicarbonate, only sodium bicarbonate decomposes to given sodium carbonate, CO_2 and H_2O. The gaseous products (CO_2 and H_2O) escape out into the atmosphere. Therefore, an apparent loss in weight occurs during the reaction.

This loss in weight corresponds to the amount of gaseous products formed. From the mass of gaseous products formed, amount of sodium bicarbonate in the mixture can be obtained and thus composition of the mixture can be found out.

EXAMPLE

In an apparatus 16.8 g of sodium bicarbonate was subjected to heating till it undergoes complete decomposition, what is the expected loss in weight? When the same apparatus was fitted to a condenser, the loss in weight was different from the earlier loss in weight. Justify the difference.

SOLUTION

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

2 moles $NaHCO_3 \rightarrow$ 2 moles of gaseous product (CO_2 and H_2O)

Number of moles of $NaHCO_3 = \frac{16.8}{84 \times 2} = 0.1$

0. 1 moles $NaHCO_3 \rightarrow 0.2$ moles gaseous product $\rightarrow 0.1$ moles $CO_2 + 0.1$ moles H_2O.

$\rightarrow 4.4$ g $CO_2 + 1.8$ g H_2O

Expected loss in weight = 4.4 + 1.8 = 6.2 g.

Actual loss in weight = Amount of CO_2 formed = 4.4 g.

The difference is due to the condensation of water vapour.

EXAMPLE

At STP, a certain amount of hydrogen is produced by the reaction of 550 g of impure zinc with excess amount of HCl. The same volume of hydrogen at S.T.P. reduces Fe_3O_4 and produces 336 g of iron. Find the percentage purity of zinc. (Atomic mass of Zn is 65)

SOLUTION

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$; $4H_2 + Fe_3O_4 \rightarrow 4H_2O + 3Fe$

Amount of iron produced = 336 g $\Rightarrow$ number of moles of iron $= \frac{336}{56} = 6$

To produce 6 moles of iron it requires 8 moles of hydrogen which further requires 8 moles of Zn.

Weight of Zn = $8 \times 65.5 = 524$ g; % purity $= \frac{524}{550} \times 100 = 95.27\%$

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. What is an ideal gas? Under what conditions does a real gas behave ideally?
2. The volume occupied by 7 g of nitrogen gas at STP is _____.
3. Why do the gases exert pressure?
4. What is meant by critical temperature?
5. Find out the number of molecules in 2.5 moles of water.
6. 2 moles of CO_2 gas contain the same number of atoms as _____ moles of CO.
7. Calculate the volume occupied by 0.01 moles of helium gas at STP.
8. What is the amount of H_2SO_4 (in grams) present in 0.2 moles of sulphuric acid?
9. The percentage of sulphur in SO_2 is _____ and _____ in SO_3.
10. What is the molarity of HCl solution containing 0.4 moles in 200 ml of the solution?
11. Calculate the volume occupied by 11 g of CO_2 gas at STP.
12. If the pressure exerted on a gas is increased by 4 times and temperature is increased by 9 times, what will be the change in volume occupied by the gas?
13. The vapour density of SO_2 gas is _____ the vapour density of O_2 gas.
14. If the mole fraction of a solute in a binary solution is 0.3, what could be the mole fraction of the solvent in the solution?
15. Calculate the ratio of the rate of diffusion of sulphur dioxide gas to helium gas.
16. Find out the number of moles constituted by 1.4 g of carbon monoxide.
    Number of moles $= \frac{\text{Weight}}{\text{GMW}}$
17. The empirical formula of a compound is CH_2O. If the vapour density is 60, what would be the molecular formula of the compound?
18. When 4 ℓ of nitrogen completely reacts with hydrogen, what would be the volume of ammonia gas formed?
19. The molecular formula of a gas with vapour density 15 and empirical formula CH_3 is _____.
20. What is the amount of calcium oxide formed by the dissociation of 25 g of calcium carbonate?
21. State Avogadro's law.
22. Define amu.
23. The vapour density of a substance is 24. What is the gram molecular weight of the substance?
24. Calculate the weight of CO_2, which occupies a volume of 11.2 dm^3 at STP.
25. The mass of N molecules of helium is the same as the mass of _____ molecules of methane.
26. Percentage of calcium in calcium carbonate is _____.
27. Calculate the percentage of chlorine present in calcium chloride.
28. Define molarity.
29. State Graham's law of diffusion.
30. How many litres of oxygen at STP are required for the combustion of 4 g of methane gas? Also calculate the volume of CO_2 gas produced at STP.

Short Answer Type Questions

31. State and explain Charle's law.
32. Explain the significance of absolute zero.
33. (a) Define molarity.
    (b) Calculate the molarity of sodium carbonate solution containing 0.53 g of sodium carbonate dissolved in 200 ml of the solution.
34. Calculate the weight of
    (a) single atom of nitrogen
    (b) single atom of carbon
    (c) 1.5×10^{21} atoms of sodium
    (d) single molecule of carbon monoxide
35. What is the volume of oxygen at STP liberated when 12.25 g of potassium chlorate is subjected to heating?

PRACTICE QUESTIONS

36. Calculate the total number of atoms present in 0.49 grams of H_2SO_4.

37. What is meant by mole fraction? Find out the mole fraction of sodium hydroxide solution containing 4 g of solute in 90 g of water.

38. What is the volume of 50% (w/v) H_2SO_4 required for the liberation of 5.6 l of hydrogen gas at STP on its reaction with magnesium?

39. Calculate the percentage composition of glucose.

40. Empirical formula of a compound is CH_3N.
If the empirical formula weight is equal to one-fourth of its vapour density, find out the molecular formula of the compound.

41. Calculate the number of atoms in
(a) 4.5 g atoms of potassium
(b) 0.2 g atoms of chlorine
(c) 1.2 g molecules of nitrogen

42. How many litres of oxygen at STP are required for the combustion of 4 g of methane gas? Also calculate the volume of CO_2 gas produced at STP.

43. Find out the relative rates of diffusion of methane and sulphur dioxide under similar conditions of temperature and pressure.

44. 1.8 g of oxalic acid ($H_2C_2O_4$) is dissolved in 200 ml of a solution. Find out the molarity of the resultant solution.

45. A gaseous hydrocarbon with a vapour density of 14 contains 85.2% carbon. Calculate its molecular formula.

Essay Type Questions

46. State and explain the postulates of kinetic molecular theory of gases.

47. State and explain Graham's law of diffusion. 120 cc of SO_2 gas is diffused through a porous membrane in 40 min. Under similar conditions, 360 cc of another gas is diffused in 30 min. What is the molecular weight of the other gas?

48. State and explain
(a) Boyle's law
(b) Charle's law with graphical representation

49. Derive the ideal gas equation on the basis of laws of Boyle, Charle and Avogadro. Calculate the volume occupied by an ideal gas at STP, if 0.25 ℓ of the gas is present at a pressure of 700 mm of Hg and 273°C.

50. Explain the relation between vapour density and molecular mass.

CONCEPT APPLICATION

Level 1

***Direction for questions from 1 to 7*: State whether the following statements are true or false.**

1. Doubling the pressure of a gas at constant temperature doubles the volume occupied by the gas.

2. When a 200 ml gas, in a closed vessel, is heated to 50°C from 25°C, the volume becomes doubled.

3. The rate of diffusion of methane is double the rate of diffusion of sulphur dioxide gas.

4. 1 g atom of nitrogen contains 6.023×10^{23} atoms of nitrogen.

5. Gay-Lussac's law of combining volumes is applicable to the reaction, $2C + O_2 \rightarrow 2CO_2$.

6. Gases show deviations from ideal behaviour at high temperatures and high pressures.

7. The greater the critical temperature of a gas, the easier is the liquefaction of the gas.

***Direction for questions from 8 to 14*: Fill in the blanks.**

8. The ratio of the volumes of 11 g of CO_2 and 28 g of CO at STP is _____.

9. The number of oxygen molecules required for the complete combustion of 5 moles of methane is _____.

10. The volume of CO_2 liberated at STP is _____ on thermal decomposition of 84 g of sodium bicarbonate.

11. "ous" acid of a nonmetal "X" has 2 "O" atoms. Per acid of the same nonmetal has the formula _____.

12. The ratio of the gram atomic weight of nitrogen and oxygen is _____.

13. Pressure exerted by water vapour in moist gas is called _____.

14. Mole fraction of NaOH in an aqueous solution is 0.3. Mole fraction of water is _____.

***Direction for question 15*: Match the entries given in Column A with appropriate ones in Column B.**

15.

A. Empirical formula of glucose	( )	a. Less intermolecular forces
B. Percentage of carbon in methane	( )	b. 75%
C. Ideal gas	( )	c. 17.6%
D. High critical temperature	( )	d. Large intermolecular forces of attraction
E. Percentage of hydrogen in ammonia	( )	e. CH_2O
F. Empirical formula of oxalic acid	( )	f. CHO_2

***Direction for questions from 16 to 30*: Select the correct alternative from the given choices.**

16. The number of oxygen atoms present in 2 moles of a compound, which consists of a bivalent metal and a perchlorate ion is
(a) 4 N (b) 6 N
(c) 8 N (d) 16 N

17. When one mole each of CO and O_2 are made to react at STP, the total number of moles at the end of the reaction is
(a) 1.5 moles (b) 1 mole
(c) 4 moles (d) 2 moles

18. When 180 g of glucose is subjected to combustion, the volume of CO_2 liberated at STP is
(a) 22.4 ℓ (b) 67.2 ℓ
(c) 44 ℓ (d) 134.4 ℓ

19. 20 cc of a hydrocarbon on complete combustion gave 80 cc of CO_2 and 100 cc of H_2O at STP. The empirical formula of that compound is
(a) C_2H_5 (b) C_2H_6
(c) C_3H_8 (d) C_4H_{10}

20. How many molecules would be there in 0.01 moles of sodium hydroxide?
(a) 6.023×10^{23} (b) 6.023×10^{21}
(c) 6.023×10^{22} (d) 6.023×10^{20}

21. 44 g of CO_2 contains
(a) 2 moles of oxygen atoms
(b) 1 mole of oxygen atoms
(c) 1.5 moles of oxygen atoms
(d) 2 moles of oxygen molecules

22. 0.1225 g of potassium chlorate decomposes completely. Write the possible chemical equation and the amount of oxygen liberated.
(a) $4KClO_3 \rightarrow 4KCl + 6O_2$, 0.048 g
(b) $4KClO_3 \rightarrow 4KCl + 5O_2$, 0.48 g
(c) $2KClO_3 \rightarrow 2KCl + 3O_2$, 0.048 g
(d) $2KClO_3 \rightarrow 2KCl + 3O_2$, 0.48 g

23. The ratio by mass of sulphur and oxygen in SO_2 is
(a) 1 : 2 (b) 2 : 1
(c) 1 : 1 (d) 1 : 4

24. Critical temperatures of the gases A, B, C and D are
(a) 5.2 K (b) 33.2 K
(c) 126.3 K (d) 191.1 K

Arrange them in the ascending order of intermolecular forces of attraction.
(a) C, B, D, A (b) A, B, C, D
(c) D, C, B, A (d) A, C, B, D

25. Which of the following pairs of gases corresponds to the ratio of the rates of diffusion as $\sqrt{2}$: 1?
(a) H_2 and He (b) He and CH_4
(c) H_2 and CH_4 (d) CH_4 and SO_2

26. When ammonia gas is subjected to sudden expansion from a region of high pressure into a region of low pressure, which of the following changes is expected to take place?
(a) decrease in kinetic energy and potential energy
(b) conversion of kinetic energy to potential energy
(c) conversion of potential energy to kinetic energy
(d) increase in kinetic energy and potential energy

27. Dalton's law of partial pressures cannot hold good for
(a) $NO_2 + O_2$ (b) $H_2 + Cl_2$
(c) $CO_2 + O_2$ (d) $NH_3 + He$

PRACTICE QUESTIONS

28. A 600 ml vessel containing oxygen at 800 mm and a 400 ml vessel containing nitrogen at 600 mm at the same temperature are joined to each other. The final pressure of the mixture is
(a) 1400 mm (b) 1000 mm
(c) 720 mm (d) 700 mm

29. It is found that with an increase in temperature by 40%, the volume decreases by 20% with change in pressure. Find the percentage change in pressure.
(a) 40% decrease (b) 60% decrease
(c) 75% increase (d) 80% increase

30. 23 g of NO_2 contains same number of molecules as
(a) 8 g of oxygen
(b) 28 g of carbon monoxide
(c) 16 g of SO_2
(d) 22 g of CO_2

***Directions for questions from 31 to 45*: Select the correct alternative from the given choices.**

31. Which of the following is in the correct order according to metal reactivity series?
(a) Al < Fe < Na< Ca (b) Fe < Ca< Al < Na
(c) Fe< Al< Ca< Na (d) Na < Ca< Al< Fe

32. Arrange the following compounds in the correct order of percentage of metallic element.

(a) potassium hydroxide
(b) potassium carbonate
(c) potassium bicarbonate
(d) potassium sulphide

(a) a > b > c > d (b) b > a > c> d
(c) c > b > a > d (d) d > a > b > c

33. Empirical formula of a compound is A_2B_4. If its empirical formula weight is half of its vapour density, determine the molecular formula of the compound.
(a) A_4B_8 (b) A_8B_{16}
(c) A_2B_4 (d) A_3B_6

34. The number of oxygen atoms present in 2 moles of a compound, which consists of a bivalent metal and a perchlorate ion is
(a) 4 N (b) 6 N
(c) 8 N (d) 16 N

35. $KMnO_4 + H_2SO_4 + FeSO_4 \rightarrow K_2SO_4 + MnSO_4 + Fe_2(SO_4)_3 + H_2O$
Coefficients of sulphuric acid and ferric sulphate in the balanced equation of above reaction are ___ and ___ respectively
(a) 8, 4 (b) 5, 8
(c) 4, 3 (d) 8, 5

36. A certain mass of a gas occupies a volume of 600 ml at a certain temperature and pressure. If the temperature is increased by 80% what will be the volume occupied by the same mass of gas at the same pressure?
(a) 1080 ml (b) 108 ml
(c) 120 ml (d) 102 ml

37. The weight of an empty china dish is 39 g and when a saturated solution of potassium nitrate is poured into it, its weight is 108 g at 50°C. After evaporating the solution to dryness, if the weight of the dish along with the crystals is 72 g then the solubility of potassium nitrate at 50°C is _____.
(a) 83.9 (b) 95.6
(c) 91.6 (d) 87.4

38. If 15 mg of N_2O_3 is added to 4.82×10^{20} molecules of N_2O_3 the total volume occupied by the gas at STP is
(a) 0.044 ℓ (b) 0.022 ℓ
(c) 0.22 ℓ (d) 0.44 ℓ

39. In a 2.5 ℓ flask at 27°C temperature, the pressure of a gas was found to be 8 atm. If 2.41×10^{23} molecules of the same gas are introduced into the container, the temperature changed to T_2. The pressure of gas is found to be 10 atm. Find out the value of T_2.
(a) 253 K (b) 347 K
(c) 230 K (d) 370 K

40. A certain mass of a gas occupies a volume of 600 ml at a certain temperature and pressure. If pressure is decreased by 40% what will be the volume occupied by the same mass of the gas at the same temperature?
(a) 240 ml (b) 1000 ml
(c) 300 ml (d) 120 ml

41. Calculate the molarity of a solution obtained by mixing 250 ml of 0.5 M HCl with 750 ml of 2 M HCl.
(a) 1.8 (b) 2.0
(c) 1.6 (d) 0.8

42. 40% w/W $Ca(OH)_2$ solution has a molarity of 7.8 M. Calculate the density of the solution.
(a) 1.03 g/cc (b) 1.04 g/cc
(c) 1.54 g/cc (d) 1.44 g/cc

43. Which one of the following is different from the others with respect to valency?
(a) potassium (b) ammonium
(c) barium (d) lithium

44. Plumbous ion is represented as
(a) Pb^{+2} (b) Pb^{+4}
(c) Pb^{+3} (d) Pb^{+1}

45. 0.5 moles of a salt contains "3N" oxygen atoms. Identify the formula of the salt.
(a) MXO_3 (b) MX_2O_3
(c) M_2XO_3 (d) $M(XO_3)_2$

Level 2

1. Balloons of 2 ℓ capacity are to be filled with hydrogen at a pressure of 1 atm and 27°C temperature from an 8 ℓ cylinder containing hydrogen at 10 atm, at the same temperature. Calculate the number of balloons that can be filled.

2. When both pressure and temperature of a given mass of a gas are increased by "n" times, the volume occupied by the same mass of the gas remains the same. Justify with respect to kinetic molecular theory.

3. A gas cylinder is filled with helium at 2000 mm. Due to leakage, the pressure dropped to 1500 torr in 40 min. When the same cylinder is filled with another gas at the same pressure the pressure dropped from 2000 mm to 1500 mm in 200 min. What is the molecular weight of the gas?

4. A cation A^{+4x} and an anion B^{-2x} combine to form a compound. Similarly, C^{+2x} and D^{-4x} also combine to form a compound. When the molten compounds are subjected to electrolysis, the gaseous products obtained are in equimolar amounts. What should be the mole ratio of the compounds taken respectively?

5. A sample of a mixture of Na_2CO_3 and $NaHCO_3$ is subjected to heating till there is no further loss in weight. Assuming that the loss in weight of the sample is 22% of the initial weight of the mixture due to the evolution of CO_2, find out the relative percentages of the two components in the mixture.

6. Calculate the mass of aluminium oxide which contains double the number of oxygen atoms in 192 g of oxygen gas.

7. A vessel contains equal number of moles of helium and methane. Due to a hole in the vessel half of the gaseous mixture effused out. What is the ratio of the number of moles of helium and methane remaining in the vessel?

8. A vessel contains double the number of moles of hydrogen than oxygen. Due to a hole in the vessel, one-fourth of the gaseous mixture is effused out. What is the ratio of the number of moles of hydrogen and oxygen remaining in the vessel?

9. A salt is formed between a bivalent metal cation and an oxyacid of a nonmetal. The -ous acid of the nonmetal has two oxygen atoms per molecule. If the salt contains a radical of per acid of the same nonmetal, calculate the number of atoms of various elements present in 0.5 moles of the salt.

10. Specific gravity of 84% (w/w) pure HNO_3 is 1.54. What volume of HNO_3 is required to prepare 1 l of 0.5 M HNO_3 solution?

11. At STP, a certain amount of hydrogen is produced by the reaction of 550 g of impure zinc with excess amount of HCl. The same volume of hydrogen at STP reduces Fe_3O_4 and produces 336 g of iron. Find the percentage purity of zinc. (atomic weight of Zn is 65)

12. The percentage of oxygen in a metallic oxide of a bivalent metal is 20.1%. The molecular weight of the compound is 79.5. Write the molecular formula of the compound considering the symbol of the metal as M and find out the atomic weight of the metal.

13. A hydrocarbon on combustion gives CO_2 and H_2O in a volume ratio of 2 : 1 under similar conditions of temperature and pressure. What is the empirical formula of the hydrocarbon?

PRACTICE QUESTIONS

14. An aqueous solution is prepared by dissolving 90 g of acetic acid in water to make a 1000 ml solution. Density of solution is 0.99. Calculate the molarity of solution and mole fraction of solute in the solution.

15. A vessel contains equal masses of hydrogen, helium and methane. Find out the fractions of the partial pressures in the mixture.

***Directions for questions from 16 to 25*: Application-Based Questions**

16. The molecular mass of a salt of oxyacid of chlorine of a divalent metal which contains more number of oxygen atoms than its corresponding "-ic" acid is 239. What will the molecular masses of its
    (a) phosphate (b) iodide
    (c) bisulphate be?

17. Represent the following chemical changes in the form of chemical equations and balance them.
    (a) A copper coin is placed in a solution of corrosive sublimate, mercuric chloride. The products obtained are cupric chloride and mercury.
    (b) A piece of (a) sulphur, (b) charcoal burns vigorously when dropped in molten potassium nitrate, because potassium nitrate decomposes to form potassium nitrite and oxygen and this oxygen helps to burn charcoal and sulphur giving out carbon dioxide and sulphur dioxide respectively.
    (c) Aqueous ammonium hydroxide solution is made to react with aqueous copper sulphate solution and a bluish white precipitate of cupric hydroxide and ammonium sulphate are formed.

18. The percentage of metal in two metal oxides A and B is 74.2% and 59%, respectively. Show that the law of multiple proportions is obeyed.

19. A sample of air contains nitrogen and oxygen saturated with water vapour. The total pressure is 640 mm. The vapour pressure of water vapour is 40 mm and molar ratio of nitrogen and oxygen is 4 : 1. Find out the partial pressures of N_2 and O_2.

20. Calculate the partial pressures of each gas present in a mixture of 8 g of oxygen and 6 g of hydrogen present in 2 ℓ container at 27°C.

21. A particular compound contains only nitrogen and hydrogen. The percentage of nitrogen in the compound is 87.5%. Further, 96 g of the compound contains 18×10^{23} molecules of the substance. Find out the molecular formula of the compound.

22. When a sample of KNO_3 is subjected to heating, the volume of oxygen liberated was sufficient for the combustion of one mole of ethylene. For giving same amount of oxygen, what is the amount of lead nitrate required to be decomposed? Also find out the volume occupied by the gaseous products at STP during this decomposition.

23. Brass is an alloy of copper and zinc. A sample of brass weighing 5.793 g when treated with excess of dil H_2SO_4 gave 336 ml of hydrogen gas at 136.5 K and 785 mm pressure. If the hydrogen gas is collected over water and pressure of water vapour under the given conditions is 25 mm, find out the percentage weight of copper in the alloy.

24. 50 ml of a gaseous hydrocarbon is mixed with excess of oxygen and burnt and cooled to the laboratory temperature. The reduction in volume was found to be 150 ml. The gas is then passed into caustic potash when there is a further reduction in the volume of 150 ml. Provided all the volumes are measured at the same conditions of temperature and pressure, find out the molecular formula of the hydrocarbon.

25. X g of CO_2 is prepared by the reaction of $CaCO_3$ and HCl. How many grams of oxygen will be liberated if X grams of CO_2 completely take part in the process of photosynthesis? 144 g of water is produced in the first reaction.

    Equation for photosynthesis is $CO_2 + H_2O \rightarrow C_6H_{12}O_6 + O_2$

Level 3

1. When a fully blown balloon is subjected to sudden bursting, what do you observe? Justify your observation.

2. Under what conditions, gases deviate to a large extent from ideal behaviour? Justify with respect to kinetic molecular theory.

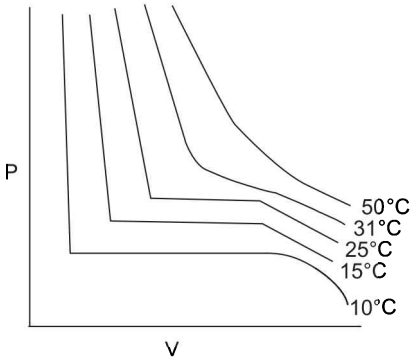
3. The vapour pressure of a solution is always less than that of the pure solvent, when the temperature of both the solution and solvent are the same with the same external pressure acting over them. Explain.

4. The experimental values of the mass (in grams) of 1 l of CO_2, NH_3 and CH_3Cl, at STP are given below:

   CO_2 → 1.9767 g
   NH_3 → 0.7712 g
   CH_3Cl → 2.3076 g

Arrange them in the ascending order of their deviation from the behaviour of ideal gas with appropriate reasons.

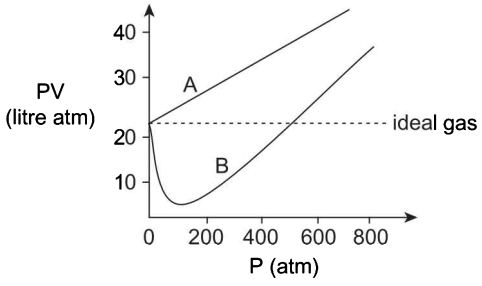
5. In the P vs V graph of CO_2 gas given below, account for the reduction in the horizontal portion of the graph with increase in temperature.



***Directions for questions from 6 to 10*: Application-Based Questions**

6. After usage for a certain period, a cooking gas cylinder was considered to be empty as no gas was coming out of it. Is the cylinder empty in its true sense? Explain what happens if the cylinder is kept in hot water or shaken vigorously. Explain by applying kinetic molecular theory.

7. From the graph given below compare the intermolecular forces of attraction in A and B.



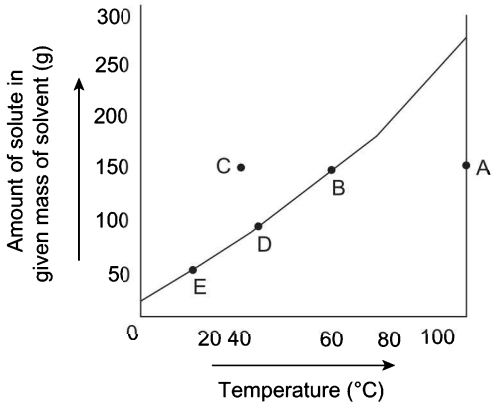
8. The various conditions required for the liquefaction of gases A, B, C and D are given below:

Gas	Temperature	Pressure
A	–4°C	10 atm
B	–4°C	5 atm
C	25°C	5 atm
D	25°C	4 atm

Arrange these gases in the ascending order of their deviation from ideal behaviour. Give reason in support of your answer.

9. The reduction of acidified solution of ferric ions by hydrogen gas takes place in the presence of zinc. Explain.

10. In the graph given below, identify the states of solution at the various points A, B, C, D and E. If the solution is cooled from point "A" at which temperature, precipitation normally starts? Also find out the amount of solute precipitated at 40°C at A and the amount of solute in the solution at point "E." What would be the maximum amount of solute that can be precipitated in the process?



PRACTICE QUESTIONS

CONCEPT APPLICATION

Level 3

True or false

1. False
2. False
3. True
4. True
5. False
6. False
7. True

Fill in the blanks

8. 1 : 4
9. 6.023×10^{24} molecules
10. 11.2 ℓ
11. HXO_4
12. 7 : 8
13. aqueous tension
14. 0.7

Match the following

15. A : e
    B : b
    C : a
    D : d
    E : c
    F : f

Multiple choice questions

16. d
17. a
18. d
19. a
20. b
21. a
22. c
23. c
24. b
25. a
26. b
27. b
28. c
29. c
30. d

Solutions for questions from 31 to 45:

31. According to the metal reactivity series, the increasing order of the reactivates of the given metals is

$$Fe < Al < Ca < Na$$

32. (a) potassium hydroxide $\rightarrow$ KOH

$$\% \text{ of potassium} = \frac{39}{56} \times 100 = 69.64\%$$

(b) potassium carbonate $\rightarrow K_2CO_3$

$$\% \text{ of potassium} = \frac{78}{138} \times 100 = 56.52\%$$

(c) potassium bicarbonate $\rightarrow KHCO_3$

$$\% \text{ of potassium} = \frac{39}{100} \times 100 = 39\%$$

(d) potassium sulphide $\rightarrow K_2S$

$$\% \text{ of potassium} = \frac{39 \times 2}{110} \times 100 = 70.90\%$$

$\therefore$ increasing order is (d) > (a) > (b) > (c)

33. Let the vapour density of compound be x

Empirical formula weight = x/2

Molecular formula weight = 2x

$$n = \frac{\text{Molecular formula weight}}{\text{Empirical formula weight}} = \frac{2x}{\left(\frac{x}{2}\right)} = 4$$

Molecular formula = $4 \times A_2B_4 = A_8B_{16}$

HINTS AND EXPLANATION

34. Let the bivalent metal ion be M^{+2}, then the formula of the compound formed will be $M(ClO_4)_2$.

1 mole of compound contains 8 N oxygen atoms.

∴ 2 moles of compound contain 16 N oxygen atoms.

Choice (d)

35. $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$

36. Initial volume, $V_1 = 600$ ml

Initial temperature, $T_1 = x$

Final temperature, $T_2 = \frac{180x}{100}$

Final volume, $V_2 = ?$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ as per Charles's law}$$

$$\frac{600}{x} = \frac{V_2 \times 100}{180x} = V_2 = 1080\,\text{ml}$$

37. The weight of saturated solution = 108 – 39 = 69 g

The weight of KNO_3 crystals = 72 – 39 = 33 g

The weight of water in saturated solution = 69 – 33 = 36 g

$$\therefore \text{Solubility of } KNO_3 = \frac{\text{Weight of } KNO_3}{\text{Weight of water}} \times 100$$

$$= \frac{33}{36} \times 100 = 91.6 \text{ at } 50°C$$

38. Gram molecular weight of N_2O_3 is 76 g and 76 g of N_2O_3 contains 6.023×10^{23} molecules

∴ Weight of 4.82×10^{20} molecules

$$= \frac{76 \times 4.82 \times 10^{20}}{6.023 \times 10^{23}} \text{g} = 0.061\,\text{g}$$

15 mg of N_2O_3 = 0.015 g

∴ Total weight of N_2O_3 = 0.061 + 0.015

= 0.076 g

76 g occupies 22.4 l at STP.

0.076 g occupies ? l at STP.

$$= \frac{0.076 \times 22.4}{76} = 0.022\ell$$

39. 6.023×10^{23} molecules correspond to 1 mole

2.41×10^{23} molecules correspond to?

$$= \frac{2.41 \times 10^{23}}{6.023 \times 10^{23}} = 0.4\,\text{moles}$$

Case (i)

$$_1V_1 = n_1.R_1. \quad T_1$$

$8(2.5) = n_1\,(0.08).(300)$

$$n_1 = \frac{8(2.5)}{(0.08)(300)}$$

$n_1 = 0.833$ moles

Total moles, $n_2 = 0.833 + 0.4$

$n_2 = 1.233$

Case (ii)

$P_2V_2 = n_2R\,T_2$

$10\,(2.5) = 1.233\,(0.08).T_2$

$T_2 = 253.4$ K

40. Initial volume, $V_1 = 600$ ml

Let initial pressure be $P_1 = x$

Final pressure, $P_2 = \frac{60x}{100}$

Final volume, V_2

As per Boyle's law, $P_1V_1 = P_2V_2 \Rightarrow V_2 = \frac{P_1V_1}{P_2}$

$$V_2 = \frac{x \times 600 \times 100}{60x}$$

$$V_2 = 1000\,\text{ml}$$

41. $N_{\text{Mixture}} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$

$$= \frac{(0.5)250 + (2 \times 750)}{250 + 750} = 1.625\,\text{N}$$

∴ Molarity = 1.625 N (as HCl is monobasic acid)

HINTS AND EXPLANATION

42. Let the density of solution be = xg/cc

Molarity = 7.8 M

Molecular mass of $Ca(OH)_2$ = 40 + 34 = 74

Mass of solute = 40 g

$$\text{Molarity} = \frac{\text{mass of solute}}{\text{molecular mass of solute}} \times \frac{1000}{\left(\frac{100}{x}\right)} 3$$

$$\left(\because v = \frac{m}{d}\right)$$

$$7.8 = \frac{40}{74} \times \frac{1000}{100} \times x$$

43. Barium's valency is 2, whereas the valency of rest of the elements is 1.

44. Suffix "ous" denotes lower valency exhibited by the metal when compared with suffix "ic" which denotes higher valency of the metal. Hence, plumbous is Pb^{+2}.

45. 0.5 moles of salt contains 3N oxygen atoms.

$\therefore$ 1mole of salt contains $= \frac{1 \times 3N}{0.5}$

= 6 N oxygen atoms

$\therefore$ The salt is $M(XO_3)_2$.

Level 2

1. (i) application of ideal gas equation
(ii) calculation of volume at 1 atmospheric pressure
(iii) determination of number of balloons
(iv) 40 balloons

2. (i) change in arrangement of molecules with increase in temperature
(ii) change in arrangement of molecules with increase in pressure
(iii) comparison of these changes

3. (i) relation between drop in pressure and rate of diffusion
(ii) relation between the rate of diffusion and molecular weight of gases
(iii) 100

4. (i) application of criss-cross method
(ii) derivation of the formulae of both the compounds
(iii) determination of the ratio of the number of atoms of B and D present in the respective molecule
(iv) determination of molar ratio of the compounds taken
(v) 1 : 2

5. (i) action of heating on the compounds Na_2CO_3 and $NaHCO_3$.
(ii) determination of the mass of Na_2CO_3 and $NaHCO_3$ from the mass of CO_2 produced
(iii) 84% $NaHCO_3$
16% Na_2CO_3

6. (i) atomicity of oxygen
(ii) chemical composition of Al_2O_3
(iii) determination of mass of Al_2O_3
(iv) 408 g

7. (i) relation between molecular weight and rate of effusion
(ii) determination of the ratio of the number of molecules of helium and methane which are effused out
(iii) calculation of the ratio of the remaining molecules
(iv) $\frac{2x}{3}$ moles

8. (i) relation between number of moles of gases
(ii) relation between number of moles of gases effused and molecular weight
(iii) comparison of number of moles of H_2 and O_2 effused
(iv) calculation of number of moles of H_2 and O_2 left over
(v) 28 : 17

9. (i) identification of acidic radical and formula of salt
(ii) determination of the formula of the "per" acid radical
(iii) determination of the formula of the salt
(iv) determination of the number of atoms of each constituent element present in one molecule of the salt
(v) determination of the number of atoms of each constituent element present in 5 moles of the salt
(vi) 4 N oxygen atoms

N chlorine atoms

10. (i) amount of HNO_3 present in 0.5 M HNO_3
(ii) calculation of volume based on given data and above amount
(iii) calculation of molarity
(iv) 20.5 ml

11. (i) reaction between Fe_3O_4 and hydrogen and weight–volume relationship between reactants and product
(ii) calculation of number of moles of iron
(iii) calculation of the corresponding number of moles of hydrogen consumed from the balanced chemical equation
(iv) calculation of number of moles of zinc taken part in the reaction
(v) calculation of percentage purity of zinc
(vi) 95.27%

12. (i) calculate the number of atoms of oxygen present in the compound
(ii) calculation of the number of atoms of oxygen present in one molecule of the metallic oxide from the percentage of oxygen given
(iii) determination of the formula of the compound
(iv) calculation of atomic weight of the metal
(v) 63.5

13. (i) relation between the ratio of the volumes and ratio of the number of moles
(ii) determination of the empirical formula based on the molar ratio of the product
(iii) CH

14. (i) number of moles of solute
(ii) calculation of weight of solution, solvent
(iii) calculation of number of moles of solvent
(iv) calculation of mole fraction and molarity
(v) 1.5 M, 0.03

15. (i) fraction of number of moles of CH_4, H_2 and He in the mixture
(ii) relation between mole fraction and total pressure
(iii) $\frac{8P}{13}, \frac{4P}{13}, \frac{P}{13}$

Solutions for questions from 16 to 25:

16. The formula of perchlorate of a divalent metal M is $M(ClO_4)_2$.

Molecular mass of $M(ClO_4)_2$ is 239.

Let x be the atomic mass of bivalent metal.

$\therefore x + 2[35.5 + 64] = 239 \Rightarrow x = 40$

$\therefore$ The element is calcium.

(a) The formula of its phosphate is $Ca_3(PO_4)_2$.
$\therefore$ Its molecular mass is $(3 \times 40) + 2[31 + 64] = 310$

(b) The formula of its iodide is CaI_2.
$\therefore$ Its molecular mass is $40 + (2 \times 127) = 294$

(c) The formula of bisulphate is $Ca(HSO_4)_2$
$\therefore$ Its molecular mass is $40 + 2[1 + 32 + 64] = 234$

17. (a) The copper displaces the mercury from mercuric chloride and forms cupric chloride and mercury.

$(Cu + HgCl_2 \rightarrow CuCl_2 + Hg)$

(b) $2\ KNO_3 \rightarrow 2\ KNO_2 + O_2$

$S + O_2 \rightarrow SO_2$

$C + O_2 \rightarrow CO_2$

(c) $2NH_4OH + CuSO_4 \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$

18.

Metal Oxides	Percentage of Metal	Percentage of Oxygen
A	74.2	25.8
B	59	41

In A, 74.2 g of metal combines with 25.8 g of oxygen

? combines with 1 g of oxygen

$$= \frac{74.2\,g}{25.8\,g} = 2.87\,g$$

In B, 59 g of metal combines with 41 g of oxygen

? combines with 1 g of oxygen

$$= \frac{59}{41}\,g = 1.43\,g$$

∴ The ratio by weight of metal combining with fixed mass of oxygen in A and B

= 2.87 : 1.43 = 2 : 1

Hence, law of multiple proportions is obeyed.

19. Total pressure, $P_{N_2} + P_{O_2} + P_{H_2O} = 640$ mm

Vapour pressure of water vapour = 40 mm

$$\therefore P_{N_{2+}} + P_{O_2} = 640 - 40 = 600\,\text{mm}$$

Mole fraction of nitrogen = 4/5

Mole fraction of oxygen $= \frac{1}{5}$

Partial pressure of N_2 = total pressure × $X_{N_2} = 600 \times \frac{4}{5} = 480\,\text{mm}$

Partial pressure of $O_2 = 600 \times \frac{1}{5} = 120\,\text{mm}$

20. No. of moles of oxygen, $n_{o_2} = \frac{8}{32} = 0.25$

No. of moles of hydrogen, $n_{H_2} = \frac{6}{3} = 2$

Total number of moles, n = 0.25 + 2 = 2.25

PV = nRT

2P = 2.25 × 0.08 × 300

P = 27 atm

Partial pressure of oxygen, p_{O2} = (mole fraction of O_2). P

$$= \left(\frac{0.25}{0.25+2}\right)27 = 3\,\text{atm}$$

$$P_{total} = P_{O_2} + P_{H_2}$$

Partial pressure of H_2 = 27 – 3 = 24 atm

21. Number of moles of the given substance $= \frac{18 \times 10^{23}}{6 \times 10^{23}} = 3$

Weight of compound = 96

Gram molecular mass of the compound $= \frac{96}{3} = 32\,\text{g}$

% of N_2 = 87.5%

Number of nitrogen atoms in 1 molecule of the compound $= \frac{87.5 \times 32}{100 \times 14} = 2$

Similarly number of hydrogen atom in 1 molecule of the compound $= \frac{12.5 \times 32}{100 \times 2} = 4$

Molecular formula is N_2H_4

22. $2KNO_3 \rightarrow 2KNO_2 + O_2$

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

1 mole of ethylene requires 3 moles of oxygen

$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2$

6 moles of $Pb(NO_3)_2$ is required to give 3 moles of oxygen

∴ Weight of $Pb(NO_3)_2$ = 6 × 330 = 1980 g

Volume occupied by gaseous (NO_2 and O_2) products

= 15 × 22.4 l at STP = 336 ℓ

23. Among Cu and Zn, only Zn displaces H_2 from H_2SO_4

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

Pressure = 785 – 25 = 760 mm

Temperature = 136.5 K, volume = 336 ml

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{760 \times 336}{136.5} = \frac{760 \times V_2}{273}$$

V_2 = 672 ml

(V_2) Vol. of H_2 liberated at STP = 672 ml

Weight of zinc required $= \frac{65.5 \times 672}{22400} = 1.965\,\text{g}$

Weight of copper in brass = 5.793 – 1.965 = 3.828 g

% of Cu in the alloy $= \frac{3.828}{5.793} \times 100 = 66\%$

24. Chemical reaction equation to combustion reaction is

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

50 ml 150 ml 150 ml

We know volume of gas has same number of moles at same temperature and pressure

50 moles 150 moles 150 moles

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

50 mole 150 mole 150 mole

Given that reduction in volume when the gases mixture is cooled to the laboratory temperature = 150 ml

$$\therefore \frac{y}{2}(50) = 150 \Rightarrow y = 6.$$

and $x(50) = 150 \Rightarrow x = 3$

$\therefore$ Hydrocarbon is C_3H_6.

25. $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

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

Number of moles of water formed in the first reaction $= \frac{144}{18} = 8$

Number of moles of CO_2 produced = 8

Number of moles of oxygen produced by using 8 moles CO_2 is 8.

Weight of oxygen liberated = $32 \times 8 = 256$ g

Level 3

1. (i) sudden expansion of the gas present inside the balloon
(ii) change in energy of the system due to the sudden expansion of the gas
(iii) effect of the change in energy on temperature
(iv) effect of this change in temperature on the surrounding
(v) phase transition of a vapour present in the surrounding

2. (i) requisite for deviation from ideal behaviour
(ii) consequences of high pressure and low temperature
(iii) comparison of actual volume occupied by real gases and ideal gases
(iv) comparison of intermolecular forces of attraction in the above said condition

3. (i) relation between the vapour pressure of the liquid and its intermolecular forces of attraction
(ii) comparison of the constituents of solution and pure solvent
(iii) comparison of the intermolecular force of attraction existing in the solution and that in the existing pure solvent
(iv) effect on vapour pressure

4. (i) calculation of the volumes of the given gases at STP
(ii) comparison of the difference in the volume of the given gases with that of the ideal gas at STP
(iii) relation between the difference in the volume and deviation in the behaviour of the gases from that of the ideal gas
(iv) determination of the ascending order of the extent of deviation of the given gases from the ideal gas

5. (i) difference between real gas and ideal gas
(ii) analysis of the pattern of the curves given in the graph
(iii) analysis of the kind of gradual change in the curves with the change of temperature
(iv) analysis of the change in volume with the change in pressure in case of each curve
(v) analysis of the reason behind the change

Solutions for questions from 6 to 10:

6. No. It is not empty in its true sense. In a cooking gas cylinder, the gas was initially at a high pressure. As the gas was drawn out from the cylinder,

the amount of gas in the cylinder decreases thereby reducing the pressure inside the cylinder. The gas will come out of the cylinder as long as the pressure of the gas inside the cylinder is more than the atmospheric pressure. When it is kept in hot water or shaken vigorously, kinetic energy of gas molecules increases and number of collisions increases. Thus, pressure increases and gas comes out of the cylinder.

7. At extremely low pressure all the gases behave almost ideally. From the graph it is known that as pressure increases, PV decreases showing that with increase in pressure the intermolecular spaces between molecules of B can be decreased to a great extent. This is possible when the intermolecular forces between the molecules are more. At a certain stage PV reaches minimum and then increases showing that further increase in pressure cannot decrease the volume to that extent. While in A though the intermolecular spaces are more, the decrease in volume of "A" with the increase of pressure is lesser than ideal gas. This shows that intermolecular forces of attraction of A are less.

8. Among A, B, C and D gases, D is the most easily liquefiable gas since the temperature required is the highest and pressure required is the lowest. The easier liquefaction indicates greater intermolecular forces of attraction and hence larger deviation from ideal behaviour. The order of ease of liquefaction is D > C > B > A, thus the ascending order of extent of deviation from ideal behaviour could be A < B < C < D.

9. Reduction of acidified solution of ferric ions by hydrogen gas does not take place. If a small amount of Zn is added to reaction mixture, the hydrogen gas is converted into nascent hydrogen by Zn. The nascent hydrogen is highly reactive and it reduces ferric ions to ferrous ions.

10. The curve indicates that the solubility of the solute at 100°C is 250 g. However, the given solution contains only 150 g of solute. The solution at point "A" is an unsaturated solution. Therefore, no precipitation takes place up to point "B" at 60°C where the solution becomes saturated, with just 150 gas solubility. Point "B" indicates saturated solution and hence precipitation normally starts at 60°C. With the fall in temperature, solubility decreases and the extra amount should get precipitated. Point "C" at 40°C indicates that the solution still contained 150g of solute which is a supersaturated solution. That means it is possible to cool a solution from 60°C to 40°C without any crystallization by creating conditions such as absence of dust particles. At 40°C, when crystallization starts, the solution ultimately becomes saturated, and this is represented by point D. At point D (40°C), the solubility is 100 g. That means, 50 g of solute would have been precipitated. At "E" also the solution remains saturated by precipitating 25 g more of solute leaving behind 75 g of solute in the solution. At 0°C when water starts to solidify, the solution still contains 5 g of solute without precipitation. That means 125 g of solute can be precipitated.

Chapter

2

Chemical Kinetics and Equilibrium

Remember

Before beginning this chapter, you should be able to:

- define a chemical reaction
- know the types of chemical reactions and how to formulate it.

Key Ideas

After completing this chapter, you should be able to:

- know the factors affecting rate of a chemical reaction and classification of chemical reactions based on it.
- study the factors influencing rate of a reaction in the light of collision theory and study about the classification of chemical reactions based on the energy changes
- study about classification of chemical reactions based on reversibility
- understand the different aspects of equilibrium such as dynamic nature, characteristics etc. and law of chemical equilibrium (law of mass action)
- understand Le Chatelier's principle and to study about factors affecting equilibrium

INTRODUCTION

Chemical reactions form an inevitable part of nature. Life on earth can never sustain without chemical reactions. Digestion of food, burning of fuel, decomposition of organic matter are some such reactions which are very essential to the existence of life. The study of the chemical reactions can have different perceptions, one of the most important aspects of the study being "rates of reactions."

Every chemical reaction can be represented in the form of a balanced chemical equation. Nevertheless, writing a chemical equation does not imply that the reaction takes place necessarily at all conditions. If that is the case, all gases in the atmosphere would react with each other and also with water. Obviously, that is not happening. For every reaction to occur, certain conditions are necessary. Moreover, some reactions may take place within a short time and some may require longer time for completion. That means, different reactions take place at different speeds.

The study of rates of chemical reactions forms an integral part of chemistry. In industry, the time taken for the completion of a particular reaction and the conditions employed to speed up the reaction determine the cost of production of a product and the economic viability of a process. Biological reactions in the presence of enzymes also take place at different rates. This aspect finds its applications in the field of medicine and agriculture.

The branch of chemistry which deals with the study of rates of reactions is called chemical kinetics. The area of chemical equilibrium deals with the kinetics of reversible reactions.

CLASSIFICATION OF REACTIONS ON THE BASIS OF RATES OF CHEMICAL REACTIONS

A chemical reaction involves transformation of reactants into products. The time taken for this transformation of reactants into products is not the same for all reactions. Based on the time taken for the completion of a reaction, the chemical reactions are classified into three categories.

(i) Instantaneous reactions

The reactions which reach completion within a fraction of a second are called *instantaneous reactions*.

Example **(a)** Precipitation reactions

Example: $2AgNO_3 + BaCl_2 \rightarrow Ba(NO_3)_2 + 2AgCl\downarrow$

(b) Burning of some active metals

Example: $2Na + O_2 \rightarrow Na_2O + Heat$

(c) Acid–base neutralization reactions involving strong acids and bases.

Example: $HCl + NaOH \rightarrow NaCl + H_2O$

(ii) Moderate reactions

The chemical reactions which require time ranging from a few minutes to hours to reach completion are called *moderate reactions*.

Examples: **(a)** digestion of food

(b) cooking of food

(c) photosynthesis in plants

(iii) Slow reactions

Some chemical reactions require a long time ranging from days to months or even years for completion. These reactions are called *slow reactions*.

Examples: **(a)** rusting of iron

(b) decomposition of organic matter

(c) formation of coal and petroleum

Rate of a Chemical Reaction

For any chemical reaction, at the start of the reaction, the concentration of the reactants is maximum and the concentration of the products is zero. As the reaction proceeds, the concentrations of the reactants decrease gradually and the concentrations of the products increase gradually. The change in concentration of the reactants or products with respect to time is known as the *rate of reaction*.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactants or products}}{\text{Time interval}}$$

$$r = \frac{\Delta C}{\Delta t}$$

$\Delta C \rightarrow$ change in concentration of reactants or products

$\Delta t \rightarrow$ time interval

If the rate of reaction is measured with respect to reactants, it is given a negative sign which indicates the decrease in concentration of reactants with time.

$$r = -\frac{\Delta C_{\text{Reactants}}}{\Delta t}$$

If the rate of reaction is measured with respect to products, it is given a positive sign which indicates the increase in concentration of products with time.

$$r = +\frac{\Delta C_{\text{Products}}}{\Delta t}$$

Units of Rate of Reaction

Since the concentration is expressed in moles/ℓ and time is expressed in seconds, the rate of reaction is expressed in mole per litre per second.

Average Reaction Rate vs Instantaneous Reaction Rate

The rate of reaction at the beginning of the reaction is proportional to the initial concentrations of the reactants. This is called the initial rate of reaction.

As the concentrations of the reactants decrease continuously, the rate of reaction is not uniform throughout the reaction. It changes continuously during the course of reaction. The rate of reaction is always taken as the change in the concentration of reactants or products in a definite interval of time. This is called the **average reaction rate**. But the average reaction rate does not give the exact idea of the rate of reaction at a particular instant of time.

At any instant, the rate of a reaction is proportional to the concentration of the reactants at that instant. As time proceeds, the concentration of the reactants decreases. With decrease in the concentration of the reactants, the rate of a reaction also decreases. Therefore, the rate of a reaction determined at a particular instant is called the **instantaneous reaction rate**.

For measuring instantaneous reaction rate, a very small interval of time, which is almost equal to zero, should be taken and the change in the concentration in that small interval of time must also be taken.

For a reaction, A → B

Rate of reaction $= \frac{\Delta C_B}{\Delta t}$, where

ΔC = change in concentration

Δt = time interval

When $\Delta t \rightarrow 0$ (Δt tends to zero)

The rate of reaction is called instantaneous rate.

Instantaneous rate (r) $= -\frac{\Delta C_A}{\Delta t}$ or $+\frac{\Delta C_B}{\Delta t}$

Example

If in a reaction A →B, ΔC_B is 0.001 moles/l and Δt is 10 s.

Average rate of reaction $= \frac{\Delta C_B}{\Delta t} = \frac{0.001}{10} = 10^{-4}$ mole l^{-1} s^{-1}

Graphical representation of average rate and instantaneous rate

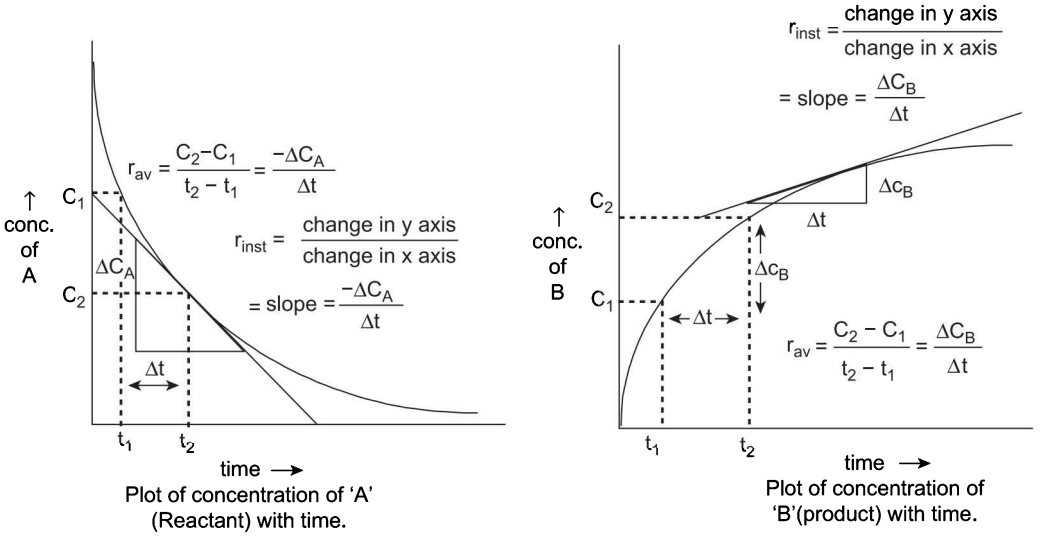


Figure 2.1 Determination of instantaneous reaction rate

Instantaneous rate at a particular time (t) can be obtained by determining the slope of the tangent drawn on the curve at the point where time = t.

Slope of the tangent $= \frac{\text{Change in y-axis}}{\text{Change in x-axis}}$

Change in "y" axis ΔC_A or ΔC_B

Change in "x" axis = Δt

Concentration of "A" vs t Concentration of "B" vs t

r_{inst} = slope $= -\frac{\Delta C_A}{\Delta t}$ r_{inst} = slope $= \frac{\Delta C_B}{\Delta t}$

Illustrations

(i) *Formation of hydrogen iodide*

$$H_2 + I_2 \rightarrow 2HI$$

The rate of the reaction may not be the same with respect to all the reactants and products. It depends upon the stoichiometric ratio of the reactants and the products. In the above case, one mole of hydrogen and one mole of iodine react to give two moles of hydrogen iodide. That means the rate of consumption of hydrogen = rate of consumption of iodine:

$$r = \frac{-\Delta[H_2]}{\Delta t} = \frac{-\Delta[H_2]}{\Delta t}$$

Rate of formation of HI = 2 × Rate of consumption of hydrogen or iodine

Rate of consumption of hydrogen or iodine = $\frac{1}{2}$ × Rate of formation of HI

$$\therefore r = \frac{-\Delta[H_2]}{\Delta t} = \frac{-\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

(ii) *Formation of nitrogen dioxide from nitric oxide*

$$2NO + O_2 \rightarrow 2NO_2$$

Rate with respect to oxygen $= \frac{-\Delta[O_2]}{\Delta t}$

Rate with respect to $O_2 = \frac{1}{2}$ × Rate with respect to NO

$$= -\frac{1}{2}\frac{\Delta[NO]}{\Delta t}$$

Rate with respect to $NO_2 = +\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}$

$$\therefore r = -\frac{1}{2}\frac{\Delta[NO]}{\Delta t} = \frac{-\Delta[O_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NO_2]}{\Delta t}$$

Therefore, while writing the equation for the rate of reaction, the stoichiometric coefficients of reactants and products are also taken into consideration.

For a general reaction, $aA + bB \rightarrow cC + dD$

$$r = -\frac{1}{a}\frac{\Delta C_A}{\Delta t} \qquad r = -\frac{1}{b}\frac{\Delta C_B}{\Delta t}$$

$$r = +\frac{1}{c}\frac{\Delta C_C}{\Delta t} \qquad r = +\frac{1}{d}\frac{\Delta C_D}{\Delta t}$$

where ΔC_A, ΔC_B, ΔC_C and ΔC_D are small changes in the concentrations of A, B, C and D that occur in time Δt.

Factors Influencing the Rate of a Reaction

Every chemical reaction has its own characteristic rate. Nevertheless, it is affected by some factors. The most important factors are listed hereunder:

(i) concentration of reactants,

(ii) temperature and

(iii) catalyst.

The reason behind different rates for different chemical reactions and factors influencing the rate of a reaction has been interpreted in terms of **collision theory of gases**. The basic concept behind this collision theory lies in kinetic molecular theory of gases.

The basic assumption of this theory is that the collisions between the reactant molecules give rise to the product.

But it is experimentally observed that the rate of reaction is much less than the frequency of collisions between the gas molecules (reactants). This observation was explained by proposing that the reactant molecules must collide with a certain minimum energy to give the product.

In 1880, Svante Arrhenius proposed that during collisions the reactant molecules must attain certain minimum amount of energy called threshold energy for the reaction to occur.

The collision model postulates that required threshold energy for the reaction can be attained from the kinetic energy of the reactant molecules before the collision.

The extra amount of energy required for the chemical reaction to occur is called the activation energy.

However, every collision with sufficient energy cannot result in the formation of the product because collision should take place with right orientation of reactants so that the product molecule(s) can be formed.

The collisions which successfully give the product are known as effective collisions and others are ineffective collisions. When the collision between the reactant molecules is effective an intermediate species called activated complex is formed before the formation of the product.

The energy of the system during the course of reaction increases and the energy associated with the activated complex is the highest. Then the energy of the system again decreases during the formation of the product from the activated complex.

Difference in the rates of different chemical reactions, i.e., slow and fast reactions can be explained satisfactorily with the help of the concept of activation energy.

The magnitude of the activation energy depends on the nature of the reactants. In case of reactions associated with high activation energy, only a small fraction of the reactant molecules possess sufficient kinetic energy and can give corresponding number of effective collisions. Such reactions are considered as slow reactions.

On the other hand, in the reactions in which the activation energy is less, an increased percentage of molecules cause effective collisions thereby giving a greater number of product molecules. These reactions are called fast reactions.

Collision theory satisfactorily accounts for the effect of change of concentration, temperature as well as the effect of catalyst on the rates of chemical reactions.

Effect of concentration: With the increase in the concentration of the reactants, the number of reactant molecules per unit volume increases. As a result, the number of collisions increases which results in the net increase of effective collisions. Therefore, the rate of a reaction increases.

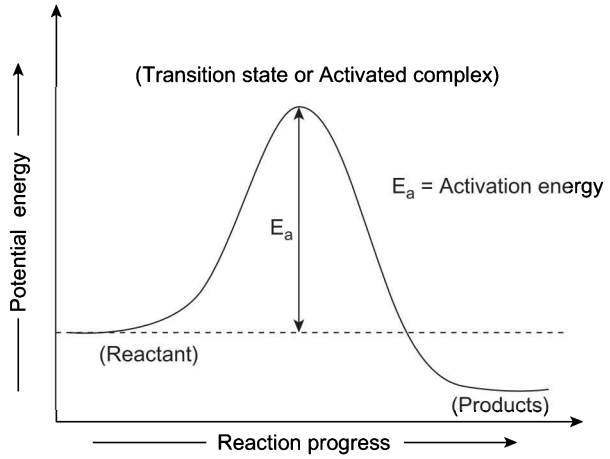


Figure 2.2 Energy profile diagram representing collision theory

Quantitative estimation of change in rate of reaction with change in concentration—Rate Law

Rate law is an expression which gives a quantitative estimation of the change in rate of reaction with the change in concentration of reactants. The establishment of quantitative relationship between the rate of reaction and concentration of the reactants cannot be obtained from the balanced chemical equation. This is because all the reactants participating in the reaction need not necessarily affect the rate of chemical reaction to the same extent. It can be done only by experimental methods.

For the general reaction

$$aA + bB \rightarrow \text{products}$$

$$r = k[A]^x [B]^y \text{ [where k is the rate constant]}$$

The power "x" is called order of the reaction with reference to "A" and the power "y" is called the order of the reaction with reference to "B." The sum of the powers (x + y) is called overall order of the reaction. It may or may not be equal to (a + b).

Order of a reaction can be defined as the sum of the powers to which the concentration terms are raised in the rate expression for that reaction.

Example

(i) $2H_2O_2 \rightarrow 2H_2O + O_2$. The rate law is $r = k[H_2O_2]^1$.
This reaction represents the dissociation of hydrogen peroxide. When the concentration of hydrogen peroxide is doubled, the rate of reaction is also doubled. Hence, the rate law can be written as $r = k[H_2O_2]^1$.

(ii) $CH_3CHO \rightarrow CH_4 + CO$
This reaction takes place in several steps. These steps take place at different rates. The slowest step of the reaction is called the rate-determining step. The overall rate of reaction is determined by the rate of the slowest step of the reaction. Consequently the rate law for this reaction does not reflect the coefficients of the balanced chemical equation.
Rate law for this reaction is

$$r = k[CH_3CHO]^{3/2}.$$

The order of reaction with respect to CH_3CHO is 3/2.

(iii) $2HI \rightarrow H_2 + I_2$

$$r = k[HI]^2$$

The decomposition of hydrogen iodide in aqueous solution takes place in the above manner. That means doubling the concentration of HI quadruples the rate of the reaction. The rate law follows the stoichiometric equation.

(iv) $H_2 + Cl_2 \xrightarrow{\text{light}} 2HCl$

In case of the above reaction of the formation of hydrogen chloride from hydrogen and chlorine, the rate of reaction is independent of concentrations of both hydrogen and chlorine. Therefore, the rate law can be written as

$$r = k[H_2]^0 [Cl_2]^0$$

Effect of temperature: For most of the chemical reactions, the rate of reaction increases with increase in number of effective collisions. When the temperature increases, the kinetic energy of molecules increases. More number of molecules attain threshold energy thereby increasing the number of fruitful collisions and hence the rate of reaction.

Experiment to Study the Effect of Temperature and Concentration on the Rate of Reaction

(i) Two boiling test tubes are taken with 3 g of zinc granules each. Graduated syringes are attached to the boiling test tubes. Further, 5 ml of 1M HCl and 5 ml of 2M HCl are added into the two test tubes. The volumes of hydrogen gas evolved in the two syringes at various time intervals are noted. It is observed that the volume of hydrogen gas evolved is more in the second case when compared to the first case. This shows that the rate of reaction increases with concentration.

(ii) The same experiment can be done by taking the same concentration of HCl at two different temperatures. Then, it is found that the volume of hydrogen evolved is more at higher temperature.

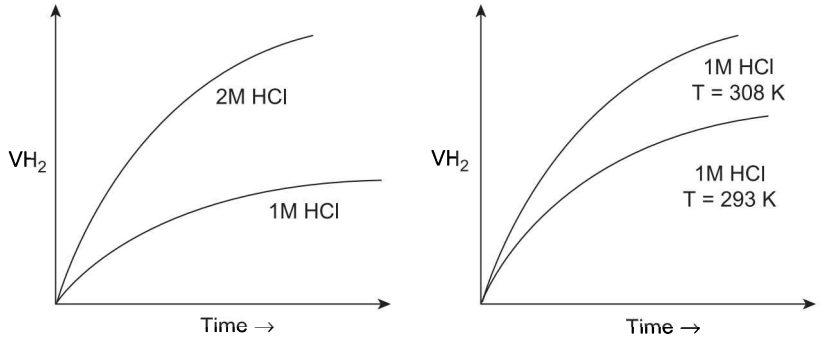


Figure 2.3 Energy profile diagram representing the effect of catalyst on rate of reaction

Effect of catalyst: The chemical reactions can be carried out at a faster rate by increasing the temperature, but this is not possible in case of all reactions. Moreover, the reactions can be carried out at a lower temperature by using a catalyst. Since the process takes place at a lower temperature, the cost of production gets reduced.

A catalyst increases the rate of reaction by providing an alternative path for the reaction. This alternative path is associated with lower activation energy when compared to the uncatalysed reaction.

In most of the reactions, catalysts increase the rate of reactions. These are called **positive catalysts**.

Examples: $2SO_2 + O2 \xrightarrow{NO} 2SO_3$

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

In case of some reactions, a catalyst only acts as a carrier of one of the reactants to the reaction site.

Example: Hydrogenation of unsaturated hydrocarbons

$$H_2C = CH_2 + H_2 \xrightarrow[\text{or Pd}]{\text{Ni or Pt}} H_3C - CH_3$$

Ethylene Ethane

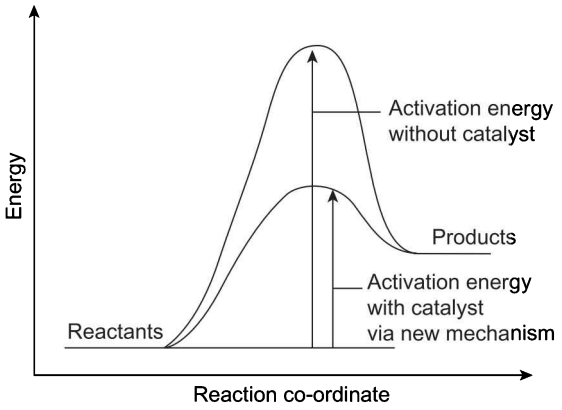


Figure 2.4 Effect of catalyst

In the above case, the hydrogen gas gets adsorbed on the metal surface and thus hydrogen gas comes into contact with the other reactant.

In some reactions, the catalyst takes part in the chemical reaction at the initial stage and gets regenerated at the end of the reaction.

Example: $2SO_2 + O_2 \xrightarrow{NO} 2SO_3$

In this reaction, nitric oxide reacts with atmospheric oxygen forming nitrogen dioxide (NO_2). This nitrogen dioxide oxidizes sulphur dioxide to sulphur trioxide. Nitric oxide is again regenerated. That means nitric oxide acts as an oxygen carrier in this reaction:

$$2NO + O_2 \rightarrow 2NO_2$$

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

There are few reactions in which catalysts can slow down the reactions. These are called **negative catalysts**.

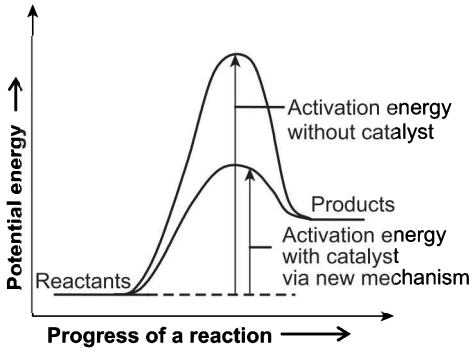
Example: Decomposition of hydrogen peroxide can be slowed down if some substances like glycerine, urea, acetanilide, sodium pyrophosphate, etc., are added to H_2O_2.

EXAMPLE

On the basis of collision theory, explain the action of a catalyst on the rate of reaction.

SOLUTION

Effect of catalyst on the rate of reaction: The chemical reactions can be carried out at a faster rate by increasing the temperature, but this is not possible in case of all reactions. Moreover, the reactions can be carried out at a lower temperature by using a catalyst. Since the process takes place at a lower temperature, the cost of production gets reduced. A catalyst increases the rate of reaction by providing an alternative path for the reaction. This alternative path is associated with lower activation energy compared to the uncatalysed reaction, which is evident from the following graph.



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EXAMPLE

Hydrogen peroxide decomposes to water and oxygen. The uncatalyzed reaction has activation energy of 86 kJ/mole. The activation energy values in the presence of acetanilide is 112 kJ/mole and in the presence of MnO_2 it is 49 kJ/mole. What conclusion can you draw from the above observations?

SOLUTION

The activation energy of a catalyzed reaction in the presence of MnO_2 catalyst is 49 kJ/mole which is much less than the activation energy of an uncatalyzed reaction that is 86 kJ/mole. This shows that the rate of decomposition of H_2O_2 is increased in the presence of MnO_2 and hence it is a positive catalyst. The activation energy of catalyzed reaction in the presence of acetanilide is 112 kJ/mole which is much greater than that of an uncatalysed reaction.

This shows that the rate of decomposition of **H_2O_2 is decreased in the presence of acetanilide and hence it is a negative catalyst.**

EXAMPLE

Assuming that $2NO + O_2$ ® $2NO_2$ is a single step reaction, what will be the rate of reaction when the volume of the reaction vessel is reduced to $1/4^{th}$ of the initial value? The original rate of reaction is 64 mole ℓ^{-1} s^{-1}.

SOLUTION

$2NO + O_2$ " $2NO_2$

The rate of the reaction $r = k[NO]^2 [O_2]$, as it is a single step reaction.

When the volume of the reaction vessel is reduced to $1/4^{th}$ of the initial volume, the concentration of each reactant is increased by 4 times. Since the reaction is 2^{nd} order with respect to NO and 1^{st}

order with respect to O_2, the rate of reaction increases by 16 times for NO and 4 times for O_2. On the whole, the rate of reaction increases by 64 times. The original rate of reaction is 64 mole ℓ^{-1} s^{-1} and the new rate of reaction is 64 times more than this.

$r_2 = 64 \times 64 = 4096 = 4.096 \times 10^3$ mole ℓ^{-1} sec^{-1}.

Chemical Equilibrium

When any liquid is taken in a closed container, the surface molecules go into vapour state due to evaporation. At the same time, at some stage, the vapour molecules condense and go back to liquid state. Therefore, the level of liquid in the container remains constant when the rate of evaporation and the rate of condensation become equal. This state is called equilibrium.

The state of equilibrium is also attained in case of chemical reactions which can take place in either direction. Such reactions in which the reaction takes place in both the directions are called reversible reactions. Due to the attainment of equilibrium state, these reactions do not reach completion.

Reversible and Irreversible Reactions

Reversible Reactions

Reactions in which the reactants are converted to products and the products are converted back to reactants are called *reversible reactions*.

The reaction in which the reactants are converted to products is called *forward reaction*. The reaction in which the products are converted back to reactants is called *backward reaction*.

Irreversible Reactions

Reactions in which the reactants are converted to products but the products cannot be converted back to reactants are called *irreversible reactions*. These reactions take place only in one direction.

Reversible reactions	Irreversible reactions
1. Can take place in both directions. 2. Equilibrium is established. 3. Can be made irreversible under some conditions. 4. Represented by two half-arrows in opposite directions ($\rightleftarrows$). ***Examples*** $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$ $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$ $2SO_{2(g)} + O2_{(g)} \rightleftarrows 2\,SO_{3(g)}$ $PCl_{5(g)} \rightleftarrows PCl_{3(g)} + Cl_{2(g)}$ $2NO_{(g)} + O_{2(g)} \rightleftarrows 2NO_{2(g)}$ $CaCO_{3(s)} \rightleftarrows CaO_{(s)} + CO_{2(g)}$	1. Can take place in one direction only. 2. No equilibrium is established. 3. Cannot be made reversible under any conditions. 4. Represented by a full arrow pointing towards the products ($\rightarrow$). ***Examples*** $4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)}$ $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$ $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$ $Sn + 2HCl \rightarrow SnCl_2 + H_2$

Dynamic Equilibrium

The rate of a reaction at any instant is proportional to the concentration of the reactants.

At the start of the reaction, the concentration of the reactants is maximum and so the rate of forward reaction is maximum. When the chemical reaction is in progress, the concentration of reactants

decreases and hence the rate of forward reaction also decreases. At the same time, during the course of reaction, the concentration of products increases thereby increasing the rate of backward reaction.

As time proceeds, a stage is reached when the rate of forward reaction becomes equal to the rate of backward reaction. At this stage, there is no net change in the molar concentrations of the reactants and the products. That means the system has attained the state of equilibrium. As the composition of the reactants and the products remains constant at this stage, it appears that the reaction has come to a standstill. However, it is not the case. The forward and backward reactions take place with equal speeds without any net change in the concentrations of reactants and products.

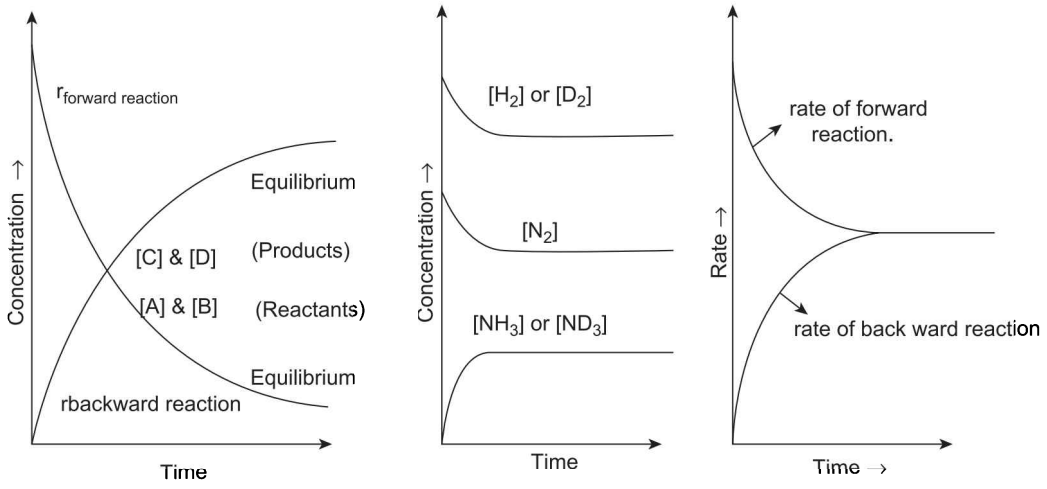


Figure 2.5 Dynamic equilibrium

Experiment to Show the Dynamic Nature of Chemical Equilibrium

Two reactions are conducted separately by taking known amounts of nitrogen and hydrogen in the first case and nitrogen and deuterium in the second case. Amounts of ammonia, N_2 and H_2 in the first reaction and amounts of ND_3, N_2 and D_2 in the second reaction are noted at regular intervals. After a certain time, the composition of reaction mixture is found to remain unaltered with time. This constancy in composition indicates the state of equilibrium. At this stage, the reaction mixtures of both the reactions are mixed together and left for some time. The analysis of the mixture showed not only the same concentration of ammonia but also existence of some deuterium containing forms of ammonia in the reaction mixture. Thus, it can be concluded that the interchange of H and D atoms has taken place because the forward and backward reactions proceed even after equilibrium is reached.

Characteristics of Dynamic Equilibrium

(i) The observable properties such as concentration, density, colour, pressure, etc., remain constant at constant temperature.

(ii) Equilibrium can be attained from either direction.

(iii) Usage of a catalyst does not alter the position of equilibrium.

(iv) Equilibrium state proceeds indefinitely unless it is disturbed by external factors.

Identification of Equilibrium

The equilibrium stage can be identified by constancy of some observable properties. Depending on the nature of various substances, a particular property is taken for observation.

Example

$$CaCO_{3(s)} + \rightleftarrows CaO_{(s)} + CO_{2(g)}$$

Since there is only one gaseous product in the above reaction, equilibrium can be identified by constancy of pressure exerted by CO_2:

$$NO_{2(g)} + CO_{(g)} \rightleftarrows NO_{(g)} + CO_{2(g)}$$

Since NO_2 is a reddish brown gas, the equilibrium can be identified by constancy of colour.

Law of Chemical Equilibrium or Law of Mass Action

Guldberg and Wage proposed a law in order to establish a quantitative relationship between the concentrations of the reactants and products at equilibrium.

The law of mass action states that the rate of a reaction is proportional to the product of the molar concentrations of the reactants.

For a reversible reaction, $xA + yB \rightleftarrows mC + nD$

$r_f \propto [A]^x [B]^y$, where r_f is the rate of forward reaction

$$r_f = K_f [A]^x [B]^y$$

$r_b \propto [C]^m [D]^n$, where r_b is rate of backward reaction

$$r_b = K_b [C]^m [D]^n$$

At equilibrium, $r_f = r_b$

$$K_f [A]^x [B]^y = K_b [C]^m [D]^n$$

$$\frac{K_f}{K_b} = K_c = \frac{[C]^m[D]^n}{[A]^x[B]^y}$$, where K_c is called equilibrium constant

Application of law of mass action to various equilibria: The chemical equilibria are basically of two types as discussed hereunder.

Homogenous equilibria: In these equilibrium reactions, all the reactants and products are in one phase only. In these cases, when all the reactants and products are in gaseous phase, the molar concentrations of all the substances are taken into consideration for writing the equilibrium constant.

Example: $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Example: $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Heterogeneous equilibria: In the reactions involving heterogeneous equilibria, the reactants and the products exist in different phases. In these cases, all the reactants and products are not taken into consideration for writing the equilibrium constant. The concentrations of the reactants and the products existing in solid state or in pure liquid state are taken in unity since their concentrations cannot be changed.

$$NH_4HS_{(s)} \rightleftarrows NH_{3(g)} + H_2S_{(g)}$$

$$K_c = \frac{[NH_3]_g[H_2S]_g}{[NH_4HS]_s}$$

Since $[NH_4HS]_s = 1$

$K_c = [NH_3][H_2S]$

Equilibrium Constant in Terms of Partial Pressure

The expression for equilibrium constant involves molar concentration of reactants and products and hence is called equilibrium constant with respect to concentration (K_c). However, in case of gas phase reactions, the concentrations of reactants and products can be expressed preferably in terms of partial pressures of the gases in the expression. Therefore it is called equilibrium constant with respect to pressure. In this case, K_c is denoted by K_p.

The ideal gas equation is PV = nRTn

$$\Rightarrow P = \frac{n}{v}RT$$

But concentration in mole/l is C = n/v

$\therefore$ P = CRT

R is constant and at constant temperature $P \alpha C_{gas}$.

Example:
$$\underset{(g)}{H_2} + \underset{(g)}{I_2} \rightleftarrows \underset{(g)}{2HI}$$

$$K_c = \frac{[HI]^2}{[H_2]\cdot[I_2]} \quad K_p = \frac{p_{HI}}{p_{H_2}\cdot p_{I_2}}$$

where p_{HI} = partial pressure of H_I

p_{H_2} = partial pressure of H_2

p_{I_2} = partial pressure of I_2

Applications of Equilibrium Constant

(i) On the basis of the value of the equilibrium constant, it is possible to predict the direction of a chemical reaction. The ratio of molar concentrations of the reactants to the products at any stage of the reaction is known as the reaction quotient (Q_c). Depending on the relative values of K_c and Q_c, it is possible to predict the direction of the equilibrium reaction.

If Qc = Kc, then the reaction is at equilibrium.

If Qc > Kc, then the reaction proceeds in the backward direction.

If Qc < Kc, then the reaction proceeds in the forward direction.

(ii) On the basis of the value of the equilibrium constant, the extent to which a chemical reaction takes place can be known. A greater value of K_c implies that the reaction mostly proceeds towards the products and the yield of the products will be more. A lower value of K_c indicates the lesser yield of products.

(iii) K_c values help in the calculation of the equilibrium concentrations of various substances in the reaction.

NUMERICAL PROBLEM

1. When two moles of hydrogen are heated with two moles of iodine, 2.96 moles of hydrogen iodide are formed. Calculate K_c for the reaction of formation of hydrogen iodide.

SOLUTION

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g)$$

At equilibrium, $2-x \quad 2-x \quad 2x$

$$2x = 2.96$$

$$x = \frac{2.96}{2} = 1.48$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(2-1.48)(2-1.48)} = \frac{4\times(1.48)^2}{0.52\times0.52} = 32.4$$

2. Calculate K_p for the following reaction if partial pressures of NH_3, N_2 and H_2 are 0.4 atm, 0.3 atm and 0.2 atm, respectively.

$$2NH_3 \rightleftarrows N_2 + 3H_2.$$

Solution

$$K_p = \frac{p^3H_2 \cdot pN_2}{P^2NH_2}$$

$$K_p = \frac{(0.2)^3 \cdot (0.3)(atm)^4}{(0.4)^2(atm)^2}$$

$$K_p = 0.015 \text{ atm}^2$$

EXAMPLE

If K_c for the formation of HI from H_2 and I_2 each is 64, then calculate K_c for the decomposition of 1 mole of HI.

SOLUTION

$H_2 + I_2 \rightleftharpoons 2HI \qquad 1/2\ H_2 + 1/2\ I_2 \rightleftharpoons HI.$

$$\Rightarrow K_{c_1} = \frac{[HI]^2}{[H_2]^1[I_2]^1} \quad \Rightarrow K_{c_2} = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$$

$$\therefore K_{c_2} = \frac{1}{\sqrt{K_{c_1}}} = \frac{1}{\sqrt{64}} = \frac{1}{8} = 0.125$$

EXAMPLE

In the reaction N_2O_4 D $2NO_2$, the dissociation of N_2O_4 was found to be 40% at equilibrium when the reaction is conducted in a 2 ℓ container at 300 K. Find the equilibrium constant and the number of moles of reactants and products.

SOLUTION

$N_2O_4 \rightleftharpoons 2NO_2$

Initial moles 1 0

Number of moles at equilibrium $1 - 0.4 = 0.6$ 0.8

Concentration at equilibrium $0.6/2 = 0.3$ $0.8/2 = 0.4$

$$\therefore K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.4)^2}{0.3} = 0.533 \text{ mole } \ell^{-1}$$

Factors Affecting The Equilibrium

The different factors which affect the chemical equilibrium are the concentration of the reactants or products, temperature and pressure. The change in the behaviour of the system at equilibrium due to the alteration of those factors was first enunciated by Le Chatelier.

Le Chatelier's principle has been proposed to explain the effect of various factors on the equilibrium.

Le Chatelier's Principle

According to this principle, when a system at equilibrium is subjected to a constraint or change, the position of the equilibrium shifts in a direction that opposes the constraints.

Effect of Concentration

When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium reaction mixture also changes in such a way as to compensate the effect of the concentration change.

Example: $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$

Addition of Hydrogen or Iodine

Addition of hydrogen or iodine at equilibrium disturbs the equilibrium concentration of the reactants. Hence, the reaction proceeds in that direction in which large amounts of hydrogen or iodine are consumed. That means the equilibrium shifts in the forward direction. The yield of HI increases. The same shift takes place by the removal of HI from the reaction mixture at equilibrium.

However, addition of HI at equilibrium results in the shift of equilibrium in the backward direction.

Example: $2K_2CrO_4 + 2HCl \rightleftarrows K_2Cr_2O_7 + 2KCl + H_2O$

Aqueous solution of potassium chromate which is yellow in colour changes to orange-coloured solution of potassium dichromate by the addition of the acid.

Addition of HCl to the reaction mixture at equilibrium shifts the reaction in the forward direction. This is indicated by the intensification of colour of the reaction mixture. Addition of water to the equilibrium mixture shifts the reaction in the backward direction. This is marked by fading of orange colour.

Effect of Pressure

According to Boyle's law, an increase in pressure leads to a decrease in volume at constant temperature.

When a system at equilibrium is subjected to increase in pressure, the reaction takes place in that direction which is associated with decrease in volume. Similarly, decrease in pressure makes the reaction proceed in that direction which is accompanied by increase in volume.

Avogadro's law states that under similar conditions of temperature and pressure equal volumes of all gases contain equal number of moles. The reactions which proceed with a change in the number of moles involve a change in volume.

Therefore, the effect of pressure is applicable to only those reactions accompanied by change in the number of moles (change in volume). Pressure has no effect on those equilibria which do not involve a change in the number of moles.

Example: $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$

$$n_R = 2n_p = 2\Delta n = n_p - n_R = 0$$

where n_R and n_P represent the number of moles of the reactants and products. Since the number of moles of reactants is equal to the number of moles of products, change in pressure has no effect on the position of equilibrium.

Reactions Associated With a Change in the Number of Moles

Case I

Increase in the number of moles (volume)

Example: PCl_5 of moles (change in volume $PCl_3 + Cl_2$)

$$n_R = 1n_P = 2\Delta\, n = n_P - n_R = 2 - 1 = 1$$

The forward reaction proceeds with an increase in the number of moles, which means that an increase in volume takes place during the reaction. Therefore, decrease in pressure favours the forward reaction and speeds up the dissociation process. Increase in pressure shifts the equilibrium in the backward direction thereby suppressing the dissociation process.

Case II

Decrease in the number of moles (volume)

Example: $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

$$n_R = 4n_P = 2\Delta n = n_P - n_R = -2$$

The forward reaction proceeds with decrease in the number of moles, i.e., decrease in volume. Hence, increase in pressure favours the forward reaction and enhances the yield of ammonia. Obviously, decrease in pressure speeds up the dissociation of ammonia into nitrogen and hydrogen. Due to this reason only, high pressure (200 to 1000 atm) is maintained during the process of the synthesis of ammonia by Haber's process. (a favourable condition for getting greater yield of the products).

Effect of Temperature

Most of the chemical reactions are associated with absorption or evolution of heat. Hence, change in temperature changes the state of equilibrium. Increase in temperature makes the reaction proceed in that direction in which more heat is absorbed. Similarly, decrease in temperature allows the reaction to take place in a direction associated with the release of heat energy.

Case I

Absorption of heat energy

Example: $N_2 + O_2 \rightleftarrows 2NO - \text{Heat}$

Since absorption of heat takes place in the forward reaction, increase in temperature shifts the equilibrium in the forward direction. It can be concluded that for all endothermic reactions, high temperature is the favourable condition for greater yield of products.

Case II

Evolution of heat energy

Example: $N_2 + 3H_2 \rightleftarrows 2NH_3 + \text{Heat}$

Since the forward reaction is accompanied by release of heat energy, decrease in temperature favours the forward reaction which means that for all exothermic reactions, low temperature is the most favourable condition.

EXAMPLE

(a) What is the effect of pressure on the equilibrium of the reaction of nitrogen and oxygen to give nitric oxide?

(b) In a reversible reaction, some amount of heat energy is liberated in the forward reaction. Name the reaction. What change in temperature favours the forward reaction?

SOLUTION

(a) $N_2 + O_2 \rightleftharpoons 2NO$

As the total number of moles on reactants side and products side is same, there is no effect of pressure on the equilibrium.

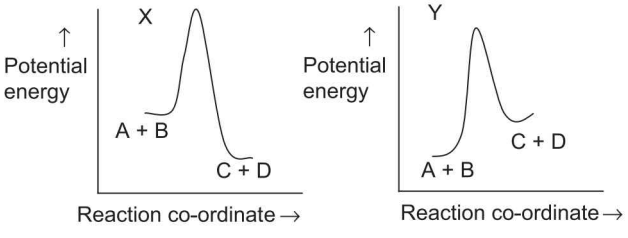
(b) In a reversible reaction, evolution of heat energy indicates that it is an exothermic reaction and ΔH = –ve.

For example, A+ B $\rightleftharpoons$ C + D + Energy

Hence, low temperature favours the formation of products.

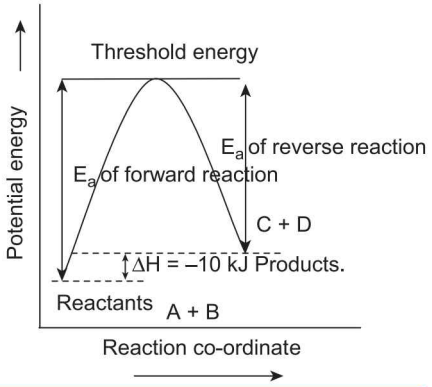
EXAMPLE

A teacher, while revising, asked Raman and Bose to sketch a potential energy diagram for a reaction A + B $\rightleftharpoons$ C + D. If ΔH for the reverse reaction is –10 kJ and E_a of the forward reaction is 40 kJ. The graph drawn by both of them are X and Y respectively. Between X and Y, which graph is correct and why? Also, explain why the other one is wrong.



SOLUTION

As the energy released in the backward reaction is 10 kJ, the backward reaction is exothermic indicating that the energy of reactants is less than the energy of products. Hence 'Y' is correct. X is wrong because as the energy of C + D is less than A + B, on the reverse reaction would be endothermic. (ΔH = +ve).



EXAMPLE

During the preparation of soap "the addition of common salt allows the precipitation of soap". Explain the principle involved. (Soap is the sodium salt of carboxylic acid)

Example: Sodium stearate $C_{17}H_{15}COONa$

SOLUTION

The addition of common salt results in the addition of Na^+ ions. Equilibrium exists between sodium stearate molecules and sodium and stearate ions. The addition of Na^+ ions shifts the equilibrium towards left and sodium stearate precipitates.

$RCOO^-Na^+ \rightleftharpoons RCOO^- + Na^+$.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. Define instantaneous reactions.
2. What are the units of rate of reaction?
3. The equation that describes mathematically the dependence of the rate of reaction on the concentration terms of reactants is _____ or _____.
4. For a reaction A → B, ΔC_B is 0.01 moles/l in 20 s, what is the average rate of reaction?
5. The reaction between Zn and H_2SO_4 is an example for _____ reaction.
6. The activation energy for an uncatalysed reaction is less than that for a catalysed reaction. What do you conclude from the above statement?
7. A _____ does not change the position of equilibrium but _____ the rate of backward as well as forward reaction.
8. Give the general expression for a balanced chemical equation by applying the law of mass action.
9. How is the attainment of equilibrium recognized in case of following equilibria?
   (i) dissociation of magnesium carbonate in a closed vessel
   (ii) dissociation of N_2O_5 in a closed vessel
10. When the reaction of synthesis of ammonia is carried out with a mixture of hydrogen and deuterium, what are the products obtained at the end of the process?
11. Write the equilibrium constant for the dissociation of $CaCO_3$.
12. In the reaction A + B → C, r = k[A], if [A] is increased by three times then the difference in the rate is _____ of the initial rate.
13. What are effective collisions?
14. _____ enables any two systems to reach a state of equilibrium more quickly.
15. The rate of _____ reactions cannot be determined experimentally.
16. Define a reversible reaction. Give an example.
17. What is meant by specific reaction rate?
18. The value of equilibrium constant for a reversible reaction is 3×10^{-2}. If the reaction quotient for the same reaction is 5×10^{-3}, predict the direction of equilibrium reaction.
19. In the reaction $2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O$, if initial concentration of hydrogen is kept constant and the concentration of NO is doubled, the rate of reaction increases by four times. This shows that rate is directly proportional to _____
20. The equilibrium $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$ is not affected by the change in _____.
21. What is the effect of pressure on the equilibrium of the reaction of nitrogen and oxygen to give nitric oxide?
22. In a reversible reaction, some amount of heat energy is liberated in the forward reaction. What change in temperature favours the forward reaction?
23. What is the effect of a catalyst on the equilibrium?
24. Active mass of a solid is taken as _____.
25. Ammonia dissociates to give nitrogen and hydrogen. What happens if the pressure is increased on the system at equilibrium?
26. What are the units for the rate of the reaction A → B?
27. If K_c for the formation of HI from H_2 and I_2 is 48, then K_c for decomposition of 1 mole of HI is _____.
28. The magnitude of _____ decreases in the presence of a catalyst.
29. Give the units of K_c for the formation of 1 mole of NH_3 from its constituents.
30. A chemical equilibrium is _____ in nature.

PRACTICE QUESTIONS

Short Answer Type Questions

31. How are the reactions classified on the basis of rates of reactions? Give examples.

32. Explain the effect of temperature on the rate of reaction.

33. How do you explain the effect of concentration on the rate of reaction on the basis of collision theory?

34. Define reversible and irreversible reactions. Give examples.

35. Discuss how the chemical equilibrium is dynamic by giving graphical representation.

36. Explain the action of a catalyst on the rate of reaction on the basis of collision theory.

37. What are the characteristics of dynamic equilibrium?

38. How is it possible to make reversible reaction irreversible?

39. Apply the law of mass action to the following equilibria:

(i) formation of SO_3 from SO_2 and O_2

(ii) formation of NO_2 from nitric oxide and oxygen

40. How does a catalyst influence the equilibrium constant?

41. "The quantitative estimation of change in the rate of reaction with change in concentration does not always follow stoichiometric equation." Justify.

42. Product the shift in equilibrium when the volume is decreased on the following equilibrium reactions:

(i) $Pcl_{3\,(g)} + Cl_{2\,(g)} \rightleftarrows PCl_{5\,(g)}$

(ii) $N_{2\,(g)} + O_{2\,(g)} \rightleftarrows 2NO_{(g)}$

43. What are the applications of equilibrium constant?

44. Calculate K_p if the partial pressures of reactants and products in the dissociation of 1 mole of phosphorous pentachloride are 0.3 atm, 0.4 atm and 0.2 atm respectively.

45. One mole of PCl_5 is subjected to heating in a 1 l vessel. The number of moles of PCl_3 formed at equilibrium is 0.6. Calculate the equilibrium constant for the dissociation of PCl_5.

Essay Type Questions

46. State the postulates of collision theory. Explain the effect of temperature, concentration and catalyst on the rate of reaction.

47. Explain an experiment to study the effect of temperature and concentration on the rate of reaction.

48. State and explain Le Chatelier's principle. Apply the principle to the following equilibria.

(i) $2SO_2 + O_2 \rightleftarrows 2SO_3 + \text{Heat}$

(ii) $2NH_3 \rightleftarrows N_2 + 3H_2 - \text{Heat}$

49. State and explain the law of mass action. Apply it to the following equilibria:

(i) $H_{2\,(g)} + F_{2\,(g)} \rightleftarrows 2HF_{\,(g)}$

(ii) $NH_4HS_{(S)} \rightleftarrows NH_{3(g)} + H_2S_{(g)}$

(iii) $PCl_{5(s)} \rightleftarrows PCl_{3(\ell)} + Cl_{2(g)}$

50. State Le Chatlier's principle and apply it to the following equilibria:

(i) $2NO_{(g)} \rightleftarrows N_{2\,(g)} + O_{2\,(g)} + \text{Heat}$

(ii) $N_2O_{4\,(g)} \rightleftarrows 2NO_{2\,(g)} - \text{Heat}$

CONCEPT APPLICATION

Level 1

***Direction for questions from 1 to 7*: State whether the following statements are true or false.**

1. If the rate with respect to O_2, NO and NO_2 are respectively

$$\frac{-\Delta[O_2]}{\Delta t}, \frac{-1}{2}, \frac{\Delta[NO]}{\Delta t}, \frac{+1}{2}\frac{\Delta[NO_2]}{\Delta t}$$

then the corresponding chemical equation is $2NO + O_2 \rightarrow 2NO_2$.

2. The slope obtained by drawing a tangent at time "t" on the curve for the concentration of reactants vs time is equal to instantaneous rate.

3. In an equilibrium, the catalyst increases the rate of the forward reaction while decreases the rate of the backward reaction.

PRACTICE QUESTIONS

4. Threshold energy = Energy of normal molecules + Activation energy.
5. An increase in pressure increases the rate of reaction due to the increase in the number of collisions among the molecules.
6. In the reaction: $NO_2 + CO \rightleftarrows NO + CO_2$, the equilibrium state may be recognized by the constancy of colour.
7. At equilibrium the reaction quotient is greater than equilibrium constant.

***Direction for questions from 8 to 14*: Fill in the blanks.**

8. Equilibrium constant has a definite value for every reaction at a given temperature. It is independent of _____ and _____.
9. The minimum energy which two molecules should possess so that their collisions result in a chemical reaction is called _____ energy.
10. Decomposition of phosphorous pentachloride is an example of _____ equilibria.
11. K_c changes with change in _____.
12. _____ in temperature favours an endothermic reaction.
13. The equilibrium constant of a reaction $A + B \rightleftarrows 2C$ if the concentrations of A and B together is 0.8 moles l^{-1} and that of C is 0.6 moles l^{-1} is _____
14. If K_C for the formation of ammonia is 2 moles^{-2} ℓ^2, K_c for decomposition of ammonia is _____.

***Direction for question 15*: Match the entries given in column A with appropriate ones from column B.**

15.

Column A		Column B
A. Neutralization of acids by bases	( )	a. Very slow reaction
B. Decomposition of H_2O_2	( )	b. Fruitful collisions
C. Formation of water from H_2 and O_2	( )	c. Moderately slow reaction
D. Threshold energy	( )	d. More numbers of bonds
E. Slow reaction	( )	e. Instantaneous reaction

***Direction for questions from 16 to 45*: For each of the questions, four choices have been provided. Select the correct alternative.**

16. If $r = \frac{-3}{2}\frac{\Delta[A]}{\Delta t} = \frac{-5}{2}\frac{\Delta[B]}{\Delta t} = \frac{+7}{3}\frac{[\Delta C]}{\Delta t}$, which of the following is the corresponding reaction?
    (a) 2/3 A + 2/5 B → 3/7 C
    (b) 2/3 A + 5/2 B → 7/3 C
    (c) 3/2 A + 5/2 B → 7/3 C
    (d) 7/3 C + 5/2 B → 3/2 A
17. In the reaction $N_2 + O_2 \rightleftarrows 2NO$ – Heat, which of following conditions is suitable to get a good yield of NO?
    (a) increase in temperature
    (b) decrease in temperature
    (c) increase in pressure
    (d) the addition of a catalyst
18. Which of the following is true?
    (a) In an endothermic equilibrium reaction, activation energy required for a forward reaction is higher than that for a backward reaction.
    (b) To an endothermic equilibrium reaction, activation energy required to forward reaction is lower than that for a backward reaction.
    (c) Activation energy required for both forward and backward reactions is same in equilibrium.
    (d) No activation energy is required for an exothermic backward equilibrium reaction.
19. The equilibrium constant for the given reaction, $CaCO_{3(s)}$ $CaO_{(s)} + CO_{2\,(g)}$ is given by
    (a) $K_c = \frac{[CaO]\cdot[CO_2]}{[CaCO_3]}$
    (b) $K_c = \frac{[CaO]}{[CaCO_3]}$
    (c) $K_c = [CO_2]$
    (d) $K_c = \frac{[CaO]}{[CO_2]}$
20. For a chemical reaction to occur
    (a) the reacting molecules must collide with each other
    (b) reacting molecules should have sufficient energy at the time of collision
    (c) reacting molecules must be properly oriented
    (d) all of the above

PRACTICE QUESTIONS

21. If an activated complex is formed in chemical reactions according to the collision theory, which of the following is true with respect to its stability?

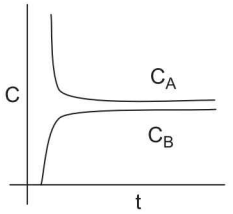
(a) It is highly stable because it has high energy.
(b) It is less stable because it has lower energy.
(c) It is less stable because it has high energy.
(d) None of the above.

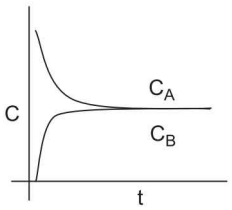
22. The equilibrium constant for the reactions $N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)}$ and $NO_{(g)} \rightleftarrows \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$ are k and k^1, respectively, the relation between k and k^1 is

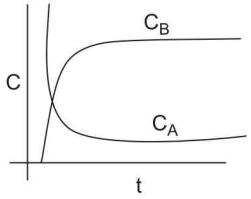
(a) $k = (k^1)^2$ (b) $k = \left(\frac{1}{k^1}\right)^2$

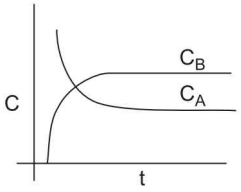
(c) $k^2 = k^1$ (d) $k^1 = \left(\frac{1}{k}\right)^2$

23. With respect to the equilibrium reaction A $\rightleftarrows$ B, which of the following graphs indicate the highest K_c value?

(a)


(b)


(c)


(d)


24. Equilibrium position of which of the following reactions is not affected by change in pressure?

(a) $I_{2(s)} + 5F_{2(g)} \rightarrow 2IF_{5(g)}$
(b) $FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(s)} + CO_{(g)}$
(c) $2Cu(NO_3)_{2(s)} \rightarrow 2CuO_{(s)} + 4NO_{2(g)} + O_{2(g)}$
(d) $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$

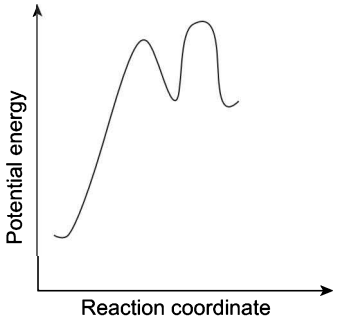
25. The equilibrium constant K_c is 10^2 for the reaction AB + C $\rightleftarrows$ AC + B

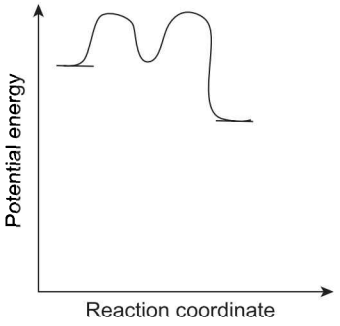
The rate constant for the forward reaction K is 106, the rate constant of backward reaction is

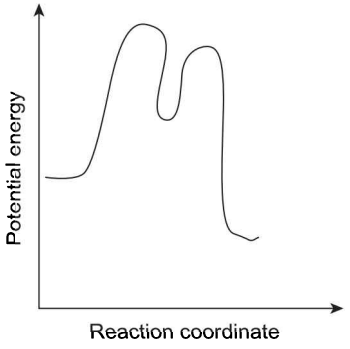
(1) 10^4 (2) 10^8

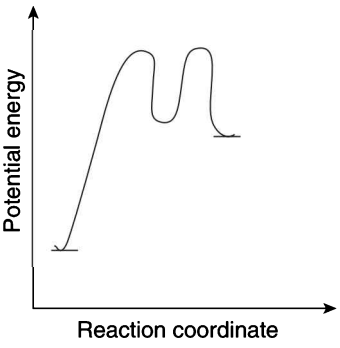
(3) 10^{-4v} (4) $\frac{1}{100}$

26. Which among the following is the graphical representation of a reaction if the ΔH for the forward reaction is twice the activation energy of the I step and activation energy of the II step is half of the I step

(a)


(b)


(c)


(d)


27. For a particular reaction, A + B → C was studied at 25°C. The following results are obtained:

[A] mole/l	[B] moles/l	Rate (mole l^{-1} s^{-1})
9×10^{-5}	1.5×10^{-2}	0.06
9×10^{-5}	3×10^{-3}	0.012
3×10^{-5}	3×10^{-3}	0.004
6×10^{-5}	x	0.024

Then the value of x is _____

(a) 6×10^{-3} m ℓ^{-1} (b) 3×10^{-3}m ℓ^{-1}

(c) 4.5×10^{-3} m ℓ^{-1} (d) 9×10^{-3} m ℓ^{-1}

28. $2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)} + Q$ kJ

In the above reaction, how can the yield of product be increased without increasing the pressure?

(a) by increasing temperature

(b) by decreasing temperature

(c) by increasing the volume of the reaction vessel

(d) by the addition of the catalyst

29. For a reaction 2A + B → 2AB, it is found that doubling the concentration of both the reactants increases the rate to eight times that of initial rate but doubling the concentration of B alone doubles the rate. Then the order of the reaction with respect to A and B is

(a) 0, 3 (b) 0, 2

(c) 2, 1 (d) 2, 2

30. In the reaction $N_2O_4 \rightleftarrows 2NO_2$, the degree of dissociation of N_2O_4 increases with

(a) increase in pressure

(b) decrease in temperature

(c) increase in volume

(d) presence of catalyst

31. Identify the correct sequence of steps in an experiment to show the effect of temperature on the rate of the reaction.

(1) Measuring the volumes of H_2 gas liberated in the two test tubes.

(2) Heating the test tube B by 10°C.

(3) Comparison of relative volumes of H_2 liberated in test tubes B and A.

(4) Addition of same concentration of HCl to the two test tubes.

(5) Taking equal masses of fine granules of zinc in two test tubes A and B.

(a) 3, 4, 5, 1, 2 (b) 5, 4, 2, 1, 3

(c) 2, 1, 3, 5, 4 (d) 5, 4, 2, 3, 1

32. The graph given below shows the change in concentration of "B" with time for the reaction A → B. Identify the steps given below in sequence for determining instantaneous rate.

(1) Find the slope of the tangent $= \frac{y_2 - y_1}{x_2 - x_1}$

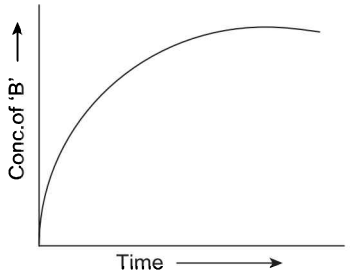
(2) Change in the y-axis, i.e., y_2–y_1 gives change in concentration of "B," whereas change in the x-axis, i.e., x_2–x_1 gives a small change in time interval.

(3) slope of the tangent is equal to instantaneous rate

(4) Draw the tangent on the curve at a particular instant of time "t."

(a) 3, 1, 2, 4 (b) 1, 2, 3, 4

(c) 4, 2, 1, 3 (d) 4, 3, 1, 2



33. For the reaction A → B, identify the correct sequence of steps for the calculation of average rate of reaction.

(1) plotting a graph of concentration of "A" at various time intervals

(2) identification of C_2 and C_1 at different time intervals t_2 and t_1, respectively by reading the graph

(3) calculation of $\frac{C_2 - C_1}{t_2 - t_1}$

(4) finding out the experimental values of concentrations of "A" at regular intervals

(a) 4, 2, 3, 1 (b) 4, 1, 2, 3

(c) 3, 2, 1, 4 (d) 1, 2, 3, 4

34. Initial number of moles of reactants taken in a closed reaction vessel is given. Percentage degree of dissociation is also given. Identify the correct sequence of steps to calculate K_c value.

(1) calculation of equilibrium concentrations of reactants and products

(2) calculation of equilibrium number of moles

(3) writing equilibrium constant expression for the reaction

(4) calculation of K_c value by using the equilibrium concentration

(a) 4, 2, 3, 1 (b) 2, 1, 3, 4

(c) 3, 2, 1, 4 (d) 2, 1, 4, 3

PRACTICE QUESTIONS

35. Which among the following reactions is an example of instantaneous reaction under normal conditions?
(a) $2H_2 + O_2 \rightarrow 2H_2O$
(b) $N_2 + O_2 \rightarrow 2NO$
(c) $NaOH + HCl \rightarrow NaCl + H_2O$
(d) $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

36. The rate for the reaction between ionic compounds cannot be determined because they are generally
(a) immeasurably slow reactions
(b) moderately slow reactions
(c) instantaneous reactions
(d) not precipitation reactions

37. For a reaction A + B → C, the rate law is written as $r = k[A]^2[B]$. Doubling the concentration of "A" without changing concentration of "B" increases the rate of reaction by
(a) 2 times (b) 4 times
(c) 8 times (d) 16 times

38. Identify the common property for a chemical reaction at dynamic equilibrium:
(a) The measurable properties like concentration, density, colour, pressure, etc., remain constant at constant temperature.
(b) The forward and backward reactions take place with the same rate.
(c) It can be achieved from both directions.
(d) All of the above.

39. Which of the following K_c values corresponds to the maximum yield of the products?
(a) 9.2×10^2 (b) 1.8×10^{-15}
(c) 2.8×10^3 (d) 3.4×10^{-25}

40. For a reaction A + B ⇄ C + D, if the activation energy of backward reaction is more than that of forward reaction, the forward reaction is
(a) endothermic
(b) exothermic
(c) reaction need not necessarily involve heat changes
(d) cannot be predicted

41. According to Le Chatelier's principle,
(a) an increase in pressure always causes a change in position of equilibrium for any reaction
(b) the yield of NH_3 decreases from its constituents at lower temperature
(c) an increase in temperature causes a decrease in the value of Kc for an exothermic reaction
(d) the K_c is decreased for the reaction $A_{(s)} + B_{(g)} \rightarrow C_{(g)}$, if the concentration of A is increased

42. In which among the following reactions, the formation of product is favoured by decreasing the temperature or volume?
(a) $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)} - q$
(b) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} - q$
(c) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$, ΔH = –ve
(d) $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$, ΔH = –ve

43. The rate of a reaction depends on the
(a) temperature of the reaction
(b) catalyst
(c) concentration of the reactants
(d) all of these

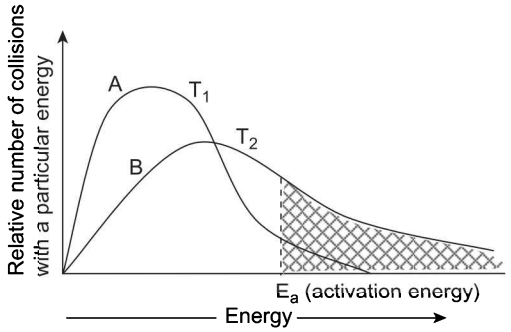
44. In the formation of NO and O_2 from NO_2 the rates of production of
(a) NO and O_2 are equal
(b) NO is double the rate of consumption of NO_2
(c) NO is twice the rate of production of O_2
(d) O_2 is twice the rate of production of NO

45. For a reaction A + B → C, the rate law is written as $r = k[A]^2[B]$. Doubling the concentrations of both of "A" and "B" increases the rate of reaction by
(a) 2 times (b) 4 times
(c) 8 times (d) 16 times

Level 1

1. Nitrogen dioxide gas dissociates to give nitric oxide and oxygen. For this reaction, when a graph is plotted between concentration of NO_2 and time, the slope of the tangent drawn at time t = 10 s is found to be 6.8×10^{-4} mole/l/s. Predict the slopes of the graphs at t =10 s when the concentration of NO and O_2 are plotted against time. Justify your answer.

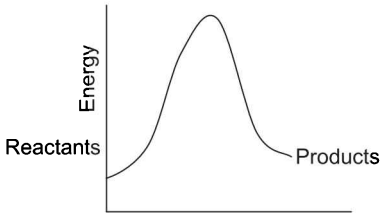
2. Based on the following curves predict in which case the rate of reaction would be more and justify?



3. Hydrogen peroxide decomposes into water and oxygen. The uncatalysed reaction has activation energy of 86 kJ/mole. The E_a value in the presence of acetanilide is 112 kJ/mole and in the presence of MnO_2 it is 49 kJ/mole. What conclusion can you draw from the above observations?

4. In the decomposition reaction, $2N_2O_5 \rightleftarrows 4NO_2 + O_2$ oxygen gas is produced at the average rate of 9.1×10^{-4} mole $l^{-1}s^{-1}$. Over the same period what is the average rate of production of NO_2 and loss of N_2O_5.

5. Energy profile diagram for a reversible chemical reaction is given. On the basis of the given diagram, explain the effect of temperature on the equilibrium.



6. For a reversible reaction, the activation energy of a forward reaction is 85 kJ/mole. The net reaction is associated with the release of 15 kJ/mole. What is the activation energy of the backward reaction? Explain it on the basis of the collision theory.

7. On what factors do the equilibrium position and equilibrium constant depend? Explain by giving appropriate reasons.

8. In the reaction $N_2O_4 \rightleftarrows 2NO_2$, the dissociation of N_2O_4 was found to be 40% at equilibrium when the reaction is conducted in a 2 l container at 300 K. Find the equilibrium constant and the number of moles of reactants and products.

9. In a gas phase reaction, the decomposition of PCl_5 takes place at 273°C and 1 atmospheric pressure. Its percentage degree of dissociation is 40%. Assuming that all gases in the reaction behave ideally, calculate the density of the equilibrium mixture. [atomic weight of phosphorus = 3 and chlorine = 35.5]

10. Carbon monoxide and water vapour react to give CO_2 and H_2 in a vessel of 2 ℓ capacity at 1090 K. Equilibrium is established and the number of moles of various components is found to be 0.8 moles, 0.6 moles, 0.4 moles and 1.2 moles, respectively. Calculate K_c value. If the concentration of CO has to be increased to 1.2 mole by increasing the concentration of CO_2 at the equilibrium, find the number of moles of CO_2 to be added to the reaction mixture at the same temperature.

11. For a gas phase reaction $Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$, the rate law is given as $r = K[Cl_2]^{1/2}[CHCl_3]$. Explain how the rate of reaction varies when the concentration of chlorine is doubled. Give units of rate constant.

12. $BRO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$. The order of reaction with respect to BrO_3^- is 2 and with respect to other reactants is one. Complete the following table.

	BrO_3^-	Br^-	H^+	Initial rates
I	0.1	0.1	0.1	?
II	0.2	0.1	0.1	1.6×10^{-3}
III		0.2	0.1	3.2×10^{-3}
IV	0.1	0.1	0.2	?

13. Assuming that $2NO + O_2 \rightarrow 2NO_2$ is a single-step reaction, what will be the change in rate of reaction when the volume of the reaction vessel is reduced to 1/4th of the initial value? The original rate of reaction is 64 mole l^{-1} s^{-1}.

14. During the preparation of soap "the addition of common salt allows the precipitation of soap." Explain the principle involved.

15. A reaction takes place in two steps. The rates of the two elementary steps are given. On the basis of these, predict the rate law and explain the trend of variation in the rates of reaction with changes in concentration. Also the given units of rate constant are

$2A_{(g)} + B_{2(g)} \rightarrow 2AB_{(g)} \rightarrow$ Overall reaction

$A + B_2 \rightarrow AB + B$, in the first step, $r = 3.2 \times 10^4$ moles/l/s

$B + A \rightarrow AB$, in the second step, $r = 1.9 \times 10^6$ moles/l/s

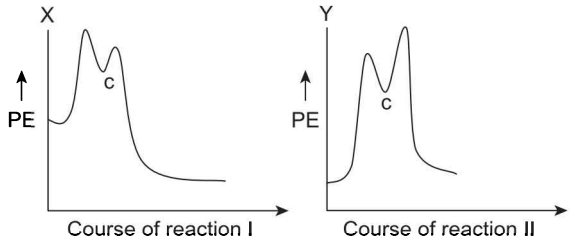
PRACTICE QUESTIONS

***Directions for questions from 16 to 25*: Application-Based Questions**

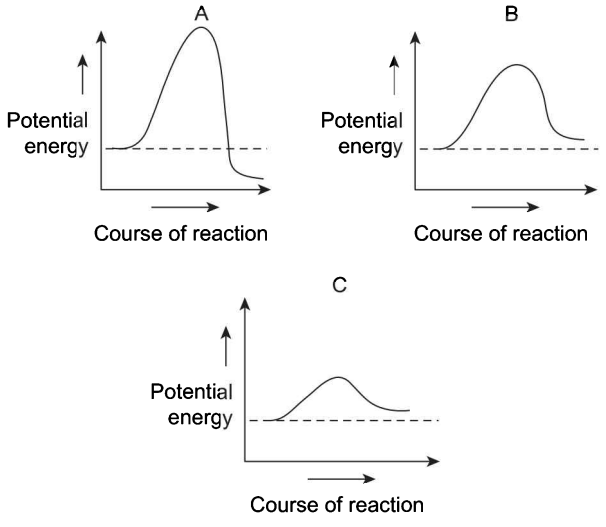
16. A chemist was studying the reaction of type $2A_{(g)} + 2B_{(g)} \rightarrow C_{(g)} + 2D_{(g)}$ experimentally. He found out that the order of the reaction is 2. Complete the following table based on the experimental results given by him.

[A]	[B]	Rates (mole l^{-1} s^{-1})
(i) 5×10^{-3} M	2.5×10^{-2} M	3.0×10^{-5}
(ii) 15×10^{-3} M	2.5×10^{-2} M	9.0×10^{-5}
(iii) 15×10^{-3} M	..... M	7.5×10^{-6}
(iv) 1.25×10^{-3} M	2.5×10^{-2} M	.....

17. Energy profile diagrams for two hypothetical reactions $2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$ and $X_{2(g)} + Y_{2(g)} \rightarrow 2XY_{(g)}$ are given below. Predict the slow and fast steps for the two reactions. Also identify the factors which favour the formation of reactants from products. Justify.



18. From the three energy profile diagrams A, B and C, find out which of the above irreversible reactions gives maximum yield within a given period of time? Justify. [Consider that the initial concentration of the reactants and temperature is same for all the reactions.]



19. Why is the oxidation of SO_2 to SO_3 not rapid in clean and dry air?

20. Change in temperature results in change in equilibrium position. However, the addition of a catalyst results in no change in the equilibrium position. Justify.

21. $Ag_2S + 4NaCN \rightleftarrows 2Na[Ag(CN)_2] + Na_2S$. Oxidation of sodium sulphide formed is the important step in the extraction of silver from its ore. Justify.

22. An absent-minded professor, Mr Waage, took elements A and B in a reaction vessel at room temperature, to study the reaction $A + 2B \rightleftharpoons 2C + D$. He took the concentration of B as 1.5 times the concentration of A. After the reaction reached equilibrium, he found that the concentrations of A and D were equal. However, he forgot to calculate K_c and removed one of the products from the mixture. Now, can you calculate K_c for the equilibrium attained in his experiment and help him out?

23. When 2.82 g of solid NH_4Cl is introduced into a 2 ℓ flask at 30°C. 40% of the solid NH_4Cl decomposes into two gaseous products, i.e., NH_3 and HCl. Calculate the Kc. What would happen if more amount of NH_4Cl is introduced into the flask?

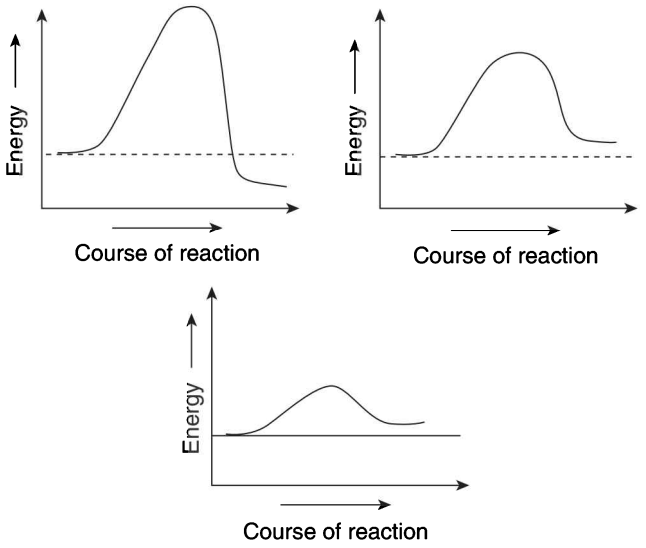
24. 0.5 moles of CO taken in a 2 ℓ flask is maintained at 750 K in the presence of a catalyst so that the following reaction can take place: $CO + 2H_2 \rightleftharpoons CH_3OH$. When hydrogen is introduced, the pressure of the system is increased to 23.629 atm from 15.129 atm at equilibrium and 0.08 moles of gaseous product, methanol is formed. Calculate K_c.

25. A mixture of 0.75 moles of N_2 and 1.20 moles of H_2 is placed in a 3 ℓ container. When the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$ reaches the equilibrium, the concentration of H_2 is 0.1M. Calculate the concentration of N_2 and NH_3 when the reaction is carried out with double the number of moles.

Level 3

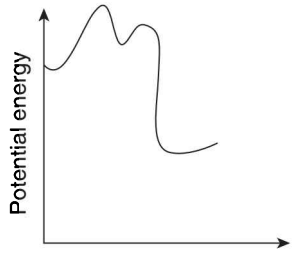
1. What is the use of a catalytic converter in automobile exhaust systems?

2. From the above three energy profile diagrams find out which of the above irreversible reactions gives maximum yield within a given period of time? Justify. [Consider that the initial concentration of the reactants and temperature is same for all the reactions.]



3. The decomposition reaction $N_2O \rightarrow N_2 + O_2$ takes place on platinum surface. Here, the rate of reaction is independent of the concentrations of the reactant. However, when this reaction is carried out in the absence of platinum surface, the rate of reaction depends on the concentration of the reactant. How do you account for this?

4. Energy profile diagram for a two-step reaction is given. On the basis of given diagram, predict the slow and fast steps in the reaction. Explain it on the basis of collision theory. Predict the factors which favour the formation of reactants from the products.

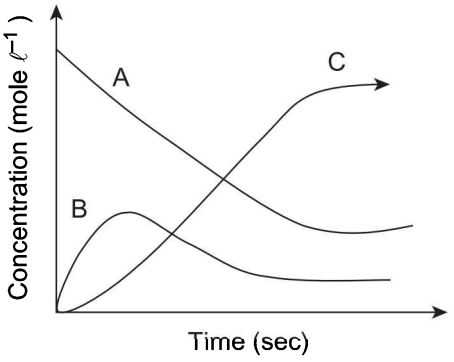


5. Explain the effect of addition of CO and O_2 and solid carbon to the equilibrium mixture separately. Also explain the effect of addition of all the three simultaneously. What happens to the equilibrium when the above changes are carried out in a container having less volume?

6. A 1 ℓ reaction vessel contained 1 mole each of solid NH_4HS, NH_3 and H_2S at a temperature of 150°C. When the decomposition of NH_4HS was carried out, equilibrium is established. Kp value at that temperature is 100. Calculate the equilibrium partial pressures of the gases in the mixture. Also calculate the pressure at which 60% dissociation of NH_4HS takes place at a lower temperature where Kp value is equal to 200 atm^2.

7. Under what conditions, addition of inert gas affects the equilibrium position in case of the following equilibria at constant temperature. Give a reason in support of your answer.
   (a) decomposition of NO to N_2 and O_2
   (b) decomposition of SO_3
   (c) formation of CH_3OH from CO and H_2

8. In a reaction, A is converted to C with the formation of an intermediate B. On the basis of the given graph compare the rate constants.



9. Nitric oxide can catalyse ozone formation in troposphere. Justify.

10. Carbon monoxide and water vapour react to give CO_2 and H_2 in a vessel of 2 l capacity at 1090 K. Equilibrium is established and the number of moles of various components is found to be 0.8, 0.6, 0.4 and 1.2, respectively. Calculate K_c value. If the concentration of CO has to be increased to 1.2 mole by increasing the concentration of CO_2 at the equilibrium, find the number of moles of CO_2 to be added to the reaction mixture at the same temperature.

CONCEPT APPLICATION

Level 1

True or false

1. True
2. True
3. False
4. True
5. True
6. True
7. False

Fill in the blanks

8. concentration, pressure
9. threshold
10. homogeneous
11. temperature
12. increase
13. 0.5625
14. 0.5 moles^2/l^2

Match the following

15. A : e
    B : c
    C : a
    D : b
    E : d

Multiple choice questions

16. a
17. a
18. a
19. c
20. d
21. c
22. b
23. c
24. b
25. a
26. c
27. d
28. 2
29. 3
30. 3

Solutions for questions from 31 to 45:

31. (i) raking equal masses of fine granules of zinc in two test tubes A and B
    (ii) addition of same concentration of HCl to the two test tubes
    (iii) heating the test tube B by 10°C
    (iv) measuring the volumes of H_2 gas liberated in the two test tubes
    (v) observation of volumes of H_2 liberated in test tubes B and A

32. (i) Draw the tangent on the curve at a particular instant of time "t."
    (ii) Change in y-axis, i.e., $y_2 - y_1$ gives change in concentration of "B," whereas change in x-axis, i.e., $x_2 - x_1$ gives change in time interval.
    (iii) find the slope of the tangent $\frac{y_2 - y_1}{x_2 - x_1}$
    (iv) slope of the tangent is equal to instantaneous rate

33. (i) finding out the experimental values of the concentrations of A at regular intervals
    (ii) plotting a graph of concentration of A at various times
    (iii) identification of C_2 and C_1 at different time intervals t_2 and t_1 by reading the graph
    (iv) calculation of $\frac{C_2 - C_1}{t_2 - t_1}$

34. (i) calculation of equilibrium number of moles
    (ii) calculation of equilibrium concentrations of reactants and products
    (iii) writing equilibrium expression for the reaction
    (iv) calculation of K_c value by using the equilibrium concentration

35. $NaOH + HCl \rightarrow NaCl + H_2O$ is a neutralization reaction between strong acid and strong base. Hence, it is an example of an instantaneous reaction.

36. The rate for the reaction between ionic compounds cannot be determined because they are generally instantaneous reactions.

37. Since the reaction is of 2nd order with respect to A, doubling the concentration of "A" increases the rate of reaction by $2^2 = 4$ times.

38. (1) The measurable properties like concentration, density, colour, pressure, etc., remain constant at constant temperature.
    (2) The forward and backward reactions take place with same rate.
    (3) It can be achieved from either direction.

39. The greater the K_c value, greater is the yield of products.

40. For a reaction A + B $\rightleftharpoons$ C + D, if the activation energy of backward reaction is more than that of forward reaction, then the forward reaction is exothermic.

41. According to Le Chatelier's principle, an increase in temperature causes a decrease in the value of K_c for an exothermic reaction.

42. In the reaction, $2NO + O_2 \rightleftharpoons 2NO_2$ + Heat
Formation of product is favoured by decreasing the temperature or volume.

43. The rate of the reaction depends on the concentration of the reactants, temperature and catalyst.

44. In the formation of NO and O_2 from NO_2, the rate of production of NO is twice the rate of production of O_2 because $2NO_2 \rightleftharpoons 2NO + O_2$.

45. Since the reaction is of 2^{nd} order with respect to A, and 1^{st} order with respect to B, the rate of reaction increases by eight times.

Level 2

1. (i) The rate of reaction in terms of reactants can be determined if the balanced equation is known.
(ii) balanced equation
(iii) rate of reaction in terms of NO, NO_2 and O_2
(iv) 3.4×10^{-4} moles/l s

2. (i) effect of temperature on average kinetic energy
(ii) comparison of average kinetic energy in both curves
(iii) comparison of effective collisions in both the curves

3. (i) effect of activation energy on rate
(ii) comparing activation energy of the reaction under different conditions
(iii) effect of change in reaction conditions on the activation energy of the reaction

4. (i) rate of reaction respective to each reactant and product
(ii) equating rates of reactions with each other on the basis of stoichiometric coefficients
(iii) 3.6×10^{-3} mole l^{-1} s^{-1}, 1.8×10^{-3} mole l^{-1} s^{-1}.

5. (i) type of reaction
(ii) compare the activation energies of forward and backward reactions
(iii) type of reaction
(iv) effect of temperature on the reaction

6. (i) relation between activation energy and effective collisions
(ii) calculation of E_a of backward reaction
(iii) comparing E_a of backward and forward reactions and its effect on effective collisions

7. difference between equilibrium position and equilibrium constant

8. (i) expression for equilibrium constant
(ii) calculation of the concentration of reactant and product at equilibrium
(iii) calculation of equilibrium constant
(iv) 0.53

9. (i) determination of total number of moles (reactants–products) at equilibrium
(ii) 3.08 g/l
(iii) calculation of the number of moles of the reactants and products present in the equilibrium mixture
(iv) calculation of weight of mixture
(v) calculation of volume of the mixture at STP
(vi) calculation of volume of equilibrium mixture at the given temperature and pressure
(vii) calculation of density

10. (i) expression for equilibrium constant
(ii) 1.5
(iii) balanced chemical reaction
(iv) calculation of equilibrium constant
(v) calculation of composition of equilibrium mixture with change in concentration of CO.

11. (i) significant of rate law
(ii) equation for rate constant
(iii) equation for rate constant with double the concentration of Cl_2
(iv) comparison of both the equations

12. (i) relation between rate law and order of a reaction
(ii) calculation of initial rate of reaction in experiment I on the change of concentration of BrO^{-3} in experiment II and the order of reaction with respect to BrO_3^-
(iii) calculation of concentration of BrO_3^- in experiment III based on the change of initial rate in experiment III, change of concentration of other reactants and the order of reaction with respect to Br^- and H^+
(iv) calculation of initial rate in experiment IV on the basis of change of concentration of all the reaction

13. (i) determination of rate law of a single-step reaction
(ii) rate law for the equation
(iii) relation between volume and concentration
(iv) effect on rate

14. (i) Le Chatelier's principle
(ii) formula of soap
(iii) equilibrium during formation of soap
(iv) ions present in common salt
(v) effect on equilibrium with the addition of salt

15. (i) rate-determining step of a reaction
(ii) determination of rate law on the basis of stoichiometry of the rate-determining step
(iii) determination of change in rate of reaction with the change of concentration of the reactions from rate law
(iv) determination of the unit of rate constant from rate law

Solutions for questions from 16 to 25: Application-Based Questions

16. Let us first find out order with respect A and B. We know $r = k\,[A]^x\,[B]^y$, x and y are orders with respect to A and B, respectively.

(i) $$\frac{r_1}{r_2} = \left[\frac{[A_1]}{[A_2]}\right]^x \Rightarrow \frac{3.0\times10^{-5}}{9.0\times10^{-5}}$$

$$= \left(\frac{(5\times10^{-3})}{(15\times10^{-3})}\right)^x$$

$$3 = (3)^x$$

$$x = 1$$

$\therefore$ Order with respect to A is 1

$\therefore$ Order with respect to B = 2 – 1 = 1

(ii) $r_1 = k\,[A]\,[B]$

$$3\times10^{-5} = k\cdot(5\times10^{-3})\times(2.5\times10^{-2})$$

$$k = \frac{3\times10^{-5}}{12.5\times10^{-5}} = 0.24\,\text{mole}^{-1}\ell\,\text{sec}^{-1}$$

(iii) $r = k\,[A_3]\cdot[B_3]$

$$7.5\times10^{-6} = 0.24\times15\times10^{-3}\times[B_3]$$

$$[B_3] = \frac{7.5\times10^{-6}}{0.24\times15\times10^{-3}}$$

$$= 2.08\times10^{-3}\,\text{mole}\,\ell^{-1}\,\text{sec}$$

(iv) From ii and iv, $\frac{[A_2]}{[A_4]} = \frac{r_2}{r_4}$

$$\Rightarrow \frac{15\times10^{-3}}{1.25\times10^{-3}} = \frac{9.0\times10^{-5}}{r_4}$$

$$\Rightarrow r_4 = 7.5\times10^{-6}\,\text{mole}\ell^{-1}\,\text{sec}^{-1}$$

[A]	[B] (mole ℓ^{-1} s^{-1})	Rate
(i) 5×10^{-3} M	2.5×10^{-2} M	3.0×10^{-5}
(ii) 15×10^{-3} M	2.5×10^{-2} M	9.0×10^{-5}
(iii) 15×10^{-3} M	2.08×10^{-3}M	7.5×10^{-6}
(iv) 1.25×10^{-3} M	2.5×10^{-2} M	7.5×10^{-6}

17. Reaction I is exothermic reaction. The first step from A to C (intermediate) is associated with higher activation energy and hence is slow. Therefore, it is the rate-determining step. Formation of reactants from products is a backward reaction which is endothermic and is associated with increase in volume. Therefore, high temperature and low pressure are the favourable conditions.

Reaction II is an endothermic reaction. The backward reaction being exothermic is favoured by low temperature. Since the reaction takes place with no change in volume, there is no effect of pressure on the equilibrium.

18. From the graphs of A, B and C, we can compare the activation energy and the energy of respective products. The product formed in graph A has the least energy and is most stable while the activation energy of the reaction in graph C is the least. The yield of the product is more for that reaction

which involves least activation energy as most of the reacting molecules undergo effective collisions and hence form a product. Thus it can be concluded that the yield of product in graph C is maximum.

19. The conversion or oxidation of SO_2 to SO_3 takes place in the presence of a catalyst. Water droplets associated with dust particles act as the catalyst for this reaction. The dust particles can adsorb the SO_2 on their surface where it can be oxidized to SO_3. Hence oxidation of SO_2 to SO_3 is not rapid in clean and dry air.

20. When the temperature is changed, the rate of forward reaction and backward reaction varies differently. If the forward reaction is exothermic, increase in temperature decreases the rate of forward reaction thereby decreasing the concentration of products. If the forward reaction is endothermic, an increase in temperature favours forward reaction and increases the concentration of products Therefore, the composition of reaction mixture at equilibrium changes. When a catalyst is added, the rate of forward reaction increases due to decrease in activation energy of the forward reaction. Since the reaction takes an alternative path, the activation energy of backward reaction also is reduced. Activated complex is formed at a lower energy state in a catalysed reaction. As both the rate of forward reaction and that of the backward reaction change to the same extent, the composition of equilibrium mixture remains constant. Therefore, the equilibrium position remains same for both catalysed and uncatalysed reactions.

21. In the extraction of silver from its ore, one of the important steps is the formation of sodium argentocyanide and sodium sulphide which is a reversible reaction. To prevent the reversibility of the reaction sodium sulphide should be subjected to oxidation. Because according to Le Chatelier's principle, with the removal of one of the products, the reaction shifts in the forward direction.

22. $A + 2B \rightleftarrows 2C + D$

Initial concentration a 1.5a 0 0

Equilibrium concentration $a - x$ $1.5a - 2x$ $2x$ x

At equilibrium, the concentration of A and that of D are equal

$\therefore a - x = x \Rightarrow a = 2x$ or $x = a/2$

$$K_c = \frac{(2x)^2 x}{(a-x)(15a-2x)^2} \text{ as } a = 2x,$$

$$\Rightarrow \frac{4x^2 \cdot x}{x \times (x)^2} \Rightarrow K_c = 4.$$

23. $NH_4Cl_{(s)} \rightleftarrows NH_{3(g)} + HCl_{(g)}$

2.82 g of NH4Cl is subjected to decomposition.

Molecular weight of NH_4Cl = 14 + 4 + 35.5 = 53.5

$$\Rightarrow \text{No. of moles of } NH_4Cl = \frac{2.82}{53.5} = 0.0527$$

Given that % dissociation of NH_4Cl is 40% 0.0527 moles decomposition corresponds to 100%

? moles decomposition corresponds to 40%

$$= \frac{40 \times 0.0527}{100} = 0.0210$$

$NH_4Cl \rightleftarrows NH_3 + HCl$

Initial number of moles	0.0527	0	0
Number of moles	0.0527		– 0.0210
	0.0210		0.0210

at equilibrium = 0.0317

$$\therefore K_c = [NH_3][HCl] = \frac{0.0210}{2} \times \frac{0.0210}{2}$$

$$= \frac{0.0210 \times 0.0210}{4} = 1.1 \times 10^{-4} \text{ moles}^2 / \text{litre}^2$$

Addition of a solid or liquid reactant at equilibrium does not affect the equilibrium. So addition of solid NH_4Cl does not affect the equilibrium.

24. $CO + 2H_2 \rightleftarrows CH_3OH$

Initial moles 0.5 a 0

At equilibrium $0.5 - x$ $a - 2x$ x

Given that x = 0.08

Moles of CO = 0.5 – 0.08 = 0.42

Moles of H_2 = a – 0.16

Moles of CH_3OH = 0.08

No. of moles of H_2 can be calculated by using PV = nRT

Pressure of hydrogen = 23.629 – 15.129 = 8.5 atm

$$n = \frac{PV}{RT} = \frac{8.5 \times 2}{0.082 \times 750} = 0.276\,(a)$$

$\therefore$ Number of moles of H_2 at equilibrium = 0.276 − 0.16 = 0.116

$$K_c = \frac{0.08/2}{\left(\frac{0.116}{2}\right)^2 \times \frac{0.42}{2}} = 56.66\,\ell^2\,mol^{-2}$$

25. $N_2 + 3H_2 \rightleftarrows 2NH_3$

Concentration of N_2 = 0.75/3 = 0.25 moles l^{-1}

Concentration of H_2 = 1.20/3 = 0.4 moles l^{-1}

$N_2 + 3H_2 \rightleftarrows 2NH_3$

Initial concentration	0.25	0.4	0
At equilibrium	0.25 − x	0.4 − 3x	2x

Concentration of H_2 at equilibrium is given as = 0.1

$\therefore$ 0.4 − 3x = 0.1 $\Rightarrow$ x = 0.1

Concentration of N_2 at equilibrium = 0.25 − 0.1 = 0.15

Concentration of NH_3 at equilibrium = 0.1 × 2 = 0.2

When the reaction is carried with double the number of moles, concentration of N_2 = 0.15 × 2 = 0.3 moles l^{-1} and concentration of NH_3 = 0.2 × 2 = 0.4 moles l^{-1}.

Level 3

1. (i) gases produced during combustion of fuels.
(ii) nature of gases that are liberated through an exhaust system
(iii) role of catalytic converter for changing the molecular composition of the exhaust gases
(iv) change in nature of the gases due to the change in the molecular composition

2. (i) role of activation energy in the formation of product
(ii) comparison of activation energy of the three reactions
(iii) relation between activation energy and yield

3. (i) role of platinum in the reaction
(ii) property of platinum
(iii) site of decomposition
(iv) comparison of mechanism of reaction in the presence and absence of a catalyst

4. (i) prediction of slow and fast steps on the basis of activation energies of the two steps
(ii) prediction of slow and fast steps on the basis of activation energies of the two steps
(iii) prediction of nature of reaction with respect to energy changes
(iv) prediction of energy changes in the net reaction
(v) nature of backward reaction

5. (i) effect of addition of product or reactant at constant volume at equilibrium
(ii) effect of addition of product or reactant at constant volume at equilibrium
(iii) effect of addition of solid reactant
(iv) Relation between volume and pressure of the system. Effect of addition of components on equilibrium at lesser volume.

Solutions for questions from 6 to 10: Application-Based Questions

6. $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$

1 − x 1 + x 1 + x

$$K_p = p_{NH_3} \times p_{H_2S}$$

Total no. of moles at equilibrium = (1 + x) + (1 + x) = 2x + 2

Partial pressure = Mole fraction × P

$$\text{Mole fraction of } NH_3 = \frac{1+x}{2x+2}$$

$$\therefore \text{ Partial pressure of } NH_3 = \frac{1+x}{2x+2} \times P$$

$$\text{Mole fraction of } H_2S = \frac{1+x}{2x+2}$$

$$\therefore \text{ Partial pressure of } H_2S = \frac{1+x}{2x+2} \times P$$

$$K_p = \left(\frac{1+x}{2x+2} \times P\right)\left(\frac{1+x}{2x+2} \times P\right)$$

$$K_p = \frac{(1+x)^2}{(2x+2)^2} = 100$$

$$\frac{(1+x)^2 P^2}{4(x+1)^2} = 100$$

$$\frac{(1+x)^2 P^2}{4(1+x)^2} = 100 \Rightarrow P^2 = 100 \times 4$$

$$P = \sqrt{400} = 20\,\text{atm}$$

$$p_{H_2S} = \frac{(1+x)20}{2(x+1)} = 10\,\text{atm}$$

$$p_{NH_3} = 10\,\text{atm}$$

60% dissociation of NH_3 and H_2S corresponds to moles each of NH_3 and H_2S.

$$K_p = p_{NH_3} \times p_{H_2S}$$

$$p_{NH_3} = \frac{1.6}{3.2} \times P, p_{H_2S} = \frac{1.6}{3.2} \times P$$

$$K_p = \frac{(1.6)^2 \times P^2}{(3.2)^2} = 200$$

$$P^2 = \frac{200 \times (3.2)^2}{(1.6)^2} = 400$$

$$P = \sqrt{400} = 20\,\text{atm}$$

7. (a) $2NO \rightleftharpoons N_2 + O_2$

The above equilibrium is associated with no change in volume. Therefore addition of inert gas has no effect on the equilibrium under any conditions.

(b) $2SO_3 \rightleftharpoons 2SO_2 + O_2$

The above equilibrium is associated with increase in volume. Addition of an inert gas has no effect at constant volume. At constant pressure, addition of inert gas favours the forward reaction since increase in volume takes place.

(c) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

The above equilibrium is associated with decrease in volume. Addition of the inert gas has no effect at constant volume. At constant pressure, addition of the inert gas favours backward reaction since increase in volume takes place.

8. From the given graph we can know that

$$A \xrightarrow{K_1} B \text{ (int ermediate)}$$

$$B \xrightarrow{K_2} C$$

That is, A is converted to C with an intermediate B.

The concentration of B first increases with time and then starts decreasing showing that after time t it acts as a reactant. The concentration of C on the other hand increases continuously with time.

So, the rate constant $k_1 \neq k_2$.

The first step is the slow step or the rate-determining step while the second step is the fast step.

Hence, $k_1 < k_2$.

9. Nitric oxide (NO) in the troposphere reacts with the oxygen forming nitrogen dioxide:

$2NO + O_2 \rightarrow 2NO_2$

Nitrogen dioxide, in the presence of light, decomposes to NO and nascent oxygen:

$$NO_2 \xrightarrow{\text{light}} NO + [O]$$

The nascent oxygen produced is highly reactive and oxidizes oxygen to ozone:

$$O_2 + [O] \rightarrow O_3$$

10. $CO + H_2O \rightleftharpoons CO_2 + H_2$

0.8 0.6 0.4 1.2

$$K_c = \frac{0.4 \times 1.2}{0.8 \times 0.6} = 1$$

but "a" moles of CO_2 is added at equilibrium. The new number of moles of CO is 1.2 showing an increase by 0.4 moles.

After the addition of "a" moles of CO_2, balanced reaction takes place:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

$(0.8+0.4)$ $(0.6+0.4)$ $(0.4+a-0.4)$ $(1.2-0.4)$

1.2 1.0 a 0.8

$$K_c = \frac{(0.6+0.4)(0.8+0.4)}{(0.4+a-0.4)(1.2-0.4)} = \frac{1 \times 1.2}{a \times 0.8} = 1$$

$$\Rightarrow a = \frac{1.2}{0.8} = 1.5$$

HINTS AND EXPLANATION

Chapter

3

Atomic Structure

Remember

Before beginning this chapter, you should be able to:

understand the concept of atom as an indivisible particle

- understand the concept of atom as an indivisible particle
- know the concept of divisibility of atom and the characteristics of subatomic particles
- primary idea on the modern atomic model

Key Ideas

After completing this chapter, you should be able to:

- observe gradual change in the perception of structure of atom based on experimental observations
- Understand the concept of spectra, quantization of energy, elliptical orbits and correlate it with stationary orbits.
- know the correlation between wave and particle nature of an electron
- identify the difference between orbit and orbital based on Heisenberg's uncertainty principle
- spot the location of electrons around the nucleus
- study the detailed concept of modern atomic model

INTRODUCTION

The atom has been found to be the smallest particle of matter which can take part in a chemical reaction. An atom is composed of three types of fundamental particles namely electrons, protons and neutrons. Many attempts have been made to propose various atomic models which depict the arrangement of these fundamental particles in an atom.

J.J. Thomson, after his discovery of the electron, proposed his atomic model according to which an atom is a spherical mass of positive charge in which electrons are embedded.

Thomson's model of atom has been disproved by Rutherford's α-ray scattering experiment. This experiment resulted in the discovery of nucleus which was a major breakthrough in the history of the structure of the atom. Rutherford's planetary model of atom has been contradicted by the laws of electrodynamics.

Neils Bohr in 1913 proposed his atomic model with the most crucial concept of stationary orbits for electrons. This concept of stationary orbits proposed by Bohr could successfully explain the stability of an atom which was the major drawback in Rutherford's atomic model.

The concept of atomic orbital developed in the later period contradicted Bohr's concept of stationary orbits. The concept of atomic orbitals originated from the wave nature of electron led to the development of quantum mechanical model of atom which gave rise to the modern atomic structure.

Bohr's Model of an Atom

Bohr proposed his atomic model based on the quantum theory of radiation. According to Bohr's model,

(i) Electrons move around the nucleus in specified circular paths called orbits or shells or energy levels.

(ii) Each orbit or shell is associated with a definite amount of energy. Hence these are also called energy levels and are designated as K, L, M and N shells.

(iii) The energy associated with a certain energy level increases with the increase of its distance from the nucleus. Hence if the energy associated with the K, L, M and N shells are E_1, E_2, E_3 and E_4, respectively, then $E_1 < E_2 < E_3$ ..... etc.

(iv) As long as the electron revolves in a particular orbit, the electron does not lose its energy. Therefore, these orbits are called stationary orbits and the electrons are said to be in stationary energy states.

(v) An electron jumps from a lower energy level to a higher energy level by absorbing energy. It jumps from a higher energy level to a lower energy level by emitting energy in the form of electromagnetic radiation.

The energy emitted or absorbed (ΔE) is given by Planck's equation, i.e., $\Delta E = h\nu$.

For example, if E_1 and E_2 are the energies of first and second orbits, respectively, then the difference in energy is equal to $h\nu$:

$$E_2 - E_1 = h\nu$$

(vi) The electron can revolve only in an orbit in which the angular momentum of the electron (mvr) is a whole-number multiple of $h/2\pi$. This is known as the principle of quantization of angular momentum.

Hence we can write angular momentum of the electron as

$$mvr = \frac{nh}{2\pi},$$

where n is an integer (n = 1, 2, 3, 4, ...) and is called principal quantum number.

where m = mass of the electron,

v = velocity of an electron in its orbit and
r = distance of the electron from the nucleus.

By applying the concept of quantization of energy, Bohr calculated the radii and the energy of the nth orbit of hydrogen atom (Z = 1).

$$r_n = \frac{n^2h^2}{4\pi^2me^2 \cdot Z}, \quad E_n = \frac{-2\pi^2me^4}{n^2h^2} \cdot Z^2$$

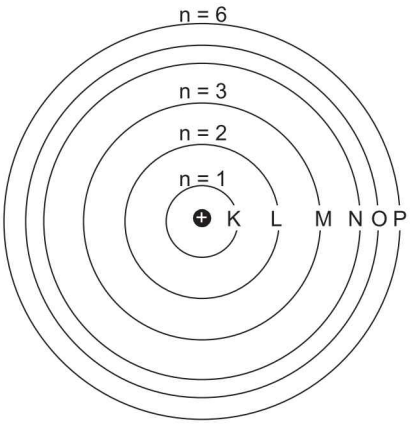


Figure 3.1 Stationary orbits of an atom

where h = Planck's constant,
m = mass of the electron and
e = charge of the electron.

With the help of these expressions, Bohr gave a satisfactory explanation for the spectra of hydrogen and hydrogen-like species (ions having one electron, for example, He^+, Li^{+2}, Be^{+3}), etc.

Limitations of Bohr's Atomic Model

(i) Bohr could not explain the spectra of the multielectronic species satisfactorily.

(ii) Bohr's model couldn't give a satisfactory justification for the assumption that electrons can revolve in those orbits where their angular momentum (mvr) is a whole-number multiple of $h/2\pi$, i.e., he could not justify the quantization of angular momentum of the electron.

(iii) According to Heisenberg's uncertainty principle, it is impossible to determine simultaneously and accurately the exact position and the momentum of the moving particle. Bohr assumed that an electron of an atom is located at a definite distance from the nucleus and revolves around the nucleus with a definite velocity which is against Heisenberg's uncertainty principle.

(iv) The atomic spectral lines are found to split into a number of closely packed lines in the presence of a magnetic field and an electric field. These effects are called Zeeman effect and Stark effect, respectively. Bohr failed to explain these effects. Each spectral line in the atomic spectrum of hydrogen consists of still finer lines when it is observed by using the instrument with high resolving power. Bohr's model failed to explain this observation.

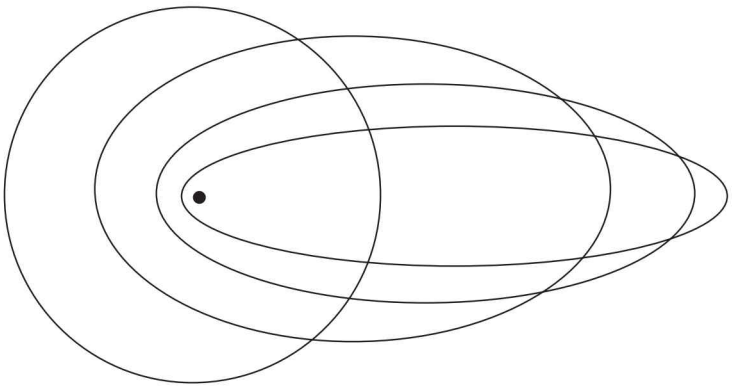


Figure 3.2 Sommerfeld's elliptical electron orbits. Sub energy levels for n = 4

Sommerfeld's Extension of Bohr's Theory

In 1915, Arnold Sommerfeld extended Bohr's atomic theory to explain the fine structure of spectral lines in the atomic spectra of hydrogen. He proposed that the electrons move in an elliptical orbit in addition to the circular orbit around the nucleus with the nucleus at one of the foci.

He suggested that the subenergy levels or subshells associated with each main energy level (expect the first main energy level) are responsible for the fine structure of the spectrum of hydrogen. These subenergy levels or subshells exist due to the difference in energies of electrons revolving in different elliptical orbits belonging to the same main energy level.

He also proposed that the energy associated with the subshells is quantized and therefore introduced a new quantum number called azimuthal quantum number to describe the angular momentum of the electrons revolving in different elliptical orbits.

To justify the assumption of the quantization of energy of the electron in the hydrogen atom, a French graduate student, Louis de Broglie, suggested in 1924 that the electrons have wave properties as well as particle properties.

EXAMPLE

What do you mean by emission and absorption spectra?

SOLUTION

When the energy emitted by an atom due to the deexcitation of electrons is observed through a spectroscope, it appears as a spectrum consisting of bright lines on a dark background, this is emission spectrum. The spectrum formed due to the absorption of energy during the excitation of electrons consists of dark lines on a bright background. This is called absorption spectrum.

EXAMPLE

What do you mean by stationary orbit?

SOLUTION

According to Bohr's atomic model an electron does not lose its energy as long as it revolves in a particular orbit. These orbits are called stationary orbits.

EXAMPLE

How did Sommerfeld explain the fine structure of hydrogen spectrum?

SOLUTION

Sommerfeld suggested that the sub energy levels or sub shells associated with each main energy level are responsible for the fine structure of hydrogen spectrum. These sub energy levels or subshells exist due to the difference in energies of electrons revolving in different elliptical orbits belonging to the same main energy level.

EXAMPLE

Sunny and Bunny have taken spectra for the following transitions. Spectra taken by sunny consisted of bright lines on a dark background. Spectra taken by Bunny consisted of dark lines on a bright

background. Identify the electronic transitions corresponding to the spectra taken by Sunny and Bunny. What are those spectra called?

(a) n = 5 to n = 2 **(b)** n = 4 to n = 6 **(c)** n = 5 to n = 7

(d) n = 3 to n = 1 **(e)** n = 1 to n = 2 **(f)** n = 5 to n = 3

SOLUTION

When an electron in an atom gains energy, it gets excited to a higher energy state from the ground state. The electron being unstable in the excited state loses energy and comes back to the ground state either directly or in steps. During this process the bright lines corresponding to the transitions are formed on the dark background. This is called emission spectrum. When the electrons get excited to higher energy levels they absorb energy and dark lines corresponding to the transitions are formed on the bright background. This is called absorption spectrum.

(a) n = 5 to n = 2 → emission spectrum **(b)** n = 4 to n = 6 → absorption spectrum

(c) n = 5 to n = 7 → absorption spectrum **(d)** n = 3 to n = 1 → emission spectrum

(e) n = 1 to n = 2 → absorption spectrum **(f)** n = 5 to n = 3 → emission spectrum

EXAMPLE

Why did Sommerfeld extend Bohr's theory?

SOLUTION

Sommerfeld extended Bohr's theory to explain the fine structure of spectral lines in the atomic spectrum of hydrogen.

EXAMPLE

"Velocity of an electron decreases as we go farther from the nucleus". Justify.

SOLUTION

According to Bohr, angular momentum is quantised.

$$mvr = \frac{nh}{2\pi} \Rightarrow v = \frac{nh}{2\pi mr}$$

From the above expression, it is obvious that velocity decreases, as we go away from the nucleus. It is due to the decrease in nuclear forces of attraction.

As the nuclear forces of attraction decreases, less velocity is required for the electron to counter balance the nuclear force of attraction.

Dual Nature of Electron—de Broglie's Theory

de Broglie derived an expression for calculating wave length (λ) of the wave which is associated with the moving electrons.

The expression is $\lambda = \dfrac{h}{\text{momentum of electron}}$

or $\lambda = \dfrac{h}{mv}$

where m = mass of electron,
v = velocity of electron and
h = Planck's constant.

This equation is called *de Broglie's equation*, and this hypothesis was experimentally confirmed by Davison and Germer who proved wave-like properties of electron in 1927. Hence the dual nature of electron, i.e., particle nature as well as wave nature was established experimentally.

Louis de Broglie pointed out that the wave behaviour of an electron is similar to that of a standing wave. The circumference of each Bohr's orbit must be equal to an integral multiple of the wave length of the wave associated with the moving electron. Orbits whose circumferences are not equal to the integral multiple of the wave length are impossible for an electron in Bohr's atom model.

In 1927, the picture of electrons moving in fixed orbits was abandoned when the German physicist, Werner Heisenberg pointed out that both the position and the momentum of subatomic particles cannot be accurately determined simultaneously.

During this period on the basis of the wave properties of electrons, Austrian physicist Erwing Schrodinger derived an equation called Schrodinger wave equation to describe the behaviour and energies of electrons in an atom.

Based on this wave equation, the three-dimensional region in space around the nucleus, where the probability of finding an electron with a particular energy is determined to be maximum is called the atomic orbital.

On the basis of Schrodinger's wave equation, a quantum mechanical model of atom has been proposed. In this model, the state of an electron in an atom can be explained with respect to four quantum numbers. Among these, three quantum numbers namely the principal quantum number, azimuthal quantum number and magnetic quantum number have been derived from Schrodinger's wave equation.

Principal Quantum Number

The principal quantum number determines the energy of the orbital and its size. Its value can be any positive integer. The larger is the principal quantum number, the higher is the energy of the electron and the greater is the average distance of the electron from the nucleus. The principal quantum number is denoted by n where n = 1, 2, 3….

Azimuthal Quantum Number

The azimuthal quantum number determines the shape of the orbitals. Except the first shell, all other shells are associated with subshells.

It is denoted by 'ℓ' where the value 'ℓ' can be any positive integer from 0 to (n – 1) [n is the principal quantum number]. For example, the shell for which n = 4, it has four subshells.

The azimuthal quantum number of these four subshells includes 0, 1, 2 and 3 and they are denoted by letters s, p, d and f, respectively.

"n" values	"ℓ" values	Representations of subshell
1	0	1s
2	0, 1	2s, 2p
3	0, 1, 2	3s, 3p, 3d
4	0, 1, 2, 3	4s, 4p, 4d, 4f

Magnetic Quantum Number

The explanation for the splitting of a single spectral line of hydrogen atom into a number of closely spaced lines in the presence of a magnetic field or an electric field was given by Lande. He postulated

that in the presence of an external electric field or a magnetic field, an electron can have different spatial orientations for a particular angular momentum. The magnetic quantum number was introduced to specify the further subdivisions of subshells or energy sublevels. It describes the spatial orientation of the orbital. The magnetic quantum number is denoted by "m" and has integral values from $-\ell$ to $+\ell$. For example, +1, +2, etc.

"n" values	"ℓ" values	"m" values	Representations of the orbital
1	0	0	1s
2	0	0	2s
	1	−1, 0, +1	$2p_x$ $2p_y$ $2p_z$
3	0	0	3s
	1	−1, 0, +1	$3p_x$ $3p_y$ $3p_z$
	2	−2, −1, 0, +1, +2	$3d_{xy}$ $3d_{yz}$ $3d_{zx}$ $3d_{X^2-Y^2}$ $3D_{Z^2}$

Spin Quantum Number

It was observed with the help of an instrument with high resolving power that the spectral lines of some atoms consist of a pair of very closely spaced lines. To account for this fact, Austrian physicist Wolfgang Pauli suggested that these two closely spaced lines are the representation of the two different states of electrons. These states were later identified as the spin of the electron.

In 1925, Uhlenbeck and Goud Smit suggested that the electron rotates around its own axis either in a clockwise or in an anticlockwise direction.

The angular momentum of the electron is not only due to its movement in the orbital but it also depends on its spinning around its own axis. Angular momentum under this condition is called spin angular momentum which is also quantized and can have two values $+\frac{1}{2}$ and $-\frac{1}{2}.\left(+\frac{1}{2}\right)$ corresponds to the anticlockwise spinning and $\left(-\frac{1}{2}\right)$ corresponds to the anticlockwise spinning of the electron.

Pauli's Exclusion Principle

Pauli's exclusion principle states that "it is impossible for two electrons in a given atom to have all the quantum numbers identical."

Relation among quantum numbers following Pauli's exclusion principle is shown hereunder.

Value of principal quantum number	Value of azimuthal quantum number	Value of magnetic quantum number	Value of spin quantum number	Total number electrons in main shells
n = 1	$\ell = 0$	m = 0	+1/2, −1/2	2
(K shell)	s subshell			
n = 2	$\ell = 0$	m = 0	+1/2, −1/2	2
(L shell)	s subshell			
	$\ell = 1$ p subshell	m = −1 m = 0 m = +1	+1/2, −1/2 +1/2, −1/2 +1/2, −1/2	2 2 } 6 2 2 + 6 = 8

n = 3	$\ell = 0$	m = 0	+1/2, –1/2	2
(M shell)	s subshell			
	$\ell = 1$ p subshell	m = –1 m = 0 m = +1	+1/2, –1/2 +1/2, –1/2 +1/2, –1/2	2 2 2 } 6
	$\ell = 2$ d subshell	m = –1 m = 0 m = –2 m = +1 m = +2	+1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2	2 2 2 2 2 } 10 2 + 6 + 10 = 18
n = 4	$\ell = 0$	m = 0	+1/2, –1/2	2
(N shell)	s subshell			
	$\ell = 1$ p subshell	m = –1 m = 0 m = +1 m = –2 m = –1	+1/2, –1/2 +1/2, –1/2 +1/2, –1/2	2 2 2 } 6
	$\ell = 2$ d subshell	m = 0 m = +1 m = +2	+1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2	2 2 2 2 2 } 10
	$\ell = 3$ f subshell	m = –3 m = –2 m = –1 m = 0 m = +1 m = +2 m = +3	+1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2 +1/2, –1/2	2 2 2 2 2 2 2 } 14 2 + 6 + 10 + 14 = 32

Representation of an Orbital

Since atomic orbital is a three-dimensional space which represents the maximum probability of finding an electron, it is difficult to give a pictorial representation of the orbital.

An atomic orbital can be generally represented by a shaded figure where the intensity of shading indicates the probability of finding an electron in that area.

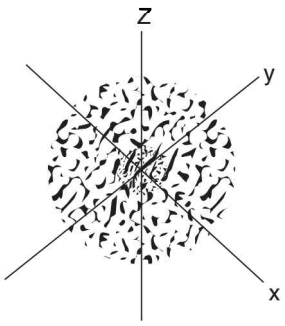


Figure 3.3 s-orbital

Shapes of the Orbitals

When a boundary is drawn enveloping the region with maximum intensity of shading, the resultant orbital diagram is called the boundary surface diagram. The atomic orbitals can be conveniently represented by these boundary surface diagrams.

s-orbitals: These orbitals have only one orientation and they are spherical. The spherical regions where the probability of finding an electron is zero are called nodal region. For an s-orbital of nth main energy level, the number of nodal regions is given by (n – 1), where n indicates the main energy level.

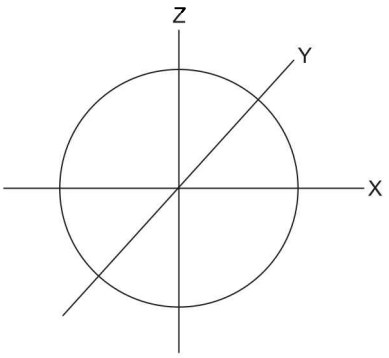


Figure 3.4 The boundary surface diagram of 1s orbital

p-orbitals: They have two lobes and there are three orientations for p-orbitals represented as p_x, p_y and p_z. The subscripts x, y and z refer to the coordinate axes along which the density of the electrons of the respective orbitals is maximum. The p-orbitals are dumb-bell shaped. The surface in which the probability of finding an electron is zero is called *nodal plane*. For example, for the p_x orbital, "yz" is the nodal plane. Each "p" orbital has one nodal plane, irrespective of the main energy level.

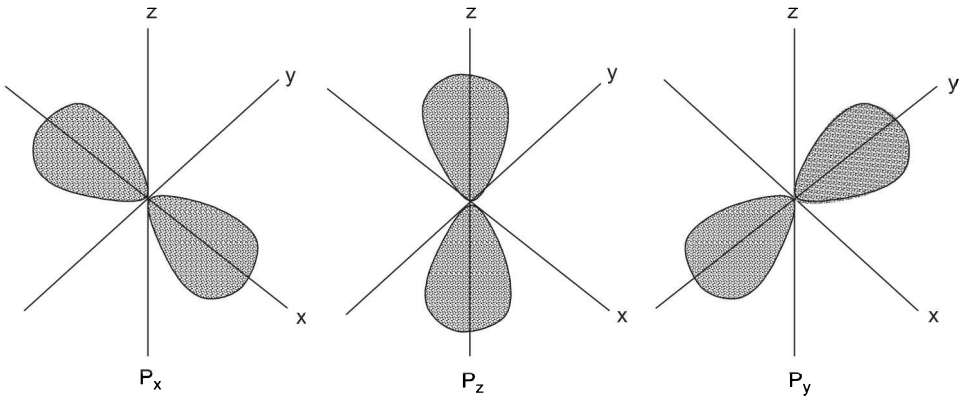


Figure 3.5 The boundary surface diagrams of the p-orbitals

d-orbitals: There are 5 d-orbitals represented as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, d_{z^2}. The orbitals d_{xy}, d_{yz} and d_{zx} have four lobes and these lobes lie symmetrically between the coordinate axes, for example, the lobes of d_{xy} lie symmetrically in between *x*- and *y*-axes.

The orbital $d_{x^2-y^2}$ also has four lobes along *x*- and *y*- axes. The orbital d_{z^2} has a unique shape with two lobes along *z*-axis and a "belt-" like space centred in the x–y plane. Each d-orbital has two nodal planes.

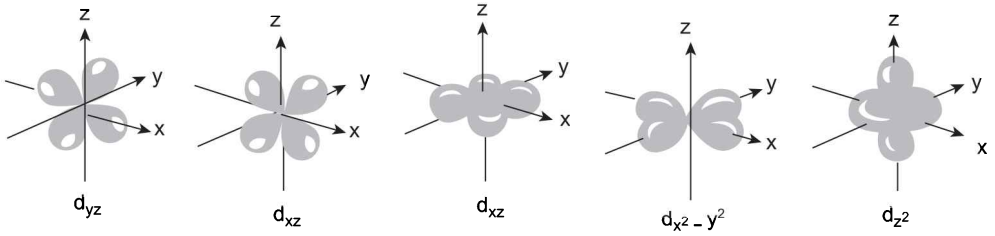


Figure 3.6 The boundary surface diagrams of five d-orbitals.

Electronic Configuration of Atoms

The distribution of electrons in the different orbitals belonging to different main energy level of an atom is known as the electronic configuration of the atom of the given element. Some rules have been laid for writing the electronic configuration of elements.

The study of the atomic spectra provided the information about the relative energies of the atomic orbitals. The increasing order of the energy of different orbitals belonging to different main energy levels was given by Aufbau principle.

"Aufbau" is a German expression which means building up or construction. According to **Aufbau principle**, "the orbitals are filled up with electrons in the order of their increasing energy." The order of filling up of various orbitals can be represented in the form of Moeller diagram.

According to Pauli's exclusion principle, two electrons in an atom can have a maximum of three quantum numbers that are same but the fourth one must be different.

According to **Hund's rule of maximum multiplicity**, pairing of electrons in a subshell starts when all the degenerate orbitals are filled with unpaired electrons with parallel spin. Hence pairing of electrons in p, d and f subshells start with the introduction of 4th, 6th and 8th electrons, respectively.

Rules for filling up of electrons in the orbitals.

(i) The maximum number of electrons in a main energy level is equal to $2n^2$, where n is the number of the main energy level.

(ii) The maximum number of electrons in a subshell or orbital like s, p, d and f is equal to $2(2\ell + 1)$, where the value of ℓ is 0, 1, 2 and 3, respectively for s, p, d and f orbitals. Hence the maximum number of electrons in s, p, d and f orbitals is 2, 6, 10 and 14, respectively.

(iii) As a working rule, a new electron enters that orbital where $(n + \ell)$ is minimum, for example, the $(n + \ell)$ value of 4s orbital is $4 + 0 = 4$ and that for the 3d orbital is $3 + 2 = 5$. Hence the electron enters 4s orbital before entering into 3d. In case $(n + \ell)$ value is equal for two orbitals, then the electron enters that orbital whose n value is less. For example $(n + \ell)$ value of $3d = 3 + 2 = 5$ and $4p = 4 + 1 = 5$, in this case, the electron prefers to enter the 3d orbital.

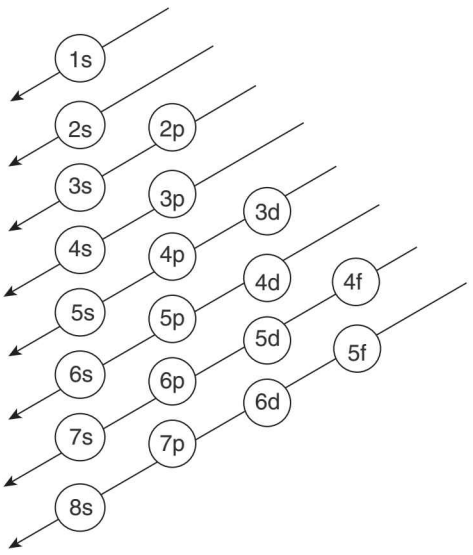


Figure 3.7 Moeller diagram

(iv) Each orbital (s, p_x, p_y, p_z, d_{xy}, d_{yz}, etc.,) can accommodate a maximum of two electrons with opposite spin as given by Pauli's exclusion principle.

The electronic configuration of an atom is written in terms of nl^x notation where n indicates the main energy level, l indicates the subshells or orbitals (s, p, d and f) and x indicates the total number of electrons present in the subshell.

(v) Electrons enter the orbitals p_x, p_y, p_z, d_{xy}, d_{yz}, etc., in such a way that maximum number of unpaired electrons remain in the subshell and the unpaired electrons spin in the same direction.

Hence in the subshells p, d and f, the electrons prefer to occupy separate orbitals rather than

getting paired in an orbital.

As a result of this, pairing takes place only with the entry of 2nd electron in the s-orbital, 4th electron in the p-orbital, 6th electron in the d-orbital and 8th in the f-orbital. These orbitals are identical in energy in the absence of any electric or magnetic field and are called as degenerate orbitals.

(vi) Half-filled or completely filled subshells impart greater stability to the atoms.

Hence, actual electronic configurations of some transition elements are different from the expected electronic configuration.

Example: Expected electronic configurations of chromium and copper are $3d^4 4s^2$ and $3d^9 4s^2$, respectively.

But their actual electronic configurations are chromium, $3d^5 4s^1$ and copper, $3d^{10} 4s^1$. Most of the exceptions to the electron configuration predicted from the Aufbau principle occur among elements with atomic number Z > 20.

Electronic Configuration of Elements up to Z = 54

Element	At. No.	K n = 1	L n = 2		M n = 3			N n = 4				O n = 5			
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f
H	1	1													
He	2	2													
Li	3	2	1												
Be	4	2	2												
B	5	2	2	1											
C	6	2	2	2											
N	7	2	2	3											
O	8	2	2	4											
F	9	2	2	5											
Ne	10	2	2	6											
Na	11	2	2	6	1										
Mg	12	2	2	6	2										
Al	13	2	2	6	2	1									
Si	14	2	2	6	2	2									
P	15	2	2	6	2	3									
S	16	2	2	6	2	4									
Cl	17	2	2	6	2	5									
Ar	18	2	2	6	2	6									
K	19	2	2	6	2	6		1							
Ca	20	2	2	6	2	6		2							
Sc	21	2	2	6	2	6	1	2							
Ti	22	2	2	6	2	6	2	2							
V	23	2	2	6	2	6	3	2							
Cr	24	2	2	6	2	6	5	1							
Mn	25	2	2	6	2	6	5	2							

Fe	26	2	2	6	2	6	6	2							
Co	27	2	2	6	2	6	7	2							
Ni	28	2	2	6	2	6	8	2							
Cu	29	2	2	6	2	6	10	1							
Zn	30	2	2	6	2	6	10	2							
Ga	31	2	2	6	2	6	10	2	1						
Ge	32	2	2	6	2	6	10	2	2						
As	33	2	2	6	2	6	10	2	3						
Se	34	2	2	6	2	6	10	2	4						
Br	35	2	2	6	2	6	10	2	5						
Kr	36	2	2	6	2	6	10	2	6						
Rb	37	2	2	6	2	6	10	2	6			1			
Sr	38	2	2	6	2	6	10	2	6			2			
Y	39	2	2	6	2	6	10	2	6	1		2			
Zr	40	2	2	6	2	6	10	2	6	2		2			
Nb	41	2	2	6	2	6	10	2	6	4		1			
Mo	42	2	2	6	2	6	10	2	6	5		1			
Tc	43	2	2	6	2	6	10	2	6	5		2			
Ru	44	2	2	6	2	6	10	2	6	7		1			
Rh	45	2	2	6	2	6	10	2	6	8		1			
Pd	46	2	2	6	2	6	10	2	6	10		0			
Ag	47	2	2	6	2	6	10	2	6	10		1			
Cd	48	2	2	6	2	6	10	2	6	10		2			
In	49	2	2	6	2	6	10	2	6	10		2	1		
Sn	50	2	2	6	2	6	10	2	6	10		2	2		
Sb	51	2	2	6	2	6	10	2	6	10		2	3		
Te	52	2	2	6	2	6	10	2	6	10		2	4		
I	53	2	2	6	2	6	10	2	6	10		2	5		
Xe	54	2	2	6	2	6	10	2	6	10		2	6		

EXAMPLE

Distinguish between orbit and orbital with respect to definition.

SOLUTION

Orbit	Orbital
Orbit is a definite circular path in which electrons revolve around the nucleus.	Orbital is the three dimensional space around the nucleus in which the probability of finding an electron with a particular energy is maximum.

EXAMPLE

Why did Sommerfeld introduce azimuthal quantum number?

SOLUTION

Sommerfeld introduced azimuthal quantum number to explain the quantisation of energy associated with each subshell. Azimuthal quantum number describes the angular momentum of the electrons revolving in different elliptical orbits.

EXAMPLE

How does de Broglie's theory support Bohr's theory?

SOLUTION

According to Bohr's atomic theory, electrons revolve around the nucleus in a circular path with a fixed angular momentum. According to de Broglie, electron has a dual nature – particle nature and wave nature. The nature of the wave should be like a stationary wave if the path of the electron is circular. The circumference of the circular path of the electron should be an integral multiple of the wave length of the wave associated with the electron since the wave is a stationary wave. The energy of the wave associated with the electron moving in a particular orbit is quantized because the wavelength of it is fixed for that particular orbit.

EXAMPLE

Designations of some orbitals are given below. Identify those designations which are not possible in an atom. Arrange the orbitals with possible designations in the order in which they are filled with electrons 6s, 8p, 7s, 4d, 2p, 3d, 3f, 4f, 1p.

SOLUTION

1p, 3f are the designations which are not possible for any orbitals in an atom. All others are possible. The orbitals are occupied by electrons in increasing order of their energy. The order of energy is decided by $n + \ell$ rule.

$n + \ell$ values of orbitals

$6s \rightarrow 6 + 0 = 6$ $\quad 4d \rightarrow 4 + 2 = 6;$ $\quad 4p \rightarrow 4 + 1 = 5$ $\quad 2p \rightarrow 2 + 1 = 3$

$8p \rightarrow 8 + 1 = 9$ $\quad 3d \rightarrow 3 + 2 = 5;$ $\quad 7s \rightarrow 7 + 0 = 7$ $\quad 4f \rightarrow 4 + 3 = 7$

$2p < 3d < 4p < 4d < 6s < 4f < 7s < 8p$

EXAMPLE

The valence electronic configuration of an atom is $6s^2$. If d orbital of the penultimate shell contains two unpaired electrons, calculate the atomic number.

SOLUTION

Since the valence electronic configuration of the atom is $6s^2$ and d orbital of the penultimate shell contains two unpaired electrons, the electronic configuration is $[Xe]6s^24f^{14}5d^2$. Therefore, the atomic number of the element is 72.

EXAMPLE

An atom of an element has 3 electrons in 4p subshell. Calculate the atomic number of the element.

SOLUTION

The electronic configuration of the element having 3 electrons in 4p subshell is $[Ar]4s^2 3d^{10} 4p^3$. Therefore, the atomic number is 33.

EXAMPLE

What is the maximum number of electrons present in the main energy level in which the 'g' subshell appears for the first time? Find the atomic number of the element to be discovered in which the differentiating electron is the only electron in the first 'g' subshell.

SOLUTION

Corresponding 'ℓ' value of 'g' subshell is '4'. Principal quantum number in which 'g' subshell can exist is '5'.

The maximum number of electrons that can be accommodated in 5^{th} orbit is 2×5^2

= 50 electrons.

Orbitals to be filled before filling of '5g' subshell is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, 8s, 5g. Atomic number of the element should be 121

EXAMPLE

Arrange the following atomic numbers in the increasing order of number of unpaired electrons.

(a) 16 **(b)** 32 **(c)** 40 **(d)** 57

SOLUTION

(a) Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$; number of unpaired electrons is 2.

(b) Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$; number of unpaired electrons is 2.

(c) Electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^2$; number of unpaired electrons is 2.

(d) Electronic configuration is [Xe] $6s^2\ 5d^1$; number of unpaired electrons 1

$\therefore$ order is (i) = (ii) = (iii) > (iv)

EXAMPLE

Account for the very stable nitrogen atom in contrast to its neighbouring carbon and oxygen atoms.

SOLUTION

Nitrogen has half filled configuration $2s^2\ 2p^3$, while Carbon $2s^2\ 2p^2$ and Oxygen $2s^2\ 2p^4$ have no half filled configurations. The atoms with half filled configurations are exceptionally stable. This is due to the symmetry in the arrangement of electrons in the orbitals and mutual exchange of energy among the parallel spins of electrons which lowers the energy of system. Hence it becomes more stable.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. How are the subatomic particles arranged in an atom according to modern structure of the atom?
2. Why did Sommerfeld extend Bohr's theory?
3. What is a fine spectrum?
4. What was the requirement for introducing the magnetic quantum number?
5. What is the principal quantum number?
6. Why did the spin quantum number come into existence?
7. The region having maximum probability of finding an electron in space is known as _____.
8. What do you mean by the dual nature of an electron?
9. According to de Broglie, what is the relation between the wave length of the wave associated with the moving electron and momentum of the electron?
10. Define an atomic orbital.
11. What was the requirement for introducing the atomic orbital concept?
12. The value of ℓ for an orbital having five degenerate orbitals is _____.
13. How many orbitals are there in K, L, M and N shells? What are they?
14. What is the shape of an "s" orbital? Draw the diagram.
15. Why does L shell does not have d-orbitals?
16. What do you mean by degenerate orbitals? Give examples.
17. The valence electronic configuration of magnesium is _____.
18. How many nodal surface(s) can 5s orbital have?
19. Magnetic quantum number specifies _____.
20. In the pictorial representation of an orbital, what is the role of different intensity of shading?
21. In the degenerate orbitals, unpaired electrons have _____ spin.
22. Nitrogen atom has _____ unpaired electrons, according to _____ rule.
23. The ratio between the number of neutrons present in C^{12} and Si^{30} atoms is _____.
24. The electronic configuration of copper is _____.
25. How is the order of the energy of the atomic orbitals established?
26. In how many d-orbitals do the lobes lie in between coordinate axes? What are those?
27. When a 4p orbital is completely filled then the next electron goes to _____.
28. How will you find out the maximum number of electrons in the main energy level?
29. The number of unpaired electrons present in Fe^{+3} is _____.
30. Which one of the following (a or b) electronic configuration is more stable and why?
    (a) $3d^4\ 4s^2$ (b) $3d^5\ 4s^1$

Short Answer Type Questions

31. (a) What is azimuthal quantum number?
    (b) Why did Sommerfeld introduce this quantum number?
32. What are the drawbacks of Bohr's theory?
33. Account for the very stable nitrogen atom in contrast to its neighbouring carbon and oxygen atoms.
34. What leads to the establishment of the particle nature of electron?
35. What is Heisenberg's uncertainty principle?
36. How did Sommerfeld explain the fine structure of hydrogen spectrum?
37. According to Pauli's exclusion principle, what is the maximum number of electrons that can be present in d- and f-orbitals? Explain.
38. Write the electronic configuration of the following elements.

Element	Atomic number	Electronic configuration (nl^x)
A	23	
B	38	
C	35	
D	20	
E	18	

39. What does Hund's rule for maximum multiplicity state?
40. Explain how the Bohr's atomic model was contradictory to Heisenberg's uncertainty principle.
41. Write the electronic configurations of the noble gases starting from helium and predict their atomic numbers.
42. How many nodes are present in 3s, 3p and 3d orbitals?
43. Describe the shape of different p-orbitals.
44. Calculate the maximum number of electrons in 1st, 2nd, 3rd and 4th shells.
45. Draw the diagram of different d-orbitals.

Essay Type Questions

46. (a) Explain Zeeman effect and Stark effect.
    (b) How are they related to magnetic quantum number? Explain
47. What are the different rules for filling up the orbitals? Explain each rule in detail.
48. Discuss the four quantum numbers. Explain the interrelationship among the four quantum numbers. Also explain the significance of a quantum number.
49. What was the basis for the origin of the concept of an atomic orbital? Define atomic orbital.
50. Explain the dual nature of an electron on the basis of de Broglie's theory. State Heisenberg's uncertainty principle. How did it contradict Bohr's theory?

CONCEPT APPLICATION

Level 1

Direction for questions from 1 to 7: **State whether the following statements are true or false.**

1. The dual nature of electron was given by Sommerfeld.
2. Among 4p, 4s, 3p and 3d orbitals, 3d orbital has the least energy.
3. Azimuthal quantum number indicates the angular momentum of an electron.
4. Any two electrons in an atom can have maximum of three quantum numbers same.
5. Pairing of electrons in degenerate orbitals takes place only when the degenerate orbitals are filled with one electron each.
6. Bohr's theory can explain the spectra of multielectron species.
7. In iron, the differentiating electron enters into the orbital of a penultimate shell.

Direction for questions from 8 to 14: **Fill in the blanks.**

8. For a given value of "ℓ," the total number of "m" values is _____
9. If the azimuthal quantum number of an electron is 2 then the shape of orbital is _____.
10. The value of Planck's constant is _____.
11. The ratio of energy to frequency of electromagnetic radiation is equal to _____.
12. The minimum angular momentum of an electron with the magnetic quantum numbers –1, 0, +1 is _____.
13. Bohr's model introduced the concept of quantization of _____.
14. The ratio of the energies of two different radiations whose frequencies are 3×10^{14} HZ and 5×10^{14} HZ is _____.

PRACTICE QUESTIONS

Direction for question 15: **Match the entries given in column A with appropriate ones from column B.**

15.

	Column A			Column B
A.	Be	(·)	a.	$[He]2s^2 2p^6$
B.	Ne	(·)	b.	$[He]2s^2$
C.	Si	(·)	c.	$[Ne]3s^2 3p^3$
D.	P	(·)	d.	$[Ne]3s^2 3p^5$
E.	Cl	(·)	e.	$[Ne]3s^2 3p^2$

Direction for questions from 16 to 45: **For each of the questions, four choices have been provided. Select the correct alternative.**

16. The Bohr's model could successfully explain
(a) the stability of the atom
(b) the atomic spectra of hydrogen atom
(c) the calculation of energy of the electron in a particular orbit of hydrogen atom
(d) all the above

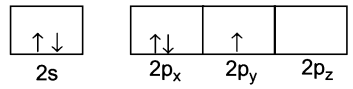
17. Among the following, the orbital that has the lowest energy is
(a) 5f (b) 4f
(c) 6s (d) 6p

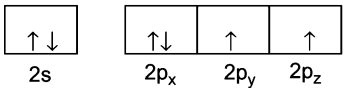
18. What is the maximum number of electrons, present in an orbit whose angular momentum is $\frac{2h}{\pi}$?
(a) 18 (b) 2
(c) 32 (d) 8

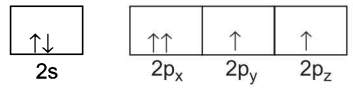
19. "The simultaneous location of both the position and the velocity of an electron in motion cannot be found with desired accuracy." This was proposed by
(a) Bohr (b) Heisenberg
(c) Sommerfeld (d) de Broglie

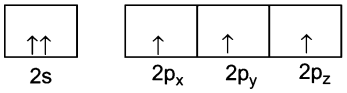
20. Which of the following sets of quantum numbers represent electron in hydrogen atom?
(a) 1, 1, 0, + ½ (b) 1, 0, 0, + ½
(c) 3, 0, 0, – ½ (d) 4, 2, 1, – ½

21. The electronic configuration of chromium is
(a) [Ar] $3d^5\ 4s^1$ (b) $3d^5\ 4s^1$
(c) [Ar] $3d^4\ 4s^2$ (d) $3d^4 4s^2$

22. The electronic configuration in which Pauli's exclusion principle or Hund's rule is not violated is
(a) 

(b) 

(c) 

(d) 

23. In the following pairs, identify the pair having a different $(n + \ell)$ value:
(a) 4s, 3p (b) 3d, 4p
(c) 4s, 3d (d) 4d, 5p

24. The maximum value of ℓ for n = 4 is
(a) 2 (b) 4
(c) 3 (d) 5

25. The maximum number of electrons that can be accommodated in p-subshell is
(a) 2 (b) 4
(c) 6 (d) 10

26. Which of the following sets of quantum numbers is correct for an electron in 3d orbital?
(a) 3, 0, 0, + ½ (b) 3, 1, 1, – ½
(c) 3, 2, 1, + ½ (d) 3, 2, 3, – ½

27. Probability of finding a d_{yz} electron is zero along the
(a) x-axis (b) y-axis
(c) z-axis (d) all of these

28. Heisenberg's uncertainty principle is not applicable to
(a) all the bodies moving with high speed
(b) protons
(c) electrons
(d) all the microparticles moving with high speed

29. If 20 electrons are present in the 4th orbit then the atomic number of that element is
(a) 58 (b) 59
(c) 56 (d) 60

30. Zeeman and Stark effects can be explained by _____ quantum number.
(a) principal (b) azimuthal
(c) magnetic (d) spin

31. Discoveries of isotopes and isobars contradict some of the postulates of _____ atomic theory.
(a) Bohr's (b) Dalton's
(c) Rutherford's (d) Thomson's

32. According to _____ atomic model positive charge is thinly spread throughout the atom.
(a) Bohr's (b) Dalton's
(c) Rutherford's (d) Thomson's

33. Which of the following statements is false?
(a) Bohr's theory explains only the spectra of single electron species.
(b) The energy of an electron remains constant during electronic transition.
(c) The angular momentum of an electron is quantized.
(d) According to Bohr's theory, electrons revolve around the nucleus in circular orbits.

34. The difference in energy of radiation emitted (or) absorbed during electronic transition is
(a) directly proportional to frequency
(b) directly proportional to wavelength
(c) inversely proportional to frequency
(d) inversely proportional to velocity of light

35. Which of the following statements regarding orbitals is false?
(a) 1s orbital has one nodal region.
(b) 2s orbital is spherical with one nodal region.
(c) 2px orbital is dumb bell with one nodal plane.
(d) 3d orbital has two nodal planes.

36. Quantum theory of radiation was proposed by
(a) Pauli (b) Planck
(c) Hund (d) Aufbau

37. The azimuthal quantum number of an electron is zero, then the shape of its orbital will be
(a) circular (b) spherical
(c) elliptical (d) dumbbell

38. The number of nodes of an s-orbital increases with
(a) the increase in n value
(b) the decrease in n value
(c) the increase in l value
(d) the decrease in l value

39. The statements given below are the postulates of various atomic models. Arrange them in their chronological order.
(1) Fine structure is due to the presence of subshells in the main energy level.
(2) The size of an atom is much larger than the size of its nucleus.
(3) As long as the electron is present in a particular orbit, its energy remains constant.
(4) Negatively charged particles are uniformly spread in the lump of positive charge.
(a) 4, 3, 2, 1 (b) 2, 3, 4, 1
(c) 4, 2, 3, 1 (d) 3, 4, 2, 1

40. (1) As long as an electron revolves in a particular orbit, the electron does not lose its energy. Therefore, these orbits are called stationary orbits and the electrons are said to be in stationary energy states.
(2) Each orbit or shell is associated with a definite amount of energy. Hence, these are also called energy levels.
(3) An electron jumps from a lower energy level to a higher energy level, by absorbing energy. It jumps from a higher energy level to a lower energy level by emitting energy in the form of electromagnetic radiation.
(4) Electrons move around the nucleus in specified circular paths called orbits or shells or energy levels and are designated as K, L, M and N shells respectively.
Arrange the above postulates of Bohr's theory in a correct sequence.
(a) 4, 1, 3, 2 (b) 4, 2, 1, 3
(c) 4, 1, 2, 3 (d) 2, 4, 1, 3

41. (1) The probability of finding an electron is maximum at certain places in space.
(2) Energy change takes place only during excitation or deexcitation of electrons.
(3) Electron has both particle and wave nature.
(4) Angular momentum of the electrons revolving in different elliptical orbits is quantized.

Arrange the above statements of different models or principles in the chronological order, which ultimately led to the development of modern structure of the atom.

(a) 1, 2, 3, 4 (b) 2, 4, 3, 1
(c) 4, 3, 2, 1 (d) 2, 3, 1, 4

42. Energy of an electron in a particular orbit of single electron species of beryllium is the same as the energy of an electron in the ground state of hydrogen atom. Identify the orbit of beryllium.

(a) 1 (b) 2
(c) 3 (d) 4

43. The difference between the angular momentum of two orbits of He^{+2} is $\frac{2h}{\pi}$. The energy of an electron present in the higher orbit is –1.51 eV. Identify the lower orbit.

(a) 1 (b) 2
(c) 3 (d) 4

44. Velocity of the electron in electron microscope is 1.6 × 106 m/s. What would be the wavelength of the electron?

(a) 5.39 Å (b) 4.55 Å
(c) 3.54 Å (d) 6.78 Å

45. An atom of an element has 9 electrons with l = 0 value, 18 electrons with l = 1 value and 10 electrons with l = 2 value. Calculate the atomic number of the element.

(a) 37 (b) 41
(c) 38 (d) 39

Level 2

1. "p" orbital has a nodal plane while "s" orbital has a nodal region. Elaborate with the help of a diagram.

2. What is the common nodal plane of d_{xy} and d_{zx}?

3. The number of nodal regions for an "s" orbital is given by (n − 1). How do you account for this?

4. Compare the energy released during direct electronic transition from 4th orbit to 1st orbit with the energy released during successive electronic transitions between the same orbits in H-atom. Is the energy of all successive transitions between the 4th orbit and 1st orbit equal?

5. "Wave nature of matter is applicable only for subatomic particles and not for larger objects." Justify this statement.

6. Are the magnetic quantum number and angular momentum of an electron related to each other? Explain.

7. What is the maximum number of electrons present in the main energy level in which the "g" subshell appears for the first time? Find the atomic number of the element to be discovered in which the differentiating electron is the only electron in the first "g" subshell.

8. If the angular momentum of an electron is 3.16×10^{-34} kg m^2/s and the radius and energy of an orbit in which the above electron is present is 0.6×10^{-10} m and 2.4×10^{-18} J, respectively then calculate the radius and energy of 2nd orbit of that atom.

9. When the electrons are successively filled in the orbitals of same shell, orbital, which is filled at the end, requires less energy to remove electron. Justify.

10. Atomic number of an element is 42. Find out the number of electrons present in the valence shell.

11. Arrange the following ions in the increasing order of unpaired electrons: Na^+, Cu^{+1}, N^{-3}, O^-, P and Cr.

12. Arrange the following orbitals in the order in which they are filled with electrons and justify the order: 6s, 5d, 6p, 7s, 5f.

13. Given that the N shell of an element contains 10 electrons, write the electronic configuration of the stable ion.

14. If an atom of an element has 8 electrons in a subshell having 5 orientations of 4th energy level, write the electronic configuration of the element and four quantum numbers for valence electrons.

15. The energy of an electron in a particular orbit of Li^{+2} is –30.6 eV. What is the energy of an electron in the same orbit of Be^{+3}?

16. Sunny and Bunny have taken spectra for the following transitions. Spectra taken by Sunny consisted of bright lines on a dark background. Spectra taken by Bunny consisted of dark lines on a bright background. Identify the electronic transitions corresponding to the spectra taken by Sunny and Bunny. What are those spectra called?

(a) n = 5 to n = 2 (b) n = 4 to n = 6
(c) n = 5 to n = 7 (d) n = 3 to n = 1
(e) n = 1 to n = 2 (f) n = 5 to n = 3

17. The angular momentum of an electron in a particular orbit of H-atom is 5.27 3 10^{-34} kg m^2/s. Calculate the radius of the particular orbit of lithium.

18. How did Sommerfeld explain the fine structure of hydrogen spectrum?

19. Electrons occupy the degenerate orbitals with parallel spins. How can you justify this statement with respect to stability?

20. "p-" orbital has a nodal plane while "s-" orbital has a nodal region. Elaborate with the help of a diagram.

21. The atomic number of an atom A is x. Valence electronic configuration of another atom B is $6s^2 5d^3$ and its atomic number is (x + 5). Write the electronic configuration of A.

22. The ratio of atomic numbers of two elements X and Y is 1 : 7. Radius of 5th orbit of single electron species of X is 3.3 Å. Write the electronic configuration of Y and four quantum numbers for the valence electrons.

23. An electron is revolving in an orbit with a velocity of 5.46 × 107 cm s^{-1}. Calculate the wavelength associated with the electron.

24. A spherical orbital has three nodal regions and it contains a pair of electrons. If this is the only orbital which is occupied with electrons in that main energy level, and the penultimate shell is completely filled, calculate its atomic number.

25. The sum of all the quantum numbers of all the valence electrons of an atom of an inert gas is 22. Identify the inert gas.

Level 3

1. "Velocity of an electron decreases as we go farther from the nucleus." Justify.

2. Energy of an electron increases with increase in distance from the nucleus. Comment on the change in kinetic energy and potential energy.

3. How does de Broglie's theory support Bohr's theory?

4. Do all the single electron species of various elements possess same energy for the electron in the ground state? Give reason.

5. Two electronic transitions were found to take place in a single electron species. One is deactivation of electron from the 5th shell to the 4th shell and the other is from the 2nd shell to the 1st shell. Do the energies emitted due to the above transitions have the same wavelength? Justify.

6. An electron is present in a hydrogen atom in the ground state and another electron is present in a single electron species of beryllium. In both the species the distance between the nucleus and electron is same. Calculate the difference in their energies.

7. One electron is made to revolve around a proton and it possesses the least possible energy and another electron is made to revolve around an α-particle with the same energy. Calculate the ratio of the distances of the electrons from the respective species.

8. The principal and azimuthal quantum numbers associated with a subshell are a and a – 4, respectively. Predict the shape of that subshell if the shape of another subshell having azimuthal quantum number a – 5 is spherical. If that subshell is half-filled, predict the atomic number of the element.

9. Are the magnetic quantum number and angular momentum of an electron related to each other? Explain.

10. "The larger the value of 'l' belonging to the same main energy, higher is the energy associated with it." Comment on this statement.

PRACTICE QUESTIONS

CONCEPT APPLICATION

Level 2

True or false

1. False
2. False
3. True
4. True
5. True
6. False
7. True

Fill in the blanks

8. $2\ell + 1$
9. double dumb-bell
10. 6.627×10^{-27} erg s or 6.627×10^{-34} joule s
11. Planck's constant
12. $\frac{h}{\pi}$
13. angular momentum and energy
14. 3:5

Match the following

15. A : b B : a C : e D : c
    E : d

Multiple choice questions

16. **d**
17. c
18. c
19. b
20. b
21. a
22. b
23. c
24. c
25. c
26. c
27. d
28. a
29. b
30. c

31. According to Dalton's atomic theory, atoms of same elements are identical in all respects, whereas atoms of different elements are different in all respects. But discovery of isotopes revealed that atoms of same element can have different mass. Discovery of isobars revealed that atoms of different elements can have same mass. These discoveries of isotopes and isobars contradict the above two postulates of Dalton's atomic theory.

32. In Thomson's model positively charged particles are thinly spread throughout the atom. Electrons are embedded in the thin positively charged mass.

33. The energy of the electron remains constant only when it is revolving around nucleus in a particular orbit. During an electronic transition, it gains or loses energy.

34. Energy $E = h\nu$

$$\therefore\ E = h\frac{c}{\lambda}$$

i.e., $E \alpha \nu : E \alpha \frac{1}{\lambda}, E \alpha c$

35. 1s orbital does not possess nodal region since it is the minimum distance at which an electron can be present.

36. Quantum theory of radiation was proposed by Planck.

37. When $\ell = 0$, the shape of the orbital is spherical (s-orbital).

38. With increase in n value, the number of nodes of s-orbital increases.

39. (i) Negatively charged particles are uniformly spread in the lump of positive charge (Thomson's model).

(ii) The size of atom is much larger than the size of its nucleus (Rutherford's model).

(iii) As long as the electron is present in a particular orbit, its energy remains constant (Bohr's model).

(iv) Fine structure is due to the presence of subshells in the main energy level (Sommerfeld's model).

40. (i) Electrons move around the nucleus in specified circular paths called orbits or shells or energy levels and are designated as K, L, M and N shells, respectively.

(ii) Each orbit or shell is associated with a definite amount of energy. Hence, these are also called energy levels.

(iii) As long as the electron revolves in a particular orbit, the electron does not lose its energy. Therefore, these orbits are called stationary orbits and the electrons are said to be in stationary energy states.

(iv) An electron jumps from a lower energy level to a higher energy level, by absorbing energy. It jumps from a higher energy level to a lower energy level by emitting energy in the form of electromagnetic radiation.

41. (i) Energy change takes place only during excitation or deexcitation of electrons.

(ii) Angular momentum of the electrons revolving in different elliptical orbits is quantized.

(iii) Electron has both particle and wave nature.

(iv) The probability of finding an electron is maximum at certain places in space.

42. Energy of an electron in Be^{+3} ion $= \frac{-13.6}{n^2} \times 4^2 ev$

Energy of the electron in ground state hydrogen atom = –13.6 ev

$$\therefore \frac{-13.6}{n^2} \times 4^2 = -13.6$$

$$\Rightarrow n^2 = 42$$

$$\Rightarrow n = 42$$

43. The energy of electron, $E = \frac{-13.6 \times Z^2}{n^2} ev$

$$\therefore 1.51 = \frac{-13.6 \times 4}{n^2}$$

$$[\because Z = 2]$$

$$\therefore n = 6.$$

The difference in angular momentum of two orbits is

$$(mvr)_x - (mvr)_y = \frac{n_x h}{2\pi} - \frac{n_y h}{2\pi}$$

$$\therefore \frac{2h}{\pi} = (n_x - n_y)\frac{h}{2\pi}$$

$$n_x - n_y = 4$$

$\therefore$ The other orbit (n_x) is the 2nd orbit.

44. $v = 1.6 \times 10^6$ m/s

$m = 9.1 \times 10^{-31}$kg

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.1 \times 10^{-31} \times 1.6 \times 10} = 4.55\,A^\circ$$

45. l = 0 corresponds to "s" subshell, l = 1 corresponds to "p" subshell, l = 2 corresponds to "d" subshell. The atom should possess "9" "s" electrons, 18 "p" electrons and 10 "d" electrons. The electronic configuration of the element should be $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 5s^2$. The atomic number of the element should be 37.

Level 3

1. (i) shape of s- and p-orbitals

(ii) orientation of lobes of p- and s-orbitals in space

(iii) areas of zero probability of electron in s- and p-orbitals

(iv) comparison of these areas of s- and p-orbitals

2. (i) shape of d_{zx} and d_{xy} orbitals

(ii) orientation of lobes of d_{xy} and d_{xz} orbitals

(iii) planes where probability of finding an electron is zero

3. nodal region for 1s orbital

4. expression for energy of electron in nth orbit

5. (i) de Broglie's wave equation
   (ii) relation between mass and wavelength
   (iii) relation between wavelength and nature of light

6. (i) significance of magnetic quantum number
   (ii) degeneracy of orbitals
   (iii) effect of a magnetic field

7. (i) "ℓ" value for g subshell
   (ii) total number of degenerate orbitals in "g" subshell
   (iii) number of electrons in "g" subshell
   (iv) main energy level in which "g" subshell first appears
   (v) orbitals which have lower energy than the first "g" orbital

8. (i) quantization of angular momentum
   (ii) calculation of principal quantum number from angular momentum
   (iii) calculation of radius
   (iv) calculation of energy of an electron

9. requisite for filling up of orbitals

10. electronic configuration of the element

11. electronic configuration of the respective ions

12. (i) Aufbau principle
   (ii) $n + \ell$ values of the given orbitals
   (iii) relation between energy and $n + \ell$ value
   (iv) relation between energy and the value of "n" for the orbitals which have the same $n + \ell$ values

13. identification of atomic number

14. identification of quantum numbers corresponding to the number of orientations

15. (i) comparison of atomic numbers
   (ii) –54.4 eV

16. When an electron in an atom gains energy, it gets excited to a higher energy state from the ground state. The electron being unstable in the excited state loses energy and comes back to the ground state either directly or in steps. During this process the bright lines corresponding to the transitions are formed on the dark background. This is called emission spectrum. When the electrons get excited to higher energy levels they absorb energy and dark lines corresponding to the transitions are formed on the bright background. This is called absorption spectrum.
   (a) n = 5 to n = 2 → emission spectrum
   (b) n = 4 to n = 6 → absorption spectrum
   (c) n = 5 to n = 7 → absorption spectrum
   (d) n = 3 to n = 1 → emission spectrum
   (e) n = 1 to n = 2 → absorption spectrum
   (f) n = 5 to n = 3 → emission spectrum

17. Angular momentum, $mvr = \dfrac{nh}{2\pi}$

$$\therefore\ 5.27\times10^{-34} = \frac{n\times6.625\times10^{-34}}{2\times\frac{22}{7}} \Rightarrow n = 5S$$

$$\text{Radius } r_n = \frac{0.529\times n^2}{Z}\,A^\circ$$

$$= \frac{0.529\times25}{3} = 4.408\,A^\circ \text{ or } 4.408\times10^{-8}\,cm$$

18. Sommerfeld suggested that the subenergy levels or subshells associated with each main energy level are responsible for the fine structure of hydrogen spectrum. These subenergy levels or subshells exist due to the difference in energies of electrons revolving in different elliptical orbits belonging to the same main energy level.

19. Degenerate orbitals are orbitals having equal energies belonging to same main energy level. Electrons can enter into any orbital. If an electron occupies one of the orbitals, the next electron necessarily takes the same spin and enters into the other vacant orbital instead of pairing up with the electron in the 1st orbital. The electrons always repel each other due to their same charge. If they rotate around their axis in the same direction, they will have similar magnetic moment and they will further repel each other and maintain maximum distance among each other which gives rise to the maximum stability.

20. "s-" orbital is spherically symmetrical and non-directional. Hence, there is no nodal plane. Only a spherical region adjacent to the orbital where the probability of finding an electron is zero is found which is called nodal region. "p-" orbital is dumb bell shaped and directional and lies along the axis. Hence for each p-orbital there is one plane where the probability of finding an electron is zero.

21. The atomic number of B is 73 because its electronic configuration is [Xe] $6s^2 4f^{14} 5d^3$.

$\therefore$ Atomic number of A is x, i.e., 73 – 5 = 68.

So, its electronic configuration is $[Xe]6s^2 5d^1 4f^{11}$

22. Radius, $r_n = \frac{0.529 \times n^2}{Z} \Rightarrow 3.3$

$$= \frac{0.529 \times 25}{Z} \Rightarrow Z = 4$$

$\therefore$ Atomic number of x is 4 and atomic number of Y is 28.

Electronic configuration of Y is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$ and valence electrons are $4s^2$ electrons.

Electron: $1 \rightarrow n = 4, 1 = 0, m = 0, s = \frac{1}{2}$,

Electron: $2 \rightarrow n = 4, 1 = 0, m = 0, s = -\frac{1}{2}$

23. $\lambda = \frac{h}{mv}$

Given that $v = 5.46 \times 10^7$ cm s^{-1}

$h = 6.625 \times 10^{-27}$ erg.s

$m = 9.1 \times 10^{-28}$ g

$$\therefore \lambda = \frac{6.625 \times 10^{-27}}{9.1 \times 10^{-28} \times 5.46 \times 10^7}$$

$$= 0.1333 \times 10^{-6} \text{cm}$$

$$\lambda = 13.3\,A^\circ$$

24. A spherical orbital which has three nodal regions and contain a pair of electrons is $4s^2$. Since this is the only orbital of that main energy level which is occupied with electron, the valence shell is 4. All the penultimate shells are completely filled. Therefore, the electronic configuration is $[Ar]3d^{10} 4s^2$. Therefore, the atomic number of that element is 30.

25. General valence electronic configuration of an inert gas is $ns^2\ np^6$. The sum of all four quantum numbers of the valence electrons of the inert gas is

Sum of principal quantum numbers = 8 × n

Sum of azimuthal quantum numbers = (2 × 0) + (6 × 1)

Sum of magnetic quantum numbers = 0

Sum of spin quantum numbers = 0

$\therefore$ 8n + 6 = 22

$$\therefore n = \frac{16}{8} = 2$$

Valence electronic configuration of the inert gas is $2s^2\ 2p^6$ and hence the inert gas is neon.

Level 3

1. (i) nuclear force of attraction
(ii) relation between velocity and nuclear force of attraction
(iii) relation between nuclear force and principal quantum number

2. factors affecting kinetic energy and potential energy of an electron

3. (i) wave nature of an electron revolving in a particular orbit
(ii) behaviour of an electron
(iii) relation between circumference of Bohr's orbit and the number of wavelengths
(iv) quantization of energy

4. reason for revolution of electron around the nucleus

5. (i) calculation of energy emitted due to the above transition
(ii) calculation of difference in energy between 5th and 4th and 2nd and 1st shells
(iii) relation between the energy and the frequency of the electromagnetic radiation
(iv) relation between frequency and the wavelength of the electromagnetic radiation

HINTS AND EXPLANATION

6. radius of hydrogen atom in 1st orbit

$$^{r}H_1 = \frac{kn^2}{Z} = kn^2 = k \cdot 1^2 = k$$

Let radius of n^{th} orbit of Be^{+3} = k

$$\therefore k = \frac{kn^2}{4}, \quad \therefore n^2 = 4, \quad \therefore n = 2$$

In order to maintain the same distance, the electron has to be present in the 2nd orbit of Be^{+3}. Energy of the electron in the 1st orbit of hydrogen

$$= \frac{-kZ^2}{n^2} = -k$$

Energy of the electron in the 2nd orbit of Be^{+3}

$$= \frac{-kZ^2}{n^2}$$

$$= -\frac{k \times 4 \times 4}{2 \times 2} = -4k$$

$\therefore$ Difference in energy = (4k – k) = 3k
= (3 × 13.6) eV
= 40.8 eV

7. Revolution of an electron around a proton at the closest distance implies that it is a hydrogen atom in its ground state.

Similarly, the other particle is He^+.

The energy of the electron revolving around the nucleus of He^+ should be –K.

$$\therefore \quad -k = \frac{-kZ^2}{n^2}$$

$$\therefore \quad n^2 = 4 [\because Z = 2]$$

$$\therefore \quad n = 2$$

The ratio of radii of the 1st orbit of hydrogen to the

$$2^{nd} \text{ orbit of } He^+ = \frac{\frac{k \times 1^2}{2}}{\frac{k \times 2^2}{2}} = 1:2$$

8. The shape of the subshell having azimuthal quantum number a – 5 is spherical. Hence, the value of a must be 5. Therefore, the subshell having principal and azimuthal quantum numbers a and (a – 4), i.e., 5 and 1 is 5p. If 5p subshell is half-filled the electronic configuration is $[Kr]5s^24d^{10}5p^3$. So, the atomic number of the element is 51. 5p orbital is dumb-bell shaped with two lobes.

9. Magnetic quantum number represents the spatial orientation of the electrons which belong to same main and subenergy levels. Angular momentum is fixed for the orbitals associated with same "n" and "l" values. The degeneracy of the orbitals gets disturbed by applying external magnetic field or electric field due to the change in angular momentum. Since the electrons are moving charged particles, they have their own magnetic field which has a particular direction and the direction of the magnetic field is different for different orbitals belonging to the same main and subenergy levels. Hence, the influence of the external magnetic or electric field is also different for different orbitals, which, in turn, changes the angular momentum of the electrons and their degeneracy gets lost.

10. When more than one electron is present in one main energy level, the energy of a particular electron is determined by the value of "l." When the electron enters into p-orbital from infinite distance, it has to work towards a weaker force of attraction than that in case of "s-" orbital due to the screening effect of the "s-" orbital belonging to the same energy level. Hence the loss of energy is less in case of electron entering the "p-" orbital than that entering the "s-" orbital. As a result the electron belonging to "p-" orbital has higher energy than that belonging to "s-" orbital. Similarly "d-" orbital is associated with higher energy than that of p and the energy of the "f-" "orbital" is the highest provided they all belong to the same main energy level.

Chapter

4

Periodic Table

Remember

Before beginning this chapter, you should be able to:

- Understand earlier versions of classification of elements with emphasis on Mendeleeff's periodic table
- Describe modern periodic table

Key Ideas

After completing this chapter, you should be able to:

- understand the historical aspects of the development of periodic table
- study different periodic laws and the arrangement of elements into groups and periods in the periodic table
- study the trends of atomic size, ionization energy, electron affinity, electropositivity, oxidising and reducing property etc among the elements in the periodic table
- learn comparison of elements based on their periodic properties.

INTRODUCTION

Chemistry involves the study of various elements and their compounds which are quite essential since they invariably find a number of applications in various fields of industry. The discovery of elements is a continuous process with new elements being added to the existing ones. There are 116 authorized elements at present and few more elements have been discovered but yet to be authorized. The study of 100 odd elements and the innumerable compounds formed by them is a tedious task. Therefore, classification of elements has been necessitated for a systematic study. This idea of classification of elements ultimately culminated into the arrangement of elements into a periodic table.

The periodic table of elements can be considered as a single document which reflects the behaviour of elements in a simple and logical way. That means, just by knowing the position of an element in the periodic table, it is possible to predict the nature and behaviour of the elements. In fact, the organization of the elements into a periodic table was a major breakthrough in the history of chemistry.

Historical Aspects

Classification of elements into metals, non-metals and metalloids could not serve the purpose because the elements within a category also show characteristic differences in properties. One of the earliest attempts of classification was made by Dobereiner on the basis of atomic weights. According to this classification, the elements are grouped into triads in which the atomic weight of the middle element is the approximate average of the atomic weights of the other two elements. This classification had a major drawback in that only few elements could be grouped into triads which reflected proper trends in properties.

Another similar attempt was made by Newland who proposed the famous law of octaves. According to Newland's law of octaves, the properties of every eighth element are a kind of repetition of the first. This classification could hold good only up to atomic weight 40 and failed beyond that. The first systematic classification of all the then known elements was made by Mendeleeff by taking atomic weight as the fundamental characteristic property.

Mendeleeff's Periodic Table

According to Mendeleeff, the properties of elements were related to their atomic weights. On this basis, he formulated his periodic law. Mendeleeff's periodic law states that the physical and chemical properties of the elements are the periodic functions of their atomic weights. Therefore, the elements have been arranged in the increasing order of their atomic weights. He compiled a periodic table by arranging the 63 elements known then in eight vertical columns called groups and seven horizontal rows known as periods. Later when the noble gases were discovered, Mendeleeff gave a modified periodic table by including the noble gases in zero group. He categorized the table into eight (columns) groups and seven periods (rows).The groups range from zero to eight and these except the zero and eighth group were further subdivided into two subgroups A and B. He numbered the periods from 1 to 7 of which the 7th period is incomplete.

Merits of Mendeleeff's Periodic Table

(i) Mendeleeff left some gaps for some undiscovered elements in the periodic table. The properties of these elements could be predicted based on the properties of other elements present in the same group. He named these missing elements as Eka boron, Eka aluminium and Eka silicon which were later discovered and named as scandium, gallium and germanium, respectively.

(ii) Mendeleeff corrected the doubtful atomic weights of some elements like indium, beryllium and uranium.

Limitations of Mendeleeff's Periodic Table

(i) In certain parts of the periodic table, element with a higher atomic weight was placed before that of the lower atomic weight in order to maintain the gradation in properties. These are known as anomalous pairs. Examples of anomalous pairs are the following:

(i) Co	Ni	(ii) Te	I	(iii) Ar	K
58·9	58·6	127·6	126·9	39·94	39·10

(ii) Isotopes of an element have different atomic weights. But there is no position for the isotopes in Mendeleeff's periodic table.

(iii) Three groups of three transition elements are placed in group VIII of the periodic table. They should have been given separate positions.

(iv) Transition elements were placed with other elements under the same group.

(v) Coinage metals were placed along with alkali metals.

Periodic System of the Elements in Groups and Periods

Series	Groups of Elements								
	0	I	II	III	IV	V	VI	VII	VIII
1	—	Hydrogen H 1.008	—	—	—	—	—	—	
2	Helium He 4.0	Lithium Li 7.03	Beryllium Be 9.1	Boron B 11.0	Carbon C 12.0	Nitrogen N 14.04	Oxygen O 16.00	Fluorine F 19.0	
3	Neon Ne 19.9	Sodium Na 23.05	Magnesium Mg 24.3	Aluminium Al 27.0	Silicon Si 28.4	Phosphorus P 31.0	Sulphur S 32.06	Chlorine Cl 35.45	
4	Argon Ar 38	Potassium K 39.1	Calcium Ca 40.1	Scandium Sc 44.1	Titanium Ti 48.1	Vanadium V 51.4	Chromium Cr 52.1	Manganese Mn 55.0	Iron Fe 55.9 Cobalt Co 59 Nickel Ni 59 (Cu)
5		Copper Cu 63.6	Zinc Zn 65.4	Gallium Ga 70.0	Germanium Ge 72.3	Arsenic As 75	Selenium Se 79	Bromine Br 79.95	
6	Krypton Kr 81.8	Rubidium Rb 85.4	Strontium Sr 87.6	Yttrium Y 89.0	Zirconium Zr 90.6	Niobium Nb 94.0	Molybdenum Mo 96.0	—	Ruthenium Ru 101.7 Rhodium Rh 103.0 Palladium Pd 106.5 (Ag)
7		Silver Ag 107.9	Cadmium Cd 112.4	Indium In 114.0	Tin Sn 119.0	Antimony Sb 120.0	Tellurium Te 127	Iodine I 127	
8	Xenon Xe 128	Caesium Cs 132.9	Barium Ba 137.4	Lanthanum La 139	Cerium Ce 140	—	—	—	— — —
9		—	—	—	—	—	—	—	

Series	Groups of Elements								
	0	I	II	III	IV	V	VI	VII	VIII
10	—	—	—	Ytterbium Yb 173	—	Tantalum Ta 183	Tungsten W 184	—	Osmium Os 191 Iridium Ir 193 Platinum Pt 194.9 (Au)
11		Gold Au 197.2	Mercury Hg 200.0	Thallium TI 204.1	Lead Pb 206.9	Bismuth Bi 208	—	—	
12	—	—	Radium Rd 224	—	Thorium Th 232	—	Uranium U 239		
Higher Saline Oxides									
	R	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Higher Gaseous Hydrogen Compounds									
					RH_4	RH_3	RH_2	RH	

Owing to these limitations and the later discovery of atomic structure, Mendeleeff's periodic table has no practical significance at present. Nevertheless, its significance lies in the fact that the concept of periodicity in properties and the resultant arrangement of elements into a periodic table originated from Mendeleeff's classification of elements.

After the discovery of fundamental particles, it has been established that electrons only take part in chemical reactions. Therefore, Moseley considered atomic number as the fundamental characteristic of elements.

Modern Periodic Table—The Long Form of the Periodic Table

In this, the atomic number, i.e., the total nuclear charge is used as the basis of the periodic table instead of the atomic weight. This observation led to the modern periodic law. The modern periodic law states that the physical and chemical properties of elements are the periodic functions of their atomic numbers or electronic configurations."

Thus, according to the modern periodic law, if the elements are arranged in the order of their increasing atomic numbers, the elements with similar properties are repeated after certain regular intervals.

The periodic table consists of 7 horizontal rows called periods and 18 vertical columns called groups. The groups are numbered from I to VIII and the zero group. The groups from I to VII are further divided into A and B. VIII group consists of three vertical columns. All the noble gases are kept in the zero group.

Periods	Description
1.	This is the very short period consisting of only two elements, hydrogen and helium. The elements have only one shell.
2.	This is a short period. These elements have two shells. It has eight elements, i.e., from Li to Ne. These are called bridge elements.
3.	This is called a short period. It has 8 elements ranging from Na to Ar. These are called the typical elements.

Periods	Description
4.	This is called a long period. It has 18 elements, i.e., from K to Kr. It consists of first transition series elements, i.e., from Sc to Zn.
5.	This is the second long period. It has 18 elements, i.e., from Rb to Xe. It consists of second transition series elements, i.e., from Y to Cd.
6.	This is the very long period. It has 32 elements, i.e., from Cs to Rn. It has the third transition series elements, i.e., from La to Hg and also the 14 inner transition elements, i.e., from Ce to Lu.
7.	Incomplete period. The elements are radioactive in nature. The elements succeeding uranium are all artificial elements. These are called transuranic elements. This period includes the elements of fourth transition series which is incomplete and the 14 inner transition series elements, i.e., from Th to Lr.

Periodic Table

Division of Periodic Table into Blocks

Depending on the subshell into which the differentiating electron enters, the elements are categorized into four blocks. The newly added electron in an atom of an element is called the differentiating electron.

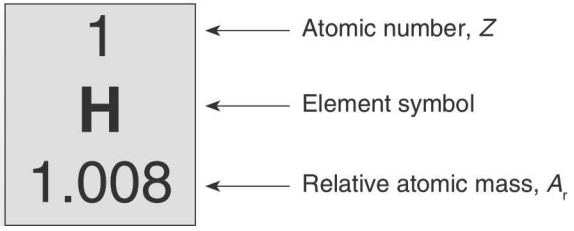
Blocks	Description	Groups
s-block	The differentiating electron enters the valence s-subshell.	Group I A → alkali metals Group II A → alkaline earth metals Left part of the periodic table. It consists of only metals.
p-block	The differentiating electron enters the valence p-subshell	III A IV A V A VI A VII A (halogens) Zero group It consists of metals, non-metals and metalloids and noble gases. p-block constitutes right part of the periodic table. s- and p-block elements except zero group are called representative elements.
d-block	The differentiating electron enters the penultimate d-subshell	III B, IV B,V B,VI B,VII B,VIII, I B, II B These are called transition elements. It consists of only metals placed in between left and right parts of the periodic table.
f-block	The differentiating electron enters the antepenultimate f-subshell	III B These are the inner transition elements kept separately at the bottom of the periodic table. It consists of only metals.

Merits of the Long Form of the Periodic Table

(i) The classification is based on the atomic number of elements, which is more fundamental than the atomic weight.

(ii) Elements belonging to the same group have same number of electrons in their valence shells and show similar chemical characteristics.

(iii) Variation of chemical properties along a period is correlated with gradual filling of electrons in a particular shell in the period.



1												13	14	15	16	17	18
1 **H** 1.008	2																2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	3	4	5	6	7	8	9	10	11	12	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.01	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.54	30 **Zn** 65.41	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.91	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** 98.91	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.40	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.30
55 **Cs** 132.91	56 **Ba** 137.34	**La–Lu**	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.98	84 **Po** 210	85 **At** 210	86 **Rn** 222
87 **Fr** 223	88 **Ra** 226.03	**Ac–Lr**	104 **Rf** [261]	105 **Db** [262]	106 **Sg** [266]	107 **Bh** [264]	108 **Hs** [277]	109 **Mt** [268]	110 **Ds** [271]	111 **Rg** [272]	112 **Uub** [285]						

Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** 146.92	62 **Sm** 150.36	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.92	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
Actinoids	89 **Ac** 227.03	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** 237.05	94 **Pu** 239.05	95 **Am** 241.06	96 **Cm** 244.07	97 **Bk** 249.08	98 **Cf** 252.08	99 **Es** 252.09	100 **Fm** 257.10	101 **Md** 258.10	102 **No** 259	103 **Lr** 262

(iv) Placement of inert gases at the end of each period is logical since it represents completion of corresponding valence shells. Inertness of these elements also could be explained on the basis of electronic configuration.

(v) Certain types of elements like
- **(a)** active metals,
- **(b)** transition metals,
- **(c)** noble gases and
- **(d)** inner transition elements (lanthanides and actinides) have their specific locations in this periodic table.

(vi) This arrangement of the elements is easy to remember and to reproduce since it is based on electronic configuration.

Defects of the Long Form of the Periodic Table

(i) The position of hydrogen in the periodic table is controversial because hydrogen with one electron in its valence shell shows similarities with both alkali metals and halogens. Therefore, placing hydrogen in IA group is not completely justifiable.

(ii) The elements lanthanides and actinides could not be placed in the main body of the modern periodic table.

(iii) This periodic table does not reflect the exact distribution of electrons of some of the transition and inner transition elements.

The properties of the elements, however, can be predicted based on their position in the periodic table.

EXAMPLE

What are the basic differences between Mendeleeff's periodic table and modern periodic table?

SOLUTION

(i) Mendeleeff's periodic table was based on atomic weight whereas modern periodic table was based on atomic number.

(ii) Mendeleef's periodic table consists of 8 groups and 7 periods whereas modern periodic table consists of 18 groups and 7 periods.

EXAMPLE

In the modern periodic table, magnesium is surrounded by elements with atomic numbers 4, 11, 13 and 20. Identify the elements. Which of these have chemical properties resembling magnesium?

SOLUTION

The element $_{12}$Mg is present in the centre of the elements having atomic numbers 4, 11, 13 and 20. The atomic number 4 and 20 resemble magnesium because they belong to same group having same number of valence electrons.

	Be = 4 (2, 2)	
Na = 11 2, 8, 1	Mg = 12 (2, 8, 2)	Al = 13 (2, 8, 3)
	Ca = 20 (2, 8, 8, 2)	

EXAMPLE

How was the problem of placement of isotopes in Mendeleeff's periodic table overcome in modern periodic table?

SOLUTION

Modern periodic table was based on the atomic number. Since isotopes have similar atomic numbers, the problem of placement of isotopes was solved.

Periodicity

The regular gradation in the properties of elements and their repetition at regular intervals is called periodicity. The properties which show such regular trend are called periodic properties.

Periodic Properties

(i) Atomic Size

Atomic size is defined in terms of atomic radius which is the distance between the nucleus and the valence shell. However, it is not possible to measure the atomic radius directly as an individual atom cannot be isolated.

There are two different ways of measuring the atomic radius:

(a) **Covalent radius**: The atomic size of the non-metals is determined by taking half the distance between the nuclei of two like atoms bonded together by a single covalent bond.

(b) **Metallic radius**: It is determined by taking half the distance between the nuclei of two adjacent metal atoms in a metallic crystal.

Variation of Atomic Size

(a) **Period**: The atomic size generally decreases from left to right along the period. This is because along a period the electrons are added to the same energy level, which leads to an increase in the effective nuclear charge on the outermost shell, thereby decreasing the size of the atom.

Exception: In the noble gases, due to interelectronic repulsions, the size is larger than the corresponding halogen.

(b) **Group**: On going down the group, a new shell is being added from one element to the other. As the electron is added to a shell farther from the nucleus, the effective nuclear force of attraction on the valence shell decreases thereby increasing the size of the atom.

Exception: Atomic sizes of the 5th period elements do not show much increase from the corresponding 4th period elements of same groups. This is because of the addition of 14 electrons in the antepenultimate "f" subshell of lanthanide elements. The contraction in atomic size among lanthanide elements is called lanthanide contraction.

(ii) Ionization Energy

Ionization energy of an element is the minimum amount of energy required to remove the outermost electron from an isolated neutral gaseous atom of that element in its lowest energy state to form a cation. This is called the first ionization potential.

The minimum amount of energy required to remove the electron from a gaseous atom is called its **first ionization potential**. The **second ionization potential** is the energy required to remove the electron from the outermost shell of a unipositively charged gaseous ion. Similarly, we can define

the third and the fourth ionization energies or ionization potentials. If the first ionization energy is considered as I_1 and the second as I_2 and so on then, $I_1 < I_2 < I_3 < I_4 < \ldots\ldots$ Theoretically, an atom can have as many ionization potentials as there are electrons in it.

This successive increase in the values of ionization potential is due to increase in effective nuclear charge from the neutral atom to the respective ions.

Variation of Ionization Potential

(a) Period: Ionization energy generally increases from left to right along a period. This is because along a period, the atomic size decreases and the valence shell is closer to the nucleus. Thus more energy is required to remove an electron from the valence shell.

(b) Group: The ionization energy decreases from top to bottom in a group because the atomic size increases down the group, thus resulting in decrease in the effective nuclear force of attraction.

Graphical Representation of Variation of IP with Atomic Numbers

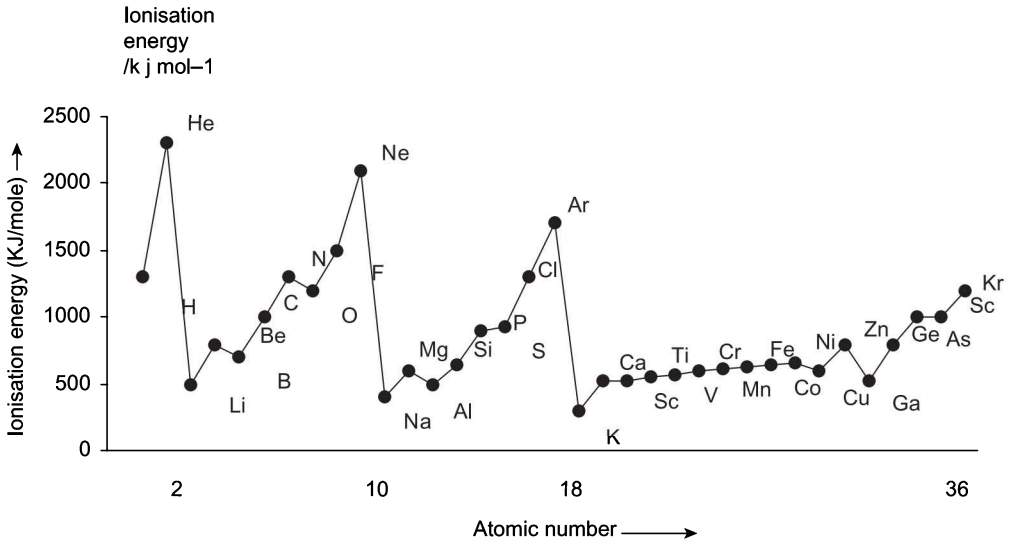


Figure 4.1 The ionization energies of the elements (hydrogen to krypton)

Conclusions from Fig. 4.1:

(a) The noble gases occupy the highest positions indicating that these have exceptionally high ionization potential values.

(b) Variation of ionization potential from nitrogen to oxygen and phosphorus to sulphur does not follow the regular trend.

(c) The variation of IP in transition metals is more regular and marginal in comparison to the representative elements.

(iii) Electron Affinity

The amount of energy released when an electron is added to an isolated neutral gaseous atom in its lowest energy state to produce an anion is called the electron affinity.

Variation of Electron Affinity

(a) Period: As the atomic size decreases and nuclear charge increases from left to right across the period, the electron affinity values generally increase.

(b) Group: The electron affinity gradually decreases from top to bottom due to the steady increase in atomic radius and the resultant decrease of effective nuclear charge.

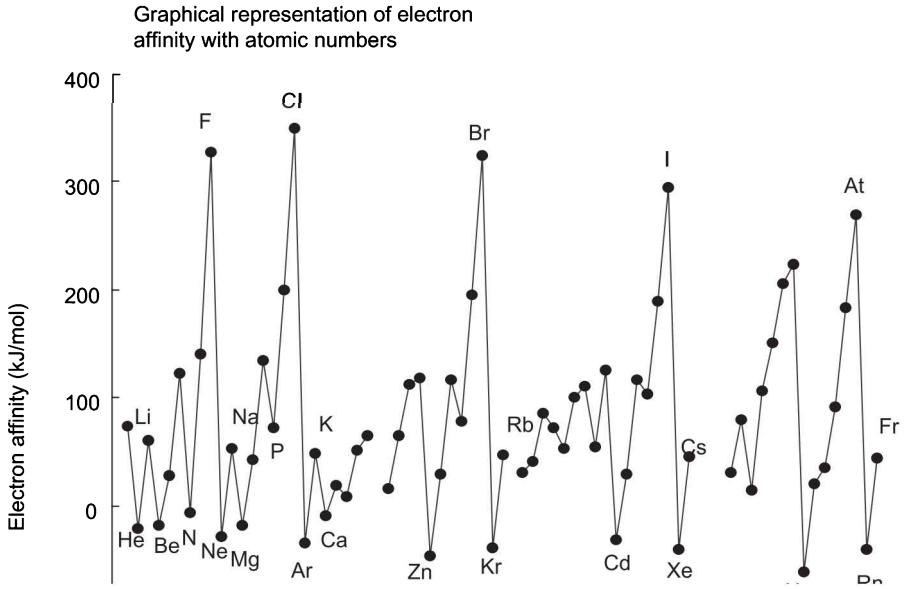


Figure 4.2 Atomic number

Conclusions drawn from Fig. 4.2:

(a) The noble gases show zero electron affinity values indicating that the addition of an electron to those atoms is not possible.

(b) The elements of IIA group show negative values for electron affinity which indicates that the addition of electron is associated with the absorption of energy.

(c) Halogens occupy the highest positions in the curve which shows maximum tendency to form negative ions.

(iv) Electronegativity

Electronegativity of an element is defined as the tendency of an atom to attract the shared pair of electrons towards itself in a bonded molecule.

Since electronegativity is a relative value, measurement of absolute value is not possible. One way of measurement of electronegativity is to take an average of ionization potential and electron affinity. In the other method, fluorine is taken as standard and the electronegativity values of other elements are calculated with respect to fluorine.

Variation of Electronegativity

(a) Period: Electronegativity increases along a period from left to right. This is due to the increase in nuclear charge and decrease in atomic size.

(b) Group: Electronegativity decreases from top to bottom in a group due to an increase in the atomic size.

(v) Electropositive Character

Electropositive character of an element is its ability to lose one or more electrons to form a positively charged ion.

The electropositive character of an element depends on its ionization potential. An element in which the atom has greater ability to lose an electron means that it has low ionization potential and high electropositivity. Such an element acts as a good reducing agent.

An element which has a high ionization potential has low electropositivity and hence cannot give out electron easily. Such an element acts as a good oxidizing agent.

Variation of Electropositive Character

(a) Period: The electropositive character decreases (the oxidizing capacity increases and the reducing capacity decreases) from left to right along a period due to the increase in ionization potential.

(b) Group: Due to the decrease of ionization potential and electron affinity down the group the electropositivity increases, oxidizing capacity decreases and reducing capacity increases.

(vi) Metallic and Non-metallic Property

Metals can generally give away electrons easily and form positive ions while non-metals generally accept electrons and form negative ions.

Variation of Metallic and Non-metallic Properties

(a) Period: As the electronegativity increases from left to right along a period, the metallic character decreases and the non-metallic character increases.

(b) Group: As the electronegativity decreases from top to bottom in a group the metallic character increases and non-metallic character decreases.

Thus the right side of the periodic table (p-block) comprises of non-metals, metalloids and metals. The left side of the table is completely occupied by metals. The middle portion (d-block) as well as the bottom portion (f-block) is comprised of metals.

This kind of distribution shows that though the periodic table is comprised of metals, non-metals and metalloids, 75% of the elements are metals. Since the metals have certain characteristic properties which clearly distinguish them from the rest of the elements, the study of metals gained significance. The metals also differ among themselves in their properties and hence they are placed in the respective positions in the periodic table.

For example, alkali metals which possess one electron in their valence shells are grouped together in group IA of the modern periodic table. Similarly, the alkaline earth metals which possess two electrons in their valence shells are placed in Group IIA of the periodic table. These two categories of metals belong to "s-" block of the periodic table.

The other two categories are transition metals and inner transition metals. These metals have certain specific properties which are not exhibited by any other groups of elements. Some of the specific properties of transition metals which clearly distinguish them from the other metals are paramagnetic nature of the atoms and ions, formation of coloured compounds and exhibition of variable oxidation states in their compounds.

Formation of Coloured Compounds

All the compounds of alkali and alkaline earth metals are colourless. However, many compounds of transition metals have their characteristic colours due to the presence of incomplete d-subshells.

Examples

$CuSO_4\ 5H_2O$	Blue
$K_2Cr_2O_7$	Orange
$KMnO_4$	Violet
$CuCl_2$	Bluish green
$FeSO_4$	Light green

These elements also do not show a regular trend in the common periodic properties studied separately. Therefore, these are placed in the "d-" block of the periodic table and are studied separately.

Comparative Study of Alkali Metals and Alkaline Earth Metals

Alkali metals and alkaline earth metals belong to "s-" block of the periodic table and they show regular gradation in the properties.

Melting and boiling points of alkali metals are lower than those of alkaline earth metals as well as transition metals to their right.

Reaction with Water

Alkali metals react vigorously with water and liberate hydrogen gas. Reaction of lithium is less vigorous:

$$M + 2H_2O \rightarrow MOH + H_2$$
(alkali metal)

Alkaline earth metals also react with water to liberate hydrogen gas:

$$M + 2H_2O \rightarrow M(OH)_2 + H_2$$
(alkaline earth metal)

The reaction is less vigorous in case of alkaline earth metals when compared to alkali metals.

Reaction with Oxygen

Alkali and alkaline earth metals burn in the presence of O_2 to give their corresponding oxides:

$$4M + O_2 \rightarrow 2M_2O$$
(alkali metals)

$$2M + O_2 \rightarrow 2MO$$
(alkaline earth metals)

Sodium (alkali metal) and barium (alkaline earth metal) also give their stable peroxides along with the oxides:

$$2Na + O_2 \rightarrow Na_2O_2$$

$$Ba + O_2 \rightarrow BaO_2$$

Reaction with Hydrogen

Alkali metals and alkaline earth metals react with H_2 and form their stable hydrides:

$$2M + H_2 \rightarrow 2MH$$
(alkali metals)

$$M + H_2 \rightarrow MH_2$$

(alkaline earth metals)

Beryllium hydride is unstable.

All the hydrides of alkali and alkaline earth metals get readily hydrolysed by water and liberate hydrogen gas.

$$2MH + 2H_2O \rightarrow 2MOH + 2H_2\uparrow$$

(alkali metals)

$$MH_2 + 2H_2O \rightarrow M(OH)_2 + 2H_2\uparrow$$

(alkaline earth metals)

Reaction with Chlorine

All the alkali metals and alkaline earth metals react with chlorine to give their corresponding chlorides:

$$2M + Cl_2 \rightarrow 2MCl$$

(alkali metals)

$$M + Cl_2 \rightarrow MCl_2$$

(alkaline earth metals)

EXAMPLE

(a) Name two elements you would expect to show chemical reactions similar to sodium.

What is the basis of your choice?

(b) Arrange the elements present in that group in the increasing order of reactivity.

Give reason.

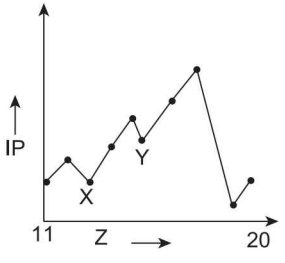
SOLUTION

(a) Lithium and potassium show same chemical properties as sodium, because all the three elements possess same number of valence electrons and belong to same group that is IA group.

(b) Increasing order of reactivity is Li < Na < K < Rb < Cs. This is due to decrease in ionization potential values from top to bottom in a group.

EXAMPLE

Teacher explained periodicity of ionization potential in a period and group with reasons. She then drew a curve of IP vs atomic number for elements with Z = 11 to Z = 20. On the basis of the curve, she asked the following questions to students.



(a) Identify the elements occupying peaks and bottommost points.

(b) Also identify 'X', and 'Y' marked in the curve.

(c) In what respect 'X' and 'Y' deviate from their preceeding elements?

When students answered these correctly, she was satisfied and told – "Now, I will give you a brain teaser to get me answer by next chemistry class". Students enthusiastically said – "yes"! Then teacher wrote the following question on board __

(d) "Why do 'X' and 'Y' show deviations from their preceeding elements in the trend of IP values"? What explanation would you give if you were there in the class?

SOLUTION

(a) Peak is occupied by noble gas, Ar. Bottom most point is occupied by alkali metal, K.

(b) 'X' is aluminium and 'Y' is sulphur

(c) Generally, with increase in atomic number, IP value should also increase. However, from magnesium to aluminium, IP value decreases. Similarly, from phosphorus to sulphur, IP value decreases.

(d) In magnesium, there is a pair of electrons in 3s orbital. Removal of electron is slightly more difficult. Moreover, since the electron to be removed belongs to 's' subshell having greater penetrating power, the IP value is relatively higher. In case of aluminium, there is an unpaired 'p' electron, the removal a which is easier. Hence IP value is less.

EXAMPLE

Ionization energy is the energy absorbed whereas electron affinity is the energy released. Explain.

SOLUTION

When an electron is present in the outermost shell of an atom, it is bound by nuclear force of attraction. In order to remove this electron, some amount of energy should be supplied to overcome the nuclear force of attraction. During the addition of an electron to a neutral atom, the electron approaches to a neutral atom due to nuclear force of attraction. This process involves work done towards the force of attraction and hence energy is released. Thus, ionization potential is the energy absorbed and electron affinity is the energy released.

EXAMPLE

(a) One mole of atoms of an element 'X' absorb 800 kJ of energy for the formation of unipositive ions. For the convertion of one mole of 'X' atoms into tripositive ions, 6800 kJ of energy is required. Second and third ionization energies are in 2 : 3 ratio. Calculate the 2^{nd} and 3^{rd} ionization energies.

(b) First and second ionization energies of $Be_{(g)}$ are 900 $kJmol^{-1}$ and 1750 $kJmol^{-1}$ respectively. Calculate approximate percentage of $Be^{2+}_{(g)}$ ions, if 1 g of $Be_{(g)}$ absorbs 150 kJ of energy [Be atomic weight is 9].

SOLUTION

(a) $x \rightarrow x^{+}$, 800 kJ/mol (IP_1)

$x \rightarrow x^{+3}$, 6800 kJ

$\therefore IP_1 + IP_2 + IP_3 = 6800 \text{ kJ} \Rightarrow IP_2 + IP_3 = 6800 - 800 = 6000$

$x^{+} \rightarrow x^{+2}$ IP_2; $x^{+2} \rightarrow x^{+3}$ IP_3

$\because IP_2 : IP_3 = 2 : 3 \Rightarrow \dfrac{IP_2}{IP_3} = \dfrac{2}{3}$

$\Rightarrow IP_2 = \frac{2}{3} . IP_3$ or $IP_3 = \frac{3IP_2}{2}$

$\Rightarrow IP_2 + IP_3 = 6000$

$\Rightarrow IP_2 + \frac{3}{2} . IP_2 = 6000 \Rightarrow 2\ IP_2 + 2\ IP_3 = 6000 \times 2$

$IP_2 = \frac{6000}{5} \times 2 = 2400$ kJ/mol; $IP_3 = \frac{6000}{5} \times 3 = 3600$ kJ/mol

(b) 1 mole (9 g) of beryllium requires 900 kJ to dislodge the 1st electron.

$\therefore$ 1 g of Be requires $= \frac{1 \times 900}{9} = 100$ kj

$\therefore$ Difference in the amount of energy absorbed = 150 – 100 = 50 kJ

To dislodge the 2nd electron from 1 mole of Beryllium ion, 1750 kJ is required.

50 kJ is sufficient for $\frac{50}{1750} \times 9 = 0.25 = 25\%$

Percentage of $Be^{2+}_{(g)}$ ions is 25%.

EXAMPLE

The ionic size of Cl^- is greater than that of K^+ ion, though they are isoelectronic. Explain.

SOLUTION

Nuclear forces of attraction on valence electrons is higher in K^+ ion, than in that in Cl^-. This is due to the greater nuclear charge of K^+ ion. So ionic size of Cl^- ion is greater than that of K^+ ion.

EXAMPLE

A sharp change in the atomic radius is observed from lithium to potassium but a gradual change in the atomic radius is observed from potassium to caesium. Explain.

SOLUTION

A sharp increase in the atomic radius is observed from lithium to potassium due to increase in the number of shells. But a gradual change is observed from potassium to caesium due to filling up of d electrons, in the pennultanate shell which increases the effective nuclear charge. Hence increase in size is gradual, not sharp.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. Why did Mendeleeff arrange the elements in the increasing order of their atomic weight in his periodic table?
2. How was the problem of placement of isotopes in Mendeleeff's periodic table overcome in the modern periodic table?
3. Why did Newland's law of octaves fail?
4. Zero group elements are known as _____ gases.
5. Why are the "s-" and "p-" blocks elements called representative elements?
6. General electronic configuration of s-block elements is _____.
7. Describe the trend of oxidizing and reducing property along a period and a group of the periodic table.
8. Name the elements whose atomic weight was corrected by Mendeleeff.
9. Describe the trend of electron affinity along a period.
10. Describe the trend of atomic size along a period and a group in the periodic table.
11. Which periods are called the short periods and which are called the long periods? Why?
12. Describe the trend of ionization potential along a period and a group in the periodic table.
13. Why are the chemical properties of the elements belonging to the same group similar?
14. Why is it that hydrogen can be placed in both I A group and VII A group of the modern periodic table?
15. An element, the atomic number with 36 belongs to _____ group and _____ period.
16. What do you mean by representative elements? Give an example.
17. Which group contains the noble gases and what are the special characteristics of these gases?
18. General electronic configuration of chalcogens is _____.
19. Describe the trend of ionization potential down the group in the periodic table.
20. Describe how the metallic and non-metallic characters vary along a period and group of the periodic table.
21. The elements present in _____ and _____ periods can exhibit diagonal relationship.
22. Ionization potential value of Cs is equal to the electron affinity value of its corresponding _____.
23. _____ block elements can exhibit variable number of oxidation states.
24. What is a covalent radius?
25. In the long form of periodic table _____ group contains the maximum number of elements.
26. Anion size is always _____ than the parent atom.
27. How does the electron affinity vary in the first transition series?
28. In the f-block elements differentiating electron enters into f-orbital of _____ shell.
29. _____ group elements are the strongest reducing agents.
30. What is metallic radius? Give the implication of measuring a metallic radius.

Short Answer Type Questions

31. What are the merits of Mendeleeff 's periodic table?
32. What are the achievements and the limitations of Newland's classification?
33. What are the advantages of the classification of elements?
34. Why are the lanthanides and the actinides given a separate position in the modern periodic table?
35. Are all the elements present in III B of same type? Explain.

PRACTICE QUESTIONS

36. Describe how effective nuclear charge changes along a period and a group in a periodic table.
37. Why is the modern periodic table also referred to as Bohr's table?
38. Why are the values of the first, the second, the third ionization energies different from each other?
39. How does electron affinity vary in halogens?
40. What is the basic difference between Mendeleeff's periodic table and modern periodic table?
41. Among all the periods which one is incomplete and what are the main important properties exhibited by all the elements present in this period?
42. What is the difference between electronegativity and electropositivity?
43. Mention different categories of elements in the long form of the periodic table.
44. What is the difference between transition and inner transition elements?
45. How does filling of valence electrons takes place in p-block, d-block and f-block elements?

Essay Type Questions

46. What are the merits and limitations of the long form of the periodic table?
47. Describe briefly Mendeleeff 's periodic table along with its merits.
48. What are the limitations of Mendeleeff 's periodic table?
49. Explain briefly the periods of the modern periodic table.
50. Explain briefly about the groups of the modern periodic table and also classify the elements depending on electron filling in s-, p-, d- and f-subshells along with the position in the periodic table.

CONCEPT APPLICATION

Level 1

Direction for questions from 1 to 7: **State whether the following statements are true or false.**

1. Modern periodic table is based on atomic number.
2. In a period, the first element has the smallest size.
3. "s" and "p" block elements except zero group are known as representative elements.
4. The inert gas present in the second long period is Xe.
5. Among the isoelectronic ions Na^+, Mg^{2+} and Al^{3+}, Na^+ ion have the largest size.
6. Alkali metals act as strong reducing agents by undergoing reduction.
7. Electronegativity is the property of an atom in a bonded molecule.

Direction for questions from 8 to 14: **Fill in the blanks.**

8. In the periodic table, vertical columns of elements are called _____ and horizontal rows of elements are called _____.
9. In the long form of the periodic table, _____ group elements can release maximum amount of energy by the addition of electron into its valence shell.
10. The ascending order of the first ionization potential of C, N, O and F is _____.
11. The total number of inner transition elements present in the 7th period are _____.
12. Amongst the species Br^-, Br, Br^+, the smallest one in size is _____.

13. In most of the lanthanides, the penultimate shell contains _____ electrons in _____orbitals.

14. Metals exhibit _____ oxidation states in their compounds.

Direction for question 15: **Match the entries in column A with the appropriate ones in column B.**

15.

Column A	Column B
A. s-block	( ) a. Radioactive metal
B. Fluorine	( ) b. Highest first IP value
C. Chlorine	( ) c. Lanthanides
D. d-block	( ) d. Highly reactive metals
E. 4f-series	( ) e. Heavy metals
F. Helium	( ) f. Always form –1 oxidation state
G. Francium	( ) g. Highest electron affinity value
H. Noble gases	( ) h. Zero group elements

Direction for questions from 16 to 45: **For each of the questions, four choices have been provided.**

Select the correct alternative.

16. ***Assertion*** (A): First ionization energy of beryllium is greater than that of boron.

Reason (R): Boron has larger size than beryllium.

(a) Both A and R are true and R is the correct explanation of A.

(b) Both A and R are true and R is not the correct explanation of A.

(c) A is true, R is false

(d) A is false, R is true

17. Which of the following properties is a periodic property?

(a) colour (b) melting point

(c) refractive index (d) atomic size

18. Which one of the following electronic configurations corresponds to the most electropositive character?

(a) $[He]2s^1$ (b) $[Ne]3s^1$

(c) $[Ar]4s^1$ (d) $[Xe]6s^1$

19. The general electronic configuration of representative elements is

(a) $ns^{1-2}\ np^{1-6}$ (b) $ns^{1-2}\ np^{1-5}$

(c) $ns^{1-2}\ (n-1)p^{1-5}$ (d) $ns^{1-2}\ (n-1)p^{1-6}$

20. Predict the formula of a compound formed between a metal "M" which has 1st, 2nd, 3rd IP values as 518, 7314, 9820 kJ mol^{-1}, respectively and a halogen "X."

(a) MX_2 (b) M_2X_3

(c) MX_3 (d) MX

21. In a period, from the left to right the electron affinity increases, but alkaline earth metals have lower electron affinity than alkali metals because

(a) alkaline earth metals have lesser atomic radius than alkali metals.

(b) alkaline earth have higher electronegativity than alkali metals.

(c) alkaline earth metals have completely filled "s-" orbitals.

(d) alkaline earth metals have lesser electronegativity than alkali metals.

22. 5f series elements are known as

(a) lanthanides

(b) representative elements

(c) transition elements

(d) actinides

23. The first ionization energies of Li, Be, B and C are in the order:

(a) Li > Be < B < C

(b) Li < Be > B < C

(c) Li > Be > B > C

(d) Li < Be > B > C

24. Predict the powerful oxidizing agent in the 3rd period:

(a) sulphur (b) sodium

(c) chlorine (d) bromine

25. An element with atomic number "32" belongs to

(a) 4th period, VIA group

(b) 3rd period, IVA group

(c) 4th period, IVA group

(d) 5th period, VA group

26. The element having the electronic configuration $[Kr]\ 4d^{10}\ 4f^{14}\ 5s^2\ 5p^6\ 5d^2\ 6s^2$ belongs to

(a) s-block (b) p-block

(c) d-block (d) f-block

PRACTICE QUESTIONS

27. The number of valence electrons that can be present in the second element of any period is
(a) 1 (b) 2
(c) 5 (d) 7

28. Transition metals can exhibit variable valency. It is because of
(a) the smaller atomic radius
(b) the high screening effect
(c) the very less energy difference between (n−1) d-subshell and ns-subshell
(d) the high nuclear charge

29. Arrange O, F, Cl and N in the descending order of their electronegativity:
(a) O > F > Cl > N (b) F > O > Cl > N
(c) F > N > O > Cl (d) Cl > Fl >O > N

30. In the sixth period, the orbitals which are completely filled are
(a) 6s, 6p, 5d, 5f (b) 6s, 6p, 6d, 6f
(c) 6s, 5f, 6d, 6p (d) 6s, 4f, 5d, 6p

31. Which of the following sequence of explanation is appropriate for explaining the reason for the periodicity of reducing property in a period or group?
(1) Tendency to undergo oxidation decreases in a period and increases in a group.
(2) In a period ionization energy increases and in a group it decreases.
(3) In a period the atomic size decreases and in a group it increases.
(4) The elements present in the left side of the periodic table have strong reducing property.
(a) 3 2 1 4 (b) 3 4 2 1
(c) 4 3 1 2 (d) 4 2 1 3

32. Which of the following triads does not follow Dobereiner's law of triads?
(a) Li, Na, K (b) Ca, Sr, Ba
(c) Be, Mg, Ca (d) Cu, Ag, Au

33. X belongs to IA or 1^{st} group and 5^{th} period and Y succeeds X in the group. Z succeeds Y in the period. Arrange the following statements in the correct sequence in order to arrange X, Y and Z in the increasing order of their atomic sizes.
(1) Effect of number of valence electrons and number of shells on the atomic size.
(2) Identification of the elements X, Y and Z.
(3) Determination of the number of shells and the number of valence electrons present in X, Y and Z.
(4) Determination of the positions of Y and Z in the periodic table based on the position of X.
(a) 4 2 3 1 (b) 2 4 3 1
(c) 3 1 4 (d) 4 3 1

34. Which among the following is not an anomalous pair in Mendeleeff 's periodic table?
(a) Co, Ni (b) Te, I
(c) Ar, K (d) Sc, Ga

35. The energy released when an electron is added to the valence shell of a neutral, gaseous, isolated atom is called _____
(a) electronegativity (b) ionization potential
(c) electron affinity (d) lattice energy

36. Which one of the following electronic configuration corresponds to the element with maximum electropositive character?
(a) $[Kr]5s^1$ (b) $[Ne]3s^1$
(c) $[Ar]4s^1$ (d) $[Xe]6s^1$

37. Which of the following elements has maximum electronegativity?
(a) P (b) S
(c) Al (d) Si

38. Which of the following elements acts as the best reducing agent?
(a) Na (b) Cl
(c) Mg (d) F

39. The elements present in d-block are
(a) metals and non-metals
(b) only metals
(c) only non-metals
(d) metals, metalloids and non-metals

40. The total number of elements present in the 6th period is
(a) 18 (b) 31
(c) 32 (d) 17

41. An element with atomic number "32" belongs to
(a) 4^{th} period, VIA group or 16^{th} group
(b) 3^{rd} period, IVA group or 14^{th} group
(c) 4^{th} period, IVA group or 14^{th} group
(d) 5^{th} period, VA group or 15^{th} group

42. The formulae of oxides formed when barium burns in presence of oxygen are
(a) Ba_2O, BaO (b) BaO, BaO_2
(c) BaO, Ba_2O_2 (d) Ba_2O, BaO_2

43. If the consecutive ionization energies of an element A are 496, 4564, 6918, 9542 kJ/mole respectively, the formula of the oxide formed by A is
(a) A_2O_3 (b) AO
(c) AO_2 (d) A_2O

44. The numerical value of ionization energy of a unipositive ion is approximately equal to
(a) IP value of neutral atom
(b) EA value of neutral atom
(c) IP value of dipositive ion
(d) EA value of dipositive ion

45. Which of the following sets of atomic numbers corresponds to elements belonging to s-, d-, f-, p-blocks respectively?
(a) 35, 37, 29, 70 (b) 35, 29, 70, 37
(c) 37, 29, 70, 35 (d) 37, 29, 35, 70

Level 2

1. Why is the atomic radius of oxygen slightly more than that of nitrogen?
2. Predict the position of an element with atomic number 55 in the periodic table and explain the chemical behaviour of that element.
3. Why is electron affinity of chlorine more than that of fluorine?
4. The ionic size of Cl^- is greater than that of K^+ ion, though they are isoelectronic. Explain.
5. Why do most of the inner transition elements exhibit stable +3 oxidation state?
6. Xenon has an octet configuration in the valence shell but it shows variable valency with the highly electronegative elements like oxygen and fluorine. Comment.
7. Though oxygen and sulphur belong to the same group, sulphur shows many oxidation states, whereas oxygen does not show a higher oxidation state than that of –2. Comment.
8. First and second ionization energies of $Be_{(g)}$ are 900 kJ mol^{-1} and 1750 kJ mol^{-1} approximately. Calculate approximate percentage of $Be^{2+}_{(g)}$ ions, if 1 g of $Be_{(g)}$ absorbs 150 kJ of energy [atomic weight of Be is 9].
9. The separation of one lanthanide from another is an extremely difficult task, almost as difficult as the separation of isotopes of one element. Justify.
10. A sharp change in the atomic radius is observed from lithium to potassium but a gradual change in the atomic radius is observed from potassium to caesium. Explain.
11. In a particular transition series, the atomic radius reaches minimum up to group VIII elements, then again increases towards the end of the series. Give appropriate reasons.
12. Ionization potential decreases down the group in representative elements while transition elements of the 6th period have greater ionization potential values compared to the elements of the 5th period. Justify.
13. The densities of transition metals are greater than the alkali and alkaline earth metals. Justify.
14. Successive ionization potentials of an element "X" are IP_1 = 520 kJ mol^{-1}, IP_2 = 7,298 kJ mol^{-1} and IP_3 = 10,815 kJ mol^{-1}. Give the probable formulae of chloride and oxide of "X."
15. An element "A" has atomic number 28. What is the electronic configuration of the elements below it in the periodic table? Predict their chemical properties.

Directions for questions from 16 to 25: **Application-Based Questions**

16. When a Dobereiner triad is considered, the sum of atomic weights of extreme elements X and Z is 177.6 and difference of Z and Y is five times the number of protons present in a neon atom. Identify X, Y and Z.
17. Iron can form two types of ions. Compare the ionic sizes of the respective ions.
18. Three elements A, B and C have atomic numbers as x, x + 1 and x + 2. The atomic size of C is greater than that of B but atomic size of B is less than that

PRACTICE QUESTIONS

of A. Predict the positions of A, B and C in the periodic table and justify the trend in atomic size.

19. A teacher while explaining the definition of ionization potential gave an example: Ionization potential value of sodium is 140 kJ/mole. That means, 140 kJ of energy is required to remove the lone electrons from "3s" orbitals of one mole of gaseous sodium atoms. Then, a student Rinku stood up immediately and asked: sodium is a solid metal. Why should we consider it in gaseous state? What explanation would have been given by the teacher?

20. Formation of X^- ion from "X" is associated with the release of 144 kJ/mole energy. However, formation of X^{-2} ion from X^- is associated with the absorption of 840 kJ of energy. How do you account for this?

21. A tripositive ion of element "X" has six electrons with l = 0 and five electrons with l = 2.

(a) Predict the group and period to which "X" belongs.

(b) Does the element show variable valencies? Justify.

22. Identify the position of the elements having outer electronic configuration:

(a) $ns^2\ np^5$ for n = 3

(b) $(n-1)d^2\ ns^2$ for n = 4

23. The steady decrease in size of lanthanide elements and their ions is called lanthanide contraction. In lanthanide elements, the differentiating electron enters into antepenultimate "f-" subshell.

(a) How does the entry of differentiating electron into antepenultimate shell affect the atomic and ionic sizes?

(b) Densities of 6th period elements are double to those of 5th period elements. Why?

24. An element "X" has three completely filled shells and forms a stable uninegative ion and the total number of electrons in the third and fourth shells is same. Identify the elements which form unipositive and dipositive ions which are isoelectronic with X^- ion. Compare the reactivities of these two elements with water. Give a reason in support of your answer.

25. Why are the electron affinities of alkaline earth metals positive?

$$M_{(g)} + e^- \rightarrow M^-_{(g)}\ \Delta H = +\ \text{(Electron affinity)}$$

Level 3

1. Generally transition elements form coloured compounds. But Sc^{+3} forms colourless compounds. Justify.

2. The first ionization energy of magnesium is greater than that of sodium, whereas the reverse is true for second ionization energy. Explain.

3. Why do some of the periodic properties like atomic size, electronegativity and ionization potential of transition and inner transition elements not show as much variation as the representative elements?

4. Why are the electron affinities of IIA group and IIB group elements less than zero?

5. The density of elements belonging to the 3rd transition series is double that of the elements belonging to the 2nd transition series provided they are in the same group unlike alkali and alkaline earth metals. Comment.

Directions for questions from 6 to 10: **Application-Based Questions**

6. In the d-block elements as we move along a period the atomic radius decreases in the beginning, reaches minimum and then increases towards the end of the series. Explain with appropriate reasons.

7. Why are the values of electron affinity of the IIA group and IIB group elements less than zero?

8. Why do some of the periodic properties like atomic size, electronegativity and ionization potential of transition and inner transition elements do not show as much variation as the representative elements?

9. Three elements X, Y and Z have atomic numbers 22, 40 and 72, respectively. Comment on the trend of change in ionization potential values from X to Y and Y to Z.

10. There is a sharp decrease in the ionization energies from boron to aluminium but it is almost the same from aluminium to gallium. Justify.

CONCEPT APPLICATION

Level 2

True or false

1. True
2. False
3. True
4. True
5. False
6. True
7. True

Fill in the blanks

8. groups, periods
9. VII
10. C, O, N, F
11. 14
12. Br^+
13. 8, s, p
14. Positive

Match the following

15. A : d
B : f
C : g
D : e
E : c
F : b
G : a
H : h

Multiple choice questions

16. b
17. d
18. d
19. c
20. d
21. c
22. d
23. b
24. **c**
25. c
26. c
27. b
28. c
29. b
30. d

Solutions for questions from 31 to 45:

31. (i) In a period the atomic size decreases and in a group it increases.
(ii) In a period ionization energy increases and in a group it decreases.
(iii) Tendency to undergo oxidation decreases in a period and increases in a group.
(iv) The elements present in the left side of the periodic table have strong reducing property.

32. Since the atomic weight of Ag is not equal to the mean of the atomic weights of Cu and Au, (Cu, Ag and Au) triad do not follow Dobereiner's law of triads.

33. (i) Determination of the positions of Y and Z in the periodic table based on the position of X.
(ii) Determination of the number of shells and the number of valence electrons present in X, Y and Z
(iii) Effect of number of valence electrons and number of shells on atomic size.

34. In case of first three pairs, the atomic weights of latter elements are greater than the former elements; so, they are called anomalous pairs. The last pair is not an anomalous pair.

35. Electron affinity is defined as the amount of energy released when an electron is added to the valence shell of gaseous, neutral and isolated atom.

36. Electropositive character increases from top to bottom in a group. Hence the element with electronic configuration [Xe] $6s^1$ has the maximum electropositive character.

37. Electronegativity increases from left to right in a period. Hence, S has the maximum value.

38. Sodium belongs to IA group which are good reducing agents.

39. All d-block elements are metals.

40. The total number of element present in the 6th period is 32 elements including 14 lanthanides.

41. Z = 32 corresponds to germanium which belongs to the IVA group (or) 4th group and 4th period. Electronic configuration is [Ar] $3d^{10}\ 4s^2\ 4p^2$.

HINTS AND EXPLANATION

42. $2Ba + O_2 \rightarrow 2BaO$ (Barium oxide)

$Ba + O_2 \rightarrow BaO_2$ (Barium peroxide)

43. In element A there is a large difference between I and II ionization energies; so, it can form the stable ion A^+. The oxide of A would be A_2O.

44. The numerical value of ionization energy of a unipositive ion is approximately equal to the electron affinity of dipositive ion.

45. Electronic configuration of an element with atomic number 37 is [Kr] $5s^1$. 29 is [Ar] $3d^{10}$ $4s^1$, 70 is [Xe] $4f^{14}$ $5d^0$ $6s^2$. 35 is [Ar] $3d^{10}$ $4s^2$ $4p^5$.

Hence, 37, 29, 70 and 35 belong to s, d, f and p, respectively.

Level 2

1. (i) comparing electronic configuration of nitrogen and oxygen
(ii) electronic arrangement in the valence shell of nitrogen and oxygen
(iii) relation between the electronic arrangement and the stability of the atom
(iv) effect of stability on size of the atom

2. (i) electronic configuration of the element and predict group and period
(ii) correlation between the position of the element in the periodic table and its chemical behaviour

3. (i) factors affecting electron affinity
(ii) electronic configuration of chlorine and fluorine
(iii) comparison of the number of valence electrons with respect to the atomic size between chlorine and fluorine

4. (i) nuclear charge is different in two ions
(ii) effect of nuclear charge on the size of the atom

5. (i) electronic configuration of inner transition elements, entry of differentiating electron
(ii) comparison of energy of valence shell and that of penultimate shell
(iii) participation of penultimate shell electrons in bonding

6. (i) Xenon belongs to the 5th period.
(ii) atomic size of xenon in comparison to the other noble gases
(iii) comparison of influence of electronegativity of fluorine and oxygen

7. (i) comparison of electronic configuration of oxygen and sulphur
(ii) presence of vacant "d" subshell and scope for excited state configuration

8. (i) amount of energy absorbed by1 g of Be to form Be^+ and Be^{+2}
(ii) energy required for conversion of 1 g $Be_{(g)}$ into Be^+ ions
(iii) calculation of additional amount of energy
(iv) conversion of Be^+ ions to Be^{+2} ions
(v) 25%

9. (i) differentiating electron of lanthanides
(ii) lanthanide contraction and its effect on atomic and ionic sizes of lanthanide elements
(iii) dependence of chemical properties on the atomic sizes
(iv) properties exploited for separation of different elements

10. (i) factors affecting the atomic radius
(ii) the effect of increase in inner shells on atomic radius

11. (i) electron filling in transition elements
(ii) effect on effective nuclear charge
(iii) relation between effective nuclear charge and atomic radius
(iv) comparison of electronic configuration in (n – 1) d subshell of the transition elements of each group
(v) effect on atomic size

12. (i) factors effecting ionization potential
(ii) comparison of the screening effects of s, p, d and f electrons

13. (i) factors affecting density
(ii) comparison of electron filling in alkali, alkaline earth and transition metals
(iii) effect on atomic size
(iv) comparison of mass with respect to atomic volume among alkali, alkaline earth and transition metals

14. (i) comparing IP values; valency of X
(ii) abrupt change in IP value
(iii) valence electronic configuration of stable ion
(iv) valencies of the corresponding positive and negative radicals

15. (i) electronic configuration of element A
(ii) electronic configuration corresponding to Z = 28
(iii) position of A in the periodic table
(iv) position of the element present below A in the periodic table and its electronic configuration
(v) determination of the properties from its position

Solutions for questions from 16 to 25: **Application-Based Questions**

16.

$$\begin{array}{l} x + z = 177 \times 6 \\ z - y = 5 \times 10 \\ \underline{(-)(+)\quad -} \\ x + y = 127.6 \end{array} \qquad \begin{array}{r} 177.6 \\ \underline{50.0} \\ 127.6 \end{array}$$

As X, Y and Z form Dobereiner triad

$y = \frac{x+z}{2}$, where x, y and z are atomic masses of X, Y and Z, respectively.

$$y = \frac{177.6}{2} = 88.8$$

$x = 127.6 - 88.8 = 38.8$

$z = 177.6 - 38.8 = 138.8$

$x = 38 \times 8 \approx 40$

$X = 40 \Rightarrow Ca$

$Y = 88 \times 80 \Rightarrow Sr$

$Z = 138 \times 6 \Rightarrow Ba$

17. Both Fe^{2+} and Fe^{3+} have the same number of protons but the number of electron in Fe^{3+} is less than that of Fe^{2+}. Hence the effective nuclear charge is more in the case of Fe^{3+} and thereby the ionic size of Fe^{3+} is less than that of Fe^{2+}.

18. As the atomic numbers of A, B and C differ by 1 unit each they must be belonging to adjacent groups. Along a period the atomic size decreases till the VII A group and then increases till the zero group. As the atomic size of C is greater than B though it differs by one unit in its atomic number it must be a zero group element. Though the atomic number of B is greater than A, it has smaller size than B and this shows that B is a halogen, i.e., VII A group and A is a chalcogen, i.e., VI A group.

19. For any element, ionization potential is considered for gaseous state only. Ionization potential corresponds to the energy required to overcome the force of attraction exerted by the nucleus on the electron without considering any other kinds of attractions. In gaseous state, the intermolecular forces of attractions being negligible, removal of electron from a neutral gaseous atom involves an amount of energy equal to IP only. In solid and liquid states, the intermolecular forces of attraction are stronger and the energy required to remove electron involves not only IP but also the energy required to overcome the other forces. Thus, for any element, IP is considered only for the isolated gaseous atoms irrespective of the state in which it exists.

20. During the addition of an electron to a neutral atom, work is done towards the nuclear force of attraction. Hence, energy is released. After the addition of an electron, the uninegative species formed, repels the 2nd electron. Hence during the addition of the second electron, work is done against the force of repulsion which requires supply of energy.

21. (a) $l = 0$ corresponds to "s" subshell and $l = 2$ corresponds to "d" subshell. Further, 6 electrons in "s" subshell and 5 electrons in "d" subshell means the ion should have the electronic configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$. Since it is a tripositive ion, the atom could have lost two electrons from 4s subshell and one electron from 3d subshell. Therefore, atomic number is 26. Electronic configuration is [Ar] $3d^6\ 4s^2$. It belongs to the VIII group and 4th period.

(b) Yes. Since Fe is a transition element it shows variable oxidation state. In transition elements, the electrons enter into the penultimate shell instead of valence shell. Energy difference between ns and (n – 1)d orbitals is very less. Hence both ns and (n – 1)d electrons are available for chemical bond formation. So, they exhibit variable valency.

22. (a) ns^2, np^5 for n = 3
$1s^2$, $2s^2$, $2p^6$, $3s^2$, sp^5
So, the period is 3rd and the group is 17th (VII A).

(b) $(n-1)\ d^2\ ns^2$ for n = 4
$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^2$
So, the period is 4th and the group is 4^{th} (IV B).

23. (a) In lanthanide elements, the newly added electron enters into anti-penultimate shell keeping the configuration of penultimate and valence shells same. The addition of electrons to inner shell should result in increased screening effect. But the "f-" subshell has a very poor screening effect. So, the addition of electrons to the inner "f-"" subshell does not result in corresponding increase in atomic size. Therefore, the increasing nuclear charge from cerium to lutetium (71) results in drastic decrease in atomic and ionic sizes.

(b) Between the 5th and 6th periods, the intervening lanthanides increase the nuclear charge and lanthanide contraction results in decrease of atomic size. As a result of this, mass of atom increases and atomic size decreases. This results in drastic increase in density of elements from the 5th to 6th periods.

24. The element "X" must be a halogen since it forms the stable X^- ion. As there are three completely filled shells in "X," the electronic configuration of "X" could be 2, 8, 18, 18, 7 and X^- is 2, 8, 18, 18, 8. Since there are 54 e^-s in X^-, the corresponding elements which form unipositive and dipositive ions should be cesium (55) and barium (56). Cesium reacts more vigorously with water than barium. This is because reactivity of alkali metals is more due to their greater atomic size when compared with alkaline earth metals. Moreover, alkaline earth metals have greater IP values than alkali metals. Hence, they react slowly with water.

25. All the electrons present in alkaline earth metals are paired. Therefore to add one extra electron to these atoms, work has to be done against the force of repulsion. Hence electron affinity of an alkaline earth metal is a positive.

Level 2

1. (i) electronic configuration of Sc
(ii) energy difference among the orbitals of "d-" subshell.
(iii) basic principle behind exhibition of colour
(iv) comparison of electronic configuration of alkali, alkaline earth and transition metals
(v) electronic configuration of Sc+3
(vi) comparison of electronic configuration of scandium ion with other transition metal ions

2. (i) electronic configuration of sodium and magnesium
(ii) comparison of atomic size of sodium and magnesium
(iii) effect of atomic size on first ionization energy
(iv) electronic configuration of stable ions of sodium and magnesium
(v) relation between the stability of ion and the respective ionization energy

3. (i) shell into which the differentiating electron enters
(ii) general electronic configuration of representative elements
(iii) comparison with general electronic configurations of transition and inner transition elements
(iv) comparison of effective nuclear charge and its effect on the periodic properties

4. (i) electronic configuration of II A and II B
(ii) change in energy that takes place due to the addition of electron to the neutral atom of the elements belonging to the Groups IIA and IIB
(iii) relation between change in energy and electron affinity values

5. (i) factors affecting density
(ii) general trend of atomic sizes in groups of transition elements
(iii) effect of inclusion of lanthanide elements on the atomic size of the elements belonging to the 3rd transition series
(iv) factors affecting the density of an atom
(v) change in atomic size of alkali and alkaline earth metals along the group
(vi) comparison of change of densities along the group among alkali, alkaline earth and transition metals

Solutions for questions from 6 to 10: **Application-Based Questions**

6. In a particular series of d-block elements, electron filling takes place in the penultimate shell. Hence their atomic size decreases up to the 7^{th} group and reaches minimum and then again increases because with the pairing of electrons, repulsive force also increases. The repulsion among the added electrons exceeds the increased force of attraction (due to

the increase of nuclear charge) after the 8th group. Hence, atomic radius increases slightly.

7. Electronic configuration of II A and II B group elements is ns^2np^0. Addition of an electron to these elements requires energy to overcome repulsive forces between completely filled ns electrons and electron going to be added. Hence, electron affinity values are less than zero.

8. In case of representative elements, from left to right in a period, the nuclear charge increases with increase in atomic number. Since the number of inner shells and inner electrons remain constant, the increased effective nuclear charge decreases the atomic size proportionately. In case of transition and inner transition elements, the electrons are being added to the penultimate and anti-penultimate shells, respectively. There is slight increase in screening effect which counterbalances the increased nuclear charge to some extent and hence the decrease in atomic size is less pronounced than in representative elements. Since the other properties in turn depend on atomic size, they also show the same trend as atomic size.

9. The respective elements X, Y and Z are Ti, Zr and Hf. They belong to IVB group of 3d, 4d and 5d series of transition elements, i.e., 4th period, 5th period and 6th period. As they belong to same group and the value of ionization potential decreases down the group, the same trend follows from Ti to Zr. However, the IP value of Hf is double to that of Zr. This is because of intervening lanthanide elements which cause lanthanide contraction. As there is no pronounced increase in atomic size due to lanthanide contraction, the increased nuclear charge increases the effective nuclear force of attraction drastically. Thus, there is a drastic increase in IP value.

10. Among IIIA group elements, boron has the highest ionization potential due to smaller size. The sharp decrease in ionization energy from boron to aluminium is due to increase in atomic radius. The atomic radius increases due to decrease in effective nuclear charge. In gallium contraction in atomic size is significant due to the presence of completely filled d-electrons in the penultimate shell. Thus, the effective nuclear charge increases. Hence both aluminium and gallium have almost equal ionization energy values.

Chapter

5

Chemical Bonding

Remember

Before beginning this chapter, you should be able to:

- understand the relation between electronic configuration and bond formation.
- represent bonds by Lewis dot structures

Key Ideas

After completing this chapter, you should be able to:

- understand the concept of ionic character in covalent bond and covalent character in ionic bond
- study the properties of ionic and covalent compounds in correlation with the type of bond present in them
- explain Lewis theory of covalent bond formation on the basis of octet rule and exceptions to octet rule
- introduce the concept of orbital overlapping to overcome the drawbacks of Lewis theory
- illustrate the theory of hybridization
- correlate the shapes of molecules with the concept of VSEPR theory
- compare various types of non-bonded forces of attraction and their relative strengths
- understand the concept of metallic bond and its effect on properties of metals
- describe the electronic concept of oxidation and reduction

INTRODUCTION

Nature is invariably associated with numerous chemical reactions. It is an established fact that an atom is the smallest particle which takes part in a chemical reaction. Nevertheless, most of the elements exist in combined state in the form of molecules. Only in case of very few elements namely noble gases, the atom has an independent existence. The existence of these elements in atomic state is attributed to the high stability associated with the completely filled octet or duple configuration in their valence shells. Obviously, the atoms of other elements have an inherent tendency to attain the above configuration by means of bond formation. This is known as an octet rule envisaged by Lewis theory. The process of bond formation is associated with the decrease in the energy of the system. This lowest energy state corresponds to the most stable state of the system. Different types of bond formation takes place depending on the nature of participant atoms.

IONIC BOND

An ionic bond is formed between two atoms, which differ much in electronegativities. One atom loses one or more electrons and the other atom gains these electrons to attain the noble gas configuration. The atom losing the electrons forms a positively charged ion (cation) and the atom gaining electrons forms a negatively charged ion (anion). The cation and anion are held together by the electrostatic force of attraction. The electrostatic force of attraction existing between the oppositely charged ions is called an ionic bond.

Energy Changes Involved in the Formation of Ionic Compounds

Ionic compounds are formed due to the transfer of one or more electrons from one atom to the other. Hence two oppositely charged ions are formed in this process and an electrostatic force of attraction is developed between them.

In addition to the force of attraction between the individual pair, forces of attraction also exist among the oppositely charged ions of different pairs which bring them close to each other. As a result of this, repulsive forces are also generated between similar ions of different pairs.

But the cation–cation distance and the anion–anion distance (measured from their centre) of different pairs is greater than the cation–anion distance of different pairs. Hence the force of attraction is greater than the repulsive forces and the ions arrange themselves in such a way that their potential energy becomes minimum. The arrangement of ions associated with minimum potential energy gives the crystalline structure of the ionic compound.

The potential energy of the ions is assumed to be zero when they are separated by an infinite distance. When the ions approach each other, each releases a certain amount of energy.

The amount of energy released when the oppositely charged gaseous ions are brought closer from an infinite distance to form one mole of ionic crystal is called lattice energy.

COVALENT BOND

When the elements do not differ much in their electronegativities, transfer of electrons is not possible between the atoms. Then, sharing of electrons takes place.

A covalent bond is formed, when two atoms attain their nearest noble gas configuration by sharing one or more electron pairs. Each of the atoms contributes equal number of electrons towards the bond formation.

Energy Changes During Covalent Bond Formation

Example: Formation of hydrogen molecule

When two hydrogen atoms are brought close together, two types of forces start acting as listed hereunder:

(i) Proton–proton and electron–electron repulsion and

(ii) proton–electron attraction.

Bond formation between two H-atoms takes place at a distance where the proton–electron attraction just balances the electron–electron repulsion and proton–proton repulsion.

At this stage the system becomes stable because it possesses the lowest possible energy, and H_2 molecule is formed. The distance between the nuclei of the hydrogen atoms, after the formation of the bond, is called the bond length.

The total energy of this system is a function of the distance between hydrogen nuclei as shown in Fig. 5.1.

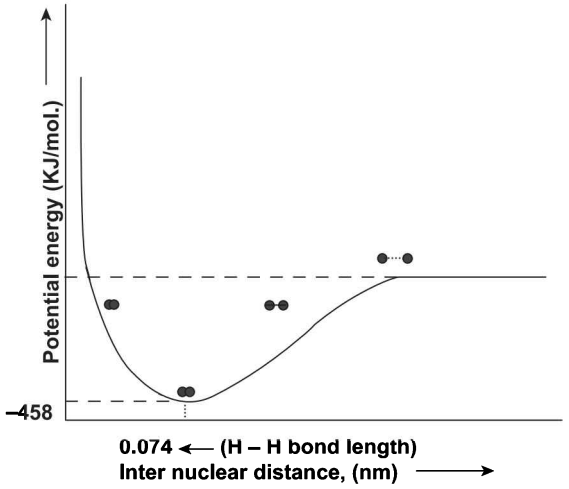


Figure 5.1 Potential energy curve representing the formation of covalent bond in hydrogen molecule

This is the way covalent bond formation takes place between two atoms.

A covalent bond can be formed between two identical atoms (atoms of same element) as well as between the atoms of two different elements.

Nonpolar Covalent Bond

In a bond between two identical atoms, the electrons are shared equally between the atoms. No separation of charge takes place in the molecule. This type of bond is called nonpolar covalent bond.

Polar Covalent Bond

A polar covalent bond is formed between non-identical atoms, which differ in electronegativities. Since the two atoms differ in their capacity to attract the shared electron pair, unequal sharing of electron density results. As a result, polarity is developed in the bond and the bond is said to have dipole moment. **Dipole moment** is the quantitative measure of the polarity of the molecule. A slight ionic character is imparted to this type of bond due to the difference in electronegativity between the bonded atoms and such type of bond is called polar covalent bond.

The relative tendency of non-identical atoms to form ionic bond or polar covalent bond depends upon the ease of the formation of cation and anion by the respective elements.

The easier is the formation of cation and anion, the more is the tendency of the formation of ionic bond. Larger size of the atom favours cation formation, whereas smaller atoms have greater tendency of attracting electrons towards it which leads to the formation of anion.

Ionic bonds are associated with some covalent character due to the attractive forces acting between the cation and the electron cloud of the anion.

The relative proportions of ionic character and covalent character of an ionic compound can be explained on the basis of the concept of polarization and Fajan's rules.

Concept of Polarization and Fajan's Rules

During the formation of an ionic compound, when a cation and anion approach each other, the nucleus of cation exerts some attractive force on the electron cloud. As a result of this, the symmetry of the electron cloud gets distorted and it shifts slightly towards the cation. This phenomenon is called *polarization*. This results in the partial sharing of electron cloud between the bonded atoms which is considered as a covalent character. This ability of a cation to distort the electron cloud of the anion is called *polarizing power* of the cation and the tendency of the anion to get distorted by the influence of the cation is called the *polarizability* of anion.

The relative proportions of ionic and covalent characters of an ionic compound depend upon the polarizing power and polarizability of the respective cation and anion which can be explained on the basis of **Fajan's rules**.

(i) Size of cation and anion

(a) A large cation and a small anion result in maximum ionic character for the bond. ***Example:*** Cs^+ and F^-

(b) A small cation and a large anion result in maximum covalent character for the bond. ***Example:*** Li^+ and I^-

(ii) Charge of cation and anion

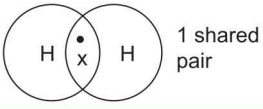
(a) Low charge on cation and anion results in maximum ionic character for the bond. ***Example:*** Na^+ Cl^-

(b) High charge on cation and anion results in greater proportion of covalent character for the bond.
Example: Al^{+3} O^{-2}

Theories of Covalent Bond Formation

Many theories have been proposed in order to explain covalent bond formation and the stability of the resultant molecules. **Octet rule** states that the atoms of the elements have a tendency to attain the nearest inert gas configuration either by the transfer of electrons or by the sharing of electrons.

Some examples of covalent molecules, the stability of which can be satisfactorily explained with the help of the octet rule are provided in the following:

Molecules	No. of valence electrons	Structure
Hydrogen (H_2)	1	

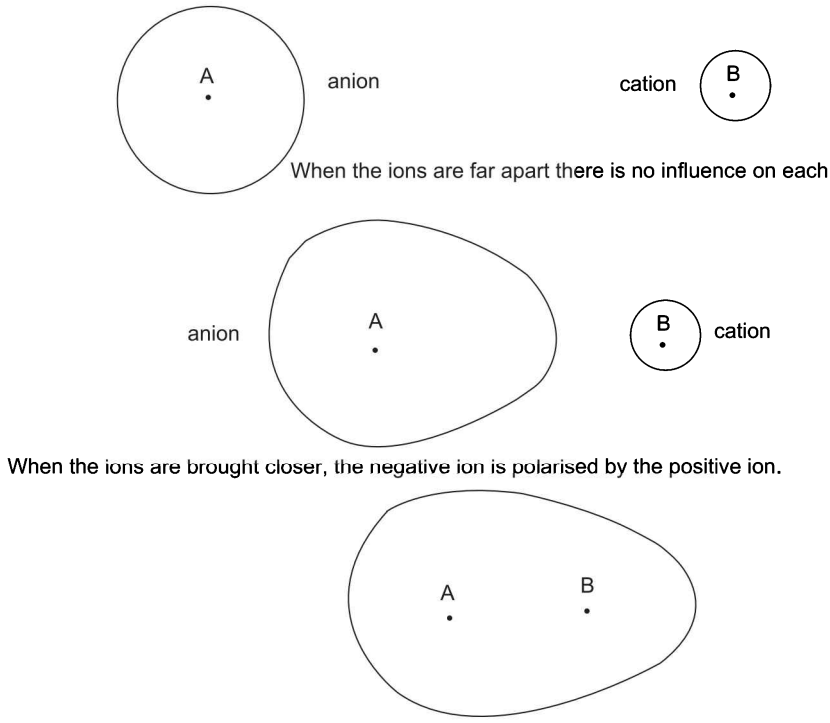


Figure 5.2 Covalant Bond Formation

Molecules	No. of valence electrons	Structure
Oxygen (O_2)	6	2 shared pairs
Nitrogen (N_2)	5	3 shared pairs
Chlorine (Cl_2)	7	1 shared pair
Water (H_2O)	H → 1, O → 6	2 shared pairs
Methane (CH_4)	C → 4, H → 1	4 shared pairs

All the above molecules are found to obey the octet rule which is visualized by writing their Lewis dot structures. Therefore, it is justified that the atoms acquire stability by gaining the octet

configuration. However, some molecules are also found in which the central atom does not acquire the octet configuration. But the fact that their stability is comparable with the stability of molecules which obey the octet rule indicates that the octet rule itself cannot completely justify formation and stability of covalent molecules.

Exceptions to the Octet Rule

The molecules may contain less than eight or more than eight electrons around the central atom. These are considered as deviations from the octet rule.

Incomplete Octet or Contracted Octet

Molecules in which the central atom possesses less than eight electrons in its valence shell.

Examples: BF_3, $BeCl_2$

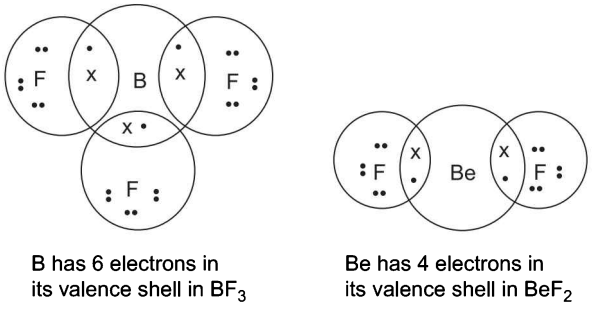


Figure 5.3 Incomplete Octet or Contracted Octet

Expanded octet

Molecules in which the central atom possesses more than eight electrons in its valence shell.

Examples: PCl_5, SF_6, IF_7

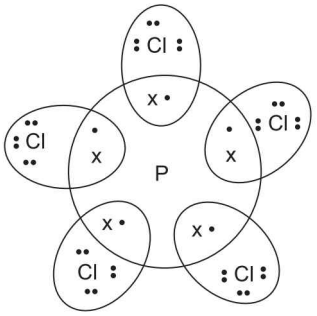


Figure 5.4 Expanded octet

P has 10 electrons in its valence shell in PCl_5.

Lewis theory explains the formation of covalent bond through sharing of electrons, but this theory does not explain the mechanism of sharing of electrons that leads to the stability of molecules. The mechanism of sharing of electrons was interpreted with the help of the concept of orbital overlapping after the quantum mechanical model of atom was proposed.

EXAMPLE

Between $CaCl_2$ and KCl, which has a stronger ionic bond? Why?

SOLUTION

Ca^{+2} ion is smaller than K^+ ion. Greater the charge on cation, the greater is the effective nuclear charge and thus smaller is the size of the cation. Hence, due to the smaller size of Ca^{+2} than K^+, $CaCl_2$ has a stronger ionic bond than KCl.

EXAMPLE

Between CuO and CuS which is more covalent and why?

SOLUTION

Between CuO and CuS, CuS is the more covalent. Since cation is same in both, the anion determines the extent of polarization. Larger anions have greater polarizability. Between O^{-2} and S^{-2} ions, S^{-2} ion is the more polarisable. Greater polarizability imparts greater covalent character to the compound.

EXAMPLE

Distinguish between polar covalent bond and nonpolar covalent bond with respect to

(a) mode of formation

(b) charge separation

(c) type of atoms involved in bond formation.

SOLUTION

(a) Polar covalent bond is a bond formed by unequal sharing of electrons between the bonded atoms. Nonpolar covalent bond is a bond formed by equal sharing of electrons between the bonded atoms.

(b) Polar covalent bond results in the formation of opposite partial charges on the bonded atoms which is called dipole. Nonpolar covalent bond does not result in charge separation between bonded atoms.

(c) Polar covalent bond is formed between atoms of different elements. Nonpolar covalent bond is formed between atoms of same element.

EXAMPLE

Ionic bond formation takes place between sodium and chlorine. But between hydrogen and chlorine, covalent bond formation takes place. Give reason.

SOLUTION

Sodium belongs to IA group and is highly electropositive. Chlorine belongs to VII A group and is highly electronegative. Sodium has very low IP value and can form Na^+ ion easily. Chlorine has very high IP value and high EA value and can form Cl^- ion easily. Thus ionic bond results between sodium and chlorine. IP value of hydrogen is not as low as alkali metals that is Na. Hence its tendency to form H^+ ion is very less. Sharing of electrons takes place between hydrogen and chlorine resulting in the formation of polar covalent bond.

Concept of Orbital Overlapping

According to this concept, covalent bond is formed when an overlap takes place between the orbital of one atom with the orbital of another atom.

Conditions required for orbital overlapping:

(i) The orbitals belonging to the valence shell only take part in overlapping.

(ii) Each of the overlapping orbitals should contain an unpaired electron.

(iii) The electrons in the overlapping orbitals should have an opposite spin.

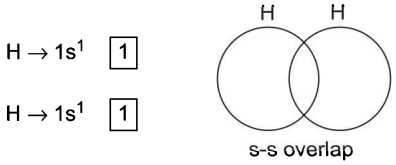
Different Types of Overlapping

(i) s–s overlapping

Example: H_2 molecule

Each hydrogen atom has only one electron ($1s^1$) which is available for bonding.

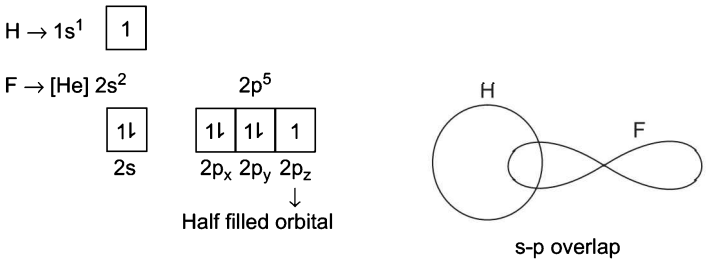
In the formation of H_2 molecules, 1s orbital of one atom overlaps with that of the other forming a single covalent bond.



(ii) s–p overlapping

Example: HF molecule

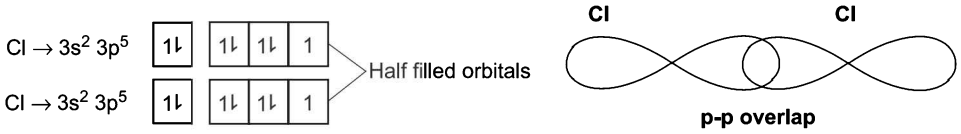
It is formed by the overlapping of 1s orbital of hydrogen atom and $2p_z$ orbital of fluorine atom, i.e., by s–p overlapping.



(iii) p–p overlapping

Examples: Cl_2, F_2, Br_2 molecules, etc.

Cl_2 molecule is formed by the overlapping of $3p_z$ orbitals of two chlorine atoms.



In the above examples (H_2, HF and Cl_2), orbitals of two atoms, each having one unpaired electron overlap to form a single covalent bond.

If the atom possesses more than one atomic orbital having unpaired electrons, then more than one covalent bond can be formed.

Strength of a Covalent Bond

The strength of a covalent bond is related to the extent to which the two combining atomic orbitals can overlap. The greater the extent of overlap between the atomic orbitals, the greater is the strength of the resulting covalent bond.

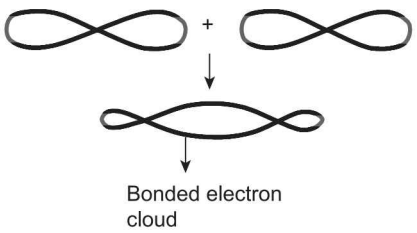
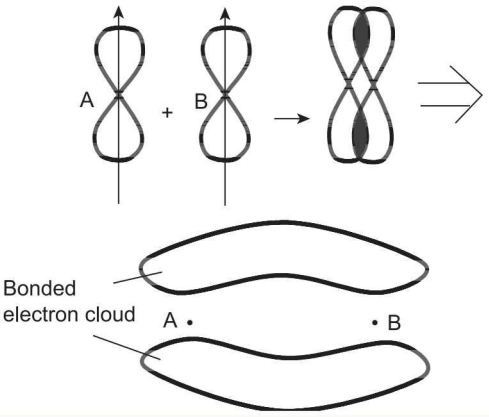
The covalent bond formed by the end to end or head on overlapping of atomic orbitals is called sigma bond. The covalent bond formed by the sidewise or lateral overlapping of atomic orbitals is called pie bond.

Sigma (σ) Bond

Sigma bond is a covalent bond formed as a result of maximum overlapping (end-to-end overlapping) of s–s, s–p and p–p orbitals along the internuclear axes. Due to the greater extent of overlapping, this type of overlapping results in a strong bond.

Pi (π) bond: A covalent bond which is formed between two atoms by lateral overlapping of orbitals perpendicular to the internuclear axis is called a *pi bond*. Due to the less extent of overlapping, this type of overlapping results in a weak bond.

Comparative Study of Sigma and pi Bonds

Sigma Bond	Pi bond
It is a strong covalent bond formed due to end-to-end overlapping of orbitals.	It is a weak covalent bond formed by lateral overlapping of orbitals.
It is denoted by σ.	It is denoted by π.
It has an independent existence.	It does not have any independent existence as it can be formed only after the formation of a σ bond.
Bond dissociation energy is high.	Bond dissociation energy is low.
Orbitals s, p and d are capable of forming bond.	Orbitals other than "s" are capable of forming a π bond.
The bonded electron cloud is distributed in a cylindrically symmetrical way around the internuclear axis. 	The bonded electron cloud is distributed in two banana-shaped regions above and below the internuclear axis. 

Explanation of sigma and pi bond with the help of formation of O_2 and N_2 molecules

O_2 molecule: The electronic configuration of an oxygen atom is $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$. Hence, the oxygen atom has two unpaired electrons. Singly occupied $2p_z$ orbital of one oxygen atom overlaps (end to end) with the same orbital of another oxygen atom to give rise to a sigma bond. Singly occupied $2p_y$ orbitals of both the oxygen atoms overlap (sidewise) along a line perpendicular to z-axis (molecular axis) to give a pi bond. Thus, a double bond is formed.

Thus an O_2 molecule has a double bond between the atoms: one is a p_z–p_z sigma bond and the other p_x–p_x pi bond called double bond.

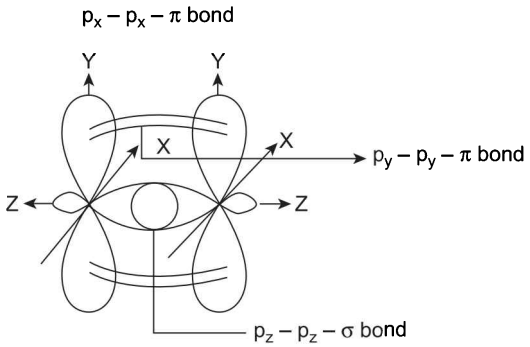


Figure 5.5 O_2 molecule (one bond and one π bond)

N_2 molecule: The electronic configuration of a nitrogen atom: $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. Hence, a nitrogen atom has three singly occupied orbitals. One $2p_z$–$2p_z$ sigma bond is formed. The other two pi bonds are $2p_x$–$2p_x$ and $2p_y$–$2p_y$. Thus N_2 molecule has three bonds—one (p_z–p_z) sigma bond and other two (p_x–p_x and p_y–p_y) pi bonds which are perpendicular to each other and perpendicular to the z-axis, i.e., the axis of the sigma bond (molecular axis). Hence, a triple bond is formed.

The concept of orbital overlapping gives satisfactory explanation for the formation of covalent bond and the stability of the molecule. But the bond formation in certain molecules like $BeCl_3$, BF_3, CH_4, etc., cannot be explained only on the basis of this concept.

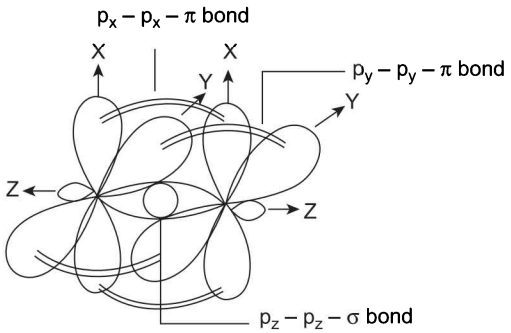


Figure 5.6 N_2 molecule (two π bonds and one σ bond)

However, the bond formation in $BeCl_2$, BF_3, CH_4, etc., can be explained by using the concept of excitation of electrons. Beryllium has no unpaired electron in its valence shell, boron has only one unpaired electron and carbon has two unpaired electrons. But the bicovalency of beryllium in $BeCl_2$, tricovalency of boron in BF_3 and tetracovalency of carbon in CH_4 is possible due to the promotion of electron from the "s" orbital to "p" orbital. The state of atom before the promotion of electron is called ground state and that after the promotion of electron is called excited state.

However, in the excited state of beryllium, one of the two unpaired electrons is present in "2s" orbital and the other one is in "2p" orbital. Hence, during the formation of $BeCl_2$ the overlapping of orbitals should take place between s–p and p–p orbitals which are nonidentical.

But the bonds in $BeCl_2$ are found to be identical in all respects. Similarly in BF_3, the three B–F bonds and in CH_4, the four C–H bonds are identical.

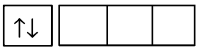
In order to explain this identical nature of the bonds, concept of hybridization and hybrid orbitals has come into existence.

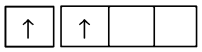
Hybridization is a process of intermixing of two or more atomic orbitals of almost equal energies (belonging to the valence shell) of an atom and their redistribution into an equal number of identical orbitals. The resultant orbitals are called hybrid orbitals.

Structure of $BeCl_2$

Electronic configuration of beryllium is $1s^2\ 2s^2\ 2p^0$.

Valence shell configuration of Be is $2s^2\ 2p^0$.

Ground state configuration of Be is 

Excited State Configuration of Be is 

Mixing up of one s-orbital and one p-orbital to give two new identical orbitals is called sp hybridization and the two orbitals formed are called "sp" hybrid orbitals.

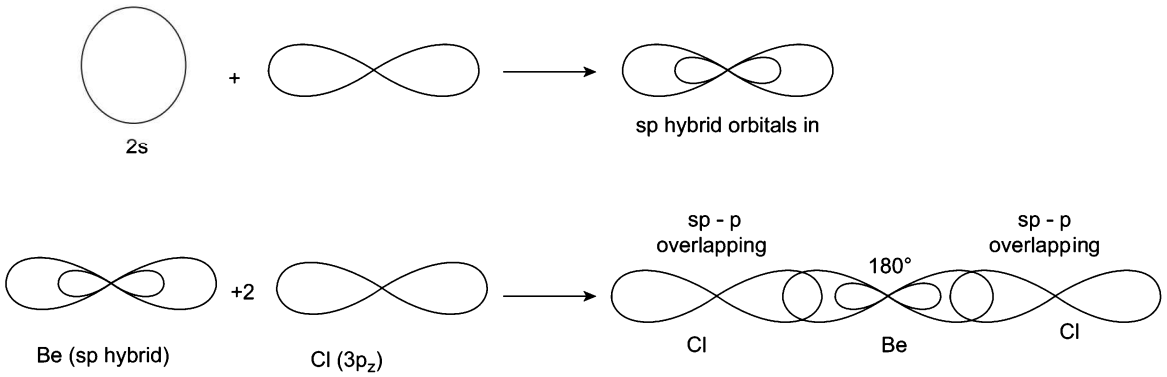
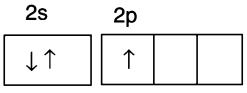
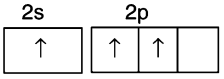


Figure 5.7 Formation of $BeCl_2$ molecule

Structure of BCl_3

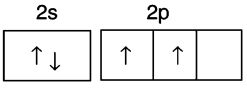
Mixing up of one s-orbital and two p-orbitals to form three new identical orbitals is called sp^2 hybridization. The orbitals so formed are called sp^2 hybrid orbitals.

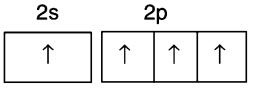
Ground state electronic configuration of "B": 

Excited state electronic configuration of "B": 

Structure of Methane

Mixing up of one s- and three p-orbitals to form four identical orbitals is called sp^3 hybridization. These three orbitals are called sp^3 hybrid orbitals.

Ground state electronic configuration of C 

Excited state electronic configuration of C 

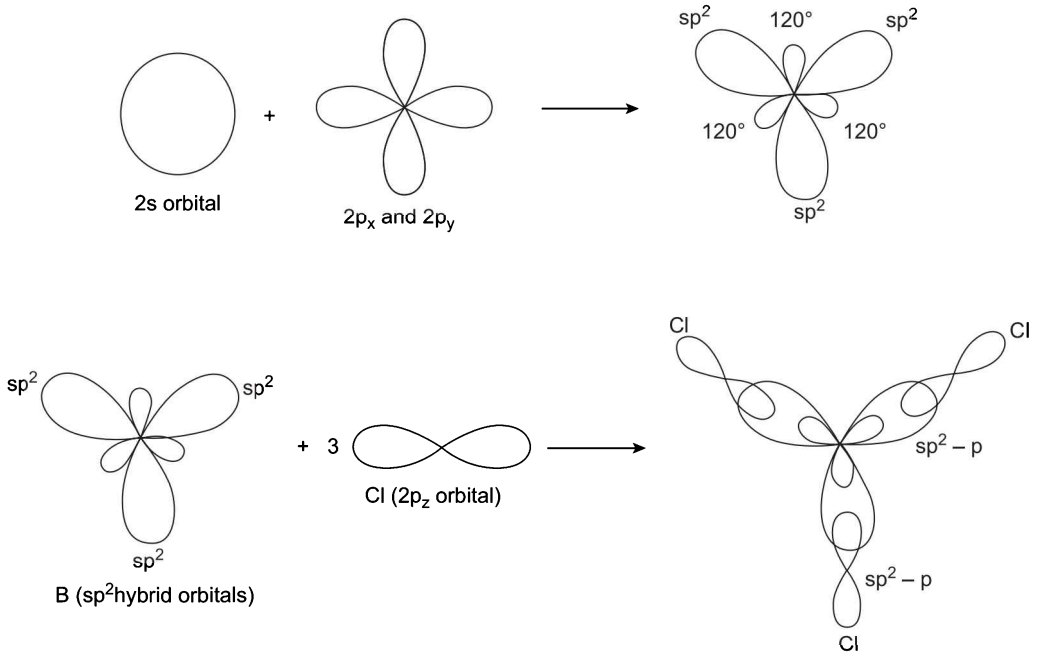


Figure 5.8 Formation of BCl_3 molecule

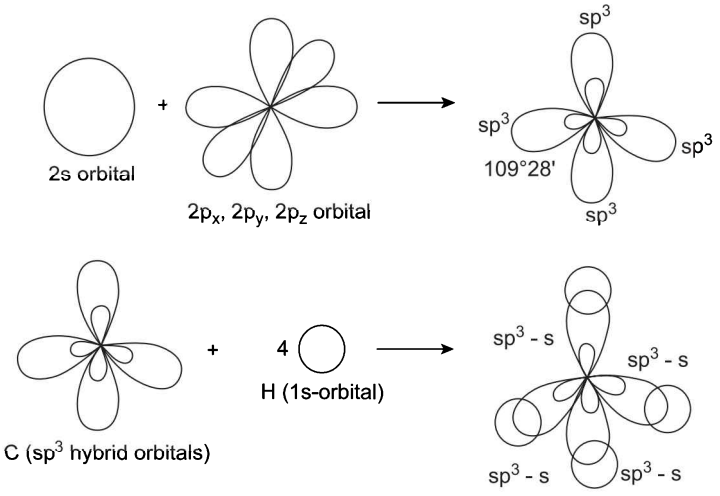


Figure 5.9 Formation of methane molecule

Shapes of the Covalent Molecules

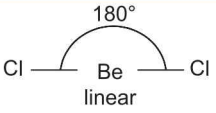
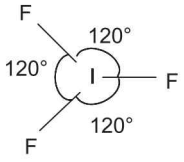
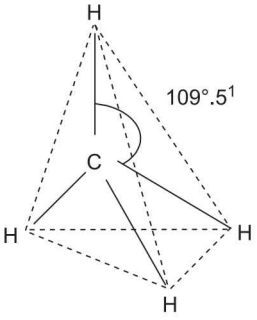
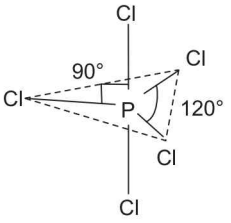
On the basis of valence shell electron pair repulsion (VSEPR) theory, the geometry and the shapes of the covalent molecules can be explained.

Postulates of the VSEPR Theory

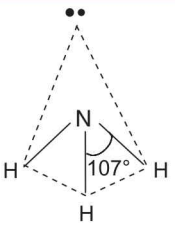
- Different geometrical shapes of the covalent molecules are generated due to the repulsion between the electron pairs present in the valence shell of the central atom of the molecules.
- These electron pairs arrange themselves in such a way that the repulsion among them becomes minimum.
- The electron pairs involved in bond formation are called bonded electron pairs.The electron pairs which are present in the valence shell of central atom but not involved in bond formation are called lone electron pairs.

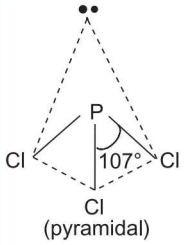
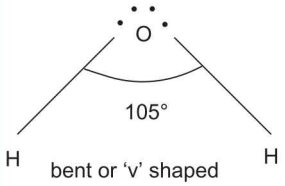
- Repulsion between two lone pairs is greater than the repulsion between a lone pair and a bond pair which is in turn greater than the repulsion between two bond pairs. Therefore, the shape of the molecule does not depend only on the number of electron pairs but also depends upon the number of bonded electron pairs and lone electron pairs on the central atom in that molecule.

Shapes of the Molecules Without Lone Pair of Electrons

Molecules	Number of bond pairs	Shapes
$BeCl_2$	2	 linear
BF_3	3	 trigonal planar
CH_4	4	
PCl_5	5	 trigonal bipyramidal

Shapes of Molecules Having Lone Pair(s) of Electrons

Molecules	Number of bond pairs	Number of lone pairs	Shapes
NH_3	3	1	 (pyramidal)

Molecules	Number of bond pairs	Number of lone pairs	Shapes
PCl_3	3	1	
H_2O	2	2	

EXAMPLE

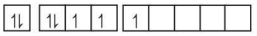
Explain how chlorine exhibits a maximum covalency of 7.

SOLUTION

Electronic configuration of Cl is [Ne] $3s^2 3p^5$. In 3rd shell, there are vacant d orbitals.

The paired electrons of 3s and 3p orbitals can be excited to 3d orbitals. Therefore the number of unparied electrons increases. As a result, covalency corresponding to the number of unparied electrons is exhibited. In the fully excited state of Cl atom, there are 7 half filled orbitals giving covalency of 7. As there is no scope for further excitation, it is the maximum covalency that chlorine can show.

Ground state : ⇒ Covalency of 1

1st excited state :  ⇒ Covalency of 3

2nd excited state : ⇒ Covalency of 5

3rd excited state : ⇒ Covalency of 7

EXAMPLE

Both helium and beryllium have ns^2 valence electronic configuration. But, berylium forms compounds and helium cannot form compounds. Explain.

SOLUTION

Both helium and beryllium have ns^2 valence electronic configuration. Berylium has an electron pair in 2s orbital and all three 2p orbitals are vacant. The paired electron of 2s orbital can be excited to 2p orbital thereby giving a covalency of 2. Helium has an electron pair in '1s' orbital and there is no scope for excitation of electrons in 1st shell. Hence Helium can not form any compounds.

EXAMPLE

Why is the repulsion between two lone pairs of electrons more than that between a lone pair and a bond pair or a bond pair and a bond pair of electrons?

SOLUTION

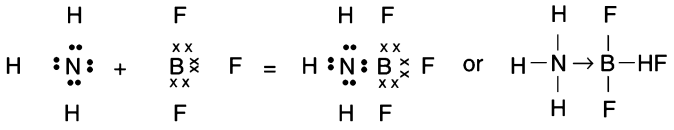
Lone pair of electrons is under the sole influence of the nucleus of one atom, but the bond pair of electrons is under the influence of the nuclei of the two atoms. Hence spreading of the electron cloud of the lone pair of electrons which is much closer to the central atom. Hence they occupy a broader orbital with greater electron density and exert greater repulsion on the adjacent electrons.

Special types of bonds and non bonded forces of attraction

Coordinate Covalent Bond

It is a special type of covalent bond in which only one of the participating atoms contributes the electron pair for sharing. The atom which gives the electron pair for sharing is called the donor and the other atom which accommodates the shared pair of electrons is called an acceptor. In this mechanism, the contribution of electron pair is one-sided, and slight polarity develops in the molecule. A coordinate bond is represented by "→," pointing from the donor atom to the acceptor atom. It is also called a *dative bond*. A coordinate bond is explained below with the help of an example.

(i) Formation of $NH_3 \rightarrow BF_3$



Nitrogen atom of ammonia has a lone pair of electrons and these are accepted by the vacant p-orbital of the boron atom of BF_3. Hence nitrogen atom is the donor and boron atom is the acceptor.

Other examples with coordinate covalent bond formation are H_3O^+, $[Fe(H_2O)_6]^{2+}$, etc.

Metallic Bond

Each atom in a metal crystal loses all its valence electrons. The electrons thus obtained form an electron pool. The resulting positively charged metal ions are believed to be held together by the electron pool. The positively charged metal ions have a definite position in the crystal lattice of the metal. The valence electrons are not attached to any individual ions, they belong to the crystal as a whole and are free to move throughout the metal crystal.

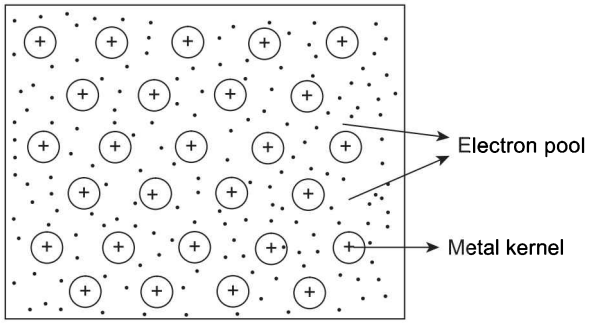


Figure 5.10 Schematic illustration of metallic bond in "electron sea model"

The electrostatic force of attraction that binds metal ions to the mobile electrons within its sphere of influence is known as a *metallic bond*.

EXAMPLE

Hydrogen bond is nothing but strong dipole-dipole attraction. Justify.

SOLUTION

When a covalent bond is formed between atoms of different elements, partial charges are developed on the bonded atoms. This molecule is called dipole. Due to the presence of opposite

partial charges on the atoms, dipole – dipole attractions exist between the molecules. In case of polar covalent bond between hydrogen and highly electronegative atom, the magnitude of partial charges will be much greater. As a result the dipole-dipole attractions become stronger and this is called hydrogen bond.

EXAMPLE

Why do NH_3 and H_2O act as electron pair donors?

SOLUTION

Ammonia molecule possesses one lone pair on nitrogen atom. Water molecule possesses two lone pairs on oxygen atom. They can therefore donate the excess electron pair to any ion or atom or molecule which has electron defficiency.

EXAMPLE

Between vanderwaal's forces and dipole- dipole attractions, which are stronger? Why?

SOLUTION

Dipole-dipole attractions are stronger as they exist between opposite partial charges. Vanderwaal's forces are weaker as they exist between the nucleus of one atom and the electrons of the other atom.

EXAMPLE

Some metals like sodium can be cut with a knife. How do you explain with respect to metallic bond?

SOLUTION

Sodium has one electron in its valence shell. Being the first element of that period, it has large size. The force of attraction binding the metal ions with electrons that means metallic bond is weaker when compared to the other metals. Therefore, sodium is soft metal and can be cut with a knife.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. Why do atoms have a tendency to form molecules?
2. Which force opposes the interionic forces of attraction between the oppositely charged ions during the formation of an ionic crystal?
3. Sharing of three electron pairs between two atoms results in the formation of a _____ bond.
4. What type of forces acts between the ions during the formation of a crystal of ionic compound?
5. What types of overlapping take place in a sigma and a pi bond?
6. Why is more energy required to break a sigma bond than a pi bond?
7. The number of non-bonded electrons present on the central atom in the molecule of ammonia is _____.
8. How is the strength of the covalent bond related to overlapping of the orbitals?
9. Why do polar covalent compounds dissolve in water?
10. If the electron pair is unequally shared between the bonded atoms, it results in _____ bond.
11. What would be the shape of XY_3 molecule if there is no lone pair on the central atom?
12. Why is the H–O–H bond angle in H_2O smaller than H–N–H bond angle in NH_3?
13. In the formation of a Br_2 molecule, the overlapping of _____ orbitals takes place.
14. How many lone pair of electrons are present on the central atom of CH_4, H_2O, NH_3, PCl_3 and PCl_5 molecules?
15. What type of bond formation takes place between the atoms of Group IA and Group VIIA?
16. Although the number of bond pair of electrons in the valence shell of phosphorus in a PCl_3 molecule is 3, its shape is not trigonal planar. Why?
17. What are the donors in a hydronium ion and ammonium ion?
18. Why do metals conduct electricity?
19. The number of σ bonds and π bonds in CO_2 molecule are _____ respectively.
20. Why does the presence of a lone pair change the shape of the molecule?
21. Why are the participating atoms of a coordinate bond called the donor and the acceptor?
22. The electrostatic forces of attraction between the metallic ions and free electrons is called _____.
23. How many electrons are present in the valence shells of the central atoms in the molecules of $BeCl_2$, BF_3 and PCl_5?
24. In PCl_5 molecule, the bond angles are _____ and _____.
25. The shape of $BeCl_2$ is _____.
26. Write the order of repulsions among the electron pairs.
27. How are the hybrid orbitals arranged in the molecules?
28. The forces of attraction between the elemental gaseous molecules are called _____.
29. How many new hybrid orbitals are formed in sp, sp^2 and sp^3 hybridizations?
30. The shape of BF_3 molecule is _____.

Short Answer Type Questions

31. "Molecules are stable only when the constituent atoms attain octet configuration." State whether the given statement is true or false and justify your answer.
32. Define an ionic bond and a covalent bond.
33. How many sigma bonds and pi bonds are there in a chlorine molecule? Justify your answer.
34. Why is a nitrogen molecule less reactive than an oxygen molecule?
35. Explain the role of electron affinity and ionization potential during the ionic and covalent bond formation?

PRACTICE QUESTIONS

36. How is the metallic or non-metallic character of an atom related to bond formation?
37. Explain the structure of $BeCl_2$ with the help of hybridization.
38. Why is $BeCl_2$ molecule linear, but BF_3 is trigonal planar?
39. Write a note on the energy changes during the formation of a hydrogen molecule.
40. Write about the partial covalent nature of ionic bond and explain it on the basis of Fajan's rules.
41. "The orbitals of two different shells of an atom combine and form one hybrid orbital." State whether the statement is true or false and justify your answer.
42. Explain the structure of CH_4 with the help of hybridization.
43. Explain the formation of hydrogen, oxygen and nitrogen molecules.
44. Mention two main striking differences between sigma and pi bonds.
45. Explain different types of bond formation in $H_3N \rightarrow BF_3$.

Essay Type Questions

46. Explain the formation of an ionic compound with respect to lattice energy.
47. (a) The strength of a covalent bond depends on which factor/factors?
    (b) Classify covalent bonds depending on the strength. Compare those bonds.
48. What are the factors on which the geometrical shapes of covalent molecules depend?

    Explain with suitable examples.
49. (a) What are the conditions required for the overlapping of the orbitals during covalent bond formation?
    (b) Describe the different types of orbital overlapping with suitable examples.
50. (a) What is hybridization?
    (b) What are the conditions for an atom to undergo hybridization?
    (c) How can we explain the shapes and bond angles of $BeCl_2$, BCl_3 and CH_4 with hybridization?

CONCEPT APPLICATION

Level 1

***Direction for questions from 1 to 7*: State whether the following statements are true or false.**

1. Ionic compounds are soluble in organic solvents.
2. All covalent compounds possess coordinate covalent bonds.
3. BF_3 does not obey the octet rule.
4. The bond angle in ammonia is 109°28.
5. A sigma (σ) bond is stronger than a pi (π) bond.
6. The hydrogen bond is always formed between the molecules of the same substance.
7. Covalent bonds are non-directional bonds.

***Direction for questions from 8 to 14*: Fill in the blanks.**

8. In CaF_2, the number of electron(s) transferred from calcium to fluorine atoms is _____.
9. The bond formed by end on overlap is _____ than the bond formed by side on overlap.
10. Linear overlapping of any two pure atomic p-orbitals lead to _____ bond formation.
11. Cl–C–Cl bond angle in CCl_4 is _____.
12. Among the hydrogen halides _____ has maximum ionic character.
13. The shape of $BeCl_2$ molecule is _____.
14. In ammonia–boron trifluoride complex, the donor molecule is _____.

***Direction for question 15*: Match the entries given in column A with appropriate ones from column B.**

15.

Column A	Column B
A. Nitrogen	( ) a. Polar covalent bond
B. Xenon	( ) b. 107°
C. Ammonia	( ) c. Octahedral
D. Sulphur hexafluoride	( ) d. 109°28
E. Hydrogen chloride	( ) e. Triple bond
F. Methane	( ) f. Two lone pairs of electrons
F. Water molecule	( ) g. Octet configuration

***Direction for questions from 16 to 45*: For each of the questions, four choices have been provided. Select the correct alternative.**

16. Expanded octet occurs in

(a) NH_3 (b) PF_5

(c) H_2O (d) O_2

17. The lesser covalency of $FeCl_2$ over $FeCl_3$ is due to

(a) lower polarizing power of Fe^{+2} than that of Fe^{+3} ion

(b) lower polarizing power of Fe^{+3} than that of Fe^{+2}

(c) higher polarizability of Fe^{+3} than Fe^{+2}

(d) higher polarizability of Fe^{+2} than Fe^{+3}

18. An element X has low ionization energy and another element Y has high electron affinity. The bond formed between them could be

(a) ionic (b) polar covalent

(c) coordinate covalent (d) non-polar covalent

19. Which of the following statements regarding pi bond is not true?

(a) It may be formed by the overlapping of p-atomic orbitals.

(b) It has no independent existence.

(c) It is weaker bond compared to σ bond.

(d) It can be formed by hybrid orbitals.

20. Arrange the following in increasing order of their bond lengths.

C–C, C=C, C≡C

(a) C≡C < C=C < C–C

(b) C=C < C–C < C≡C

(c) C≡C < C–C < C=C

(d) C–C < C=C < C≡C

21. Which of the following statements is wrong?

(a) KCl is soluble in water.

(b) HCl conducts electricity in its aqueous solution.

(c) Acetic acid is soluble in water.

(d) The bond formed between aluminum and fluorine is covalent.

22. NH^+_4 is isostructural with

(a) PCl_3 (b) CH_4

(c) BF_3 (d) NO_3^-

23. In water molecule, the bond angle of 104.5° around oxygen is accounted due to

(a) high electron affinity of oxygen

(b) very high repulsions between lone pair and bond pair of electrons

(c) very high repulsion between lone pair and lone pair electrons

(d) small size of hydrogen

24. Which of the following bonds is more polar when compared to others?

(a) O–H (b) N–H

(c) C–H (d) H–H

25. The number of sigma and pi bonds in benzene are

(a) 6σ and 3π bonds (b) 12σ and 3π bonds

(c) 9σ and 3π bonds (d) 6σ and 6π bonds

26. Which among the following pairs of molecules possess same geometry?

(a) $BeCl_2$, SiO_2 (b) CO_2, SiO_2

(c) BF_3, PCl_3 (d) F_2O, H_2S

27. The number of σ and π bonds in C_2H_2 is _____.

(a) 0 and 4 (b) 2 and 2

(c) 3 and 2 (d) 4 and 2

28. A species H_3O^+ pyramidal in shape. The number of lone pairs of electrons is

(a) 0 (b) 1

(c) 2 (d) 3

29. The shape of H_2O molecule is _____.

(a) linear (b) tetrahedral

(c) v-shaped (d) trigonal planar

30. The covalency of "N" in NH_4^+ ion is equal to number of

(a) covalent bonds

(b) coordinate bonds

(c) covalent bonds and coordinate bonds

(d) valence electrons

31. Two substances X and Y are dissolved in water under suitable conditions. X is a gas while Y is a solid under normal conditions. Solution of Y is found to conduct electricity but not "X." Based on the conclusion identify the nature of bond present in X and Y with appropriate reasons as given below.

Arrange the steps given below in a sequence.

(1) Y is a solid at room temperature and its aqueous solution conducts electricity. This shows that it is an ionic compound.

(2) X on dissolution in water doesn't conduct electricity and is a gas at room temperature. Hence it should be a nonpolar covalent molecule.

(3) Aqueous solutions of both ionic compounds and polar covalent compounds conduct electricity because of the presence of free ions.

(4) All ionic compounds are solids and most of the nonpolar covalent molecules are gases or solids at room temperature. Polar covalent compounds are liquids or gases.

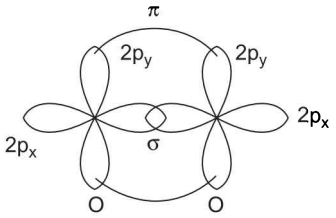
(a) 3 4 2 1 (b) 1 4 3 2

(c) 1 3 2 4 (d) 3 1 2 4

32. The formation of double bond in an oxygen molecule is explained below. Arrange the given points in a sequential order.

(1) $2p_y$ orbitals of each oxygen atom overlap laterally/sidewise to form a pi bond.

(2) Thus, double bond between two oxygen atoms in which one p_z–p_z sigma bond and p_y–p_y pi bond is formed.



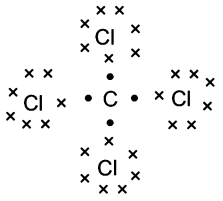
(3) All the three 2p orbitals are perpendicular to each other. Hence $2p_z$ orbitals of each oxygen atom overlap end to end to form a sigma bond.

(4) The electronic configuration of oxygen is O: $1s^2 2s^2 2p_x^1 2p_y^2 2p_z^1$.

(a) 3 1 4 2 (b) 4 3 1 2

(c) 3 4 2 1 (d) 3 4 1 2

33. The necessary steps required to show the formation of CCl_4 by Lewis electron dot diagram have been jumbled. Arrange them in a sequence.



(1) Thus, an electron pair is shared between C and Cl. This is the Lewis electron dot diagram for CCl_4.

(2) Write the symbol of chlorine and represent its valence electrons with the help of crosses, i.e.,

(3) Write the symbol of carbon and represent its valence electrons with the help of dots, i.e.,

(4) When carbon combines with four chlorine atoms, the carbon atom contributes four electrons for sharing, whereas each chlorine atom contributes only one electron for sharing. Thus, both the atoms in CCl_4 attain an octet.

(a) 1 3 2 4 (b) 2 1 3 4

(c) 4 3 2 1 (d) 3 2 4 1

34. Which among the following substances does not conduct electricity in its aqueous solution state?

(a) glucose (b) alcohol

(c) hydrochloric acid (d) common salt

35. The ease of formation of which of following chlorides is maximum?

(a) NaCl (b) KCl

(c) RbCl (d) CsCl

36. During the formation of sodium chloride from its constituents,

(a) Na undergoes oxidation and acts as an oxidizing agent.

(b) Na undergoes reduction and Cl undergoes oxidation.

PRACTICE QUESTIONS

(c) Cl undergoes reduction and acts as a reducing agent.

(d) Na acts as a reducing agent and Cl acts as an oxidizing agent.

37. The valence electronic configurations of two elements are $4s^1$ and $3s^2\ 3p^5$, respectively. The type of bond expected to be present between them is

(a) polar covalent bond

(b) nonpolar covalent bond

(c) metallic bond

(d) ionic bond

38. The angular shape of water molecule is due to

(a) high electron affinity of oxygen

(b) very high repulsions between lone pair and bond pair of electrons

(c) very high repulsion between lone pair and lone pair electrons

(d) small size of hydrogen

39. The element which has the strongest metallic bond among $_{11}A^{23}$, $_{12}B^{24}$, $_{13}C^{27}$ and $_{19}D^{39}$ is _____.

(a) A (b) B

(c) C (d) D

40. Identify the compound that exhibits maximum ionic character among the following:

(a) $MgCl_2$ (b) $BaCl_2$

(c) NaCl (d) CsCl

41. Identify the favourable conditions for the formation of ionic bond:

(a) low IP value of metal, low EA value of nonmetal

(b) high IP value of metal, high EA value of nonmetal

(c) low IP value of metal, high EA value of nonmetal

(d) high IP value of metal, low IP value of nonmetal

42. Among the following molecules, p–p overlap takes place in

(a) H_2 (b) $BeCl_2$

(c) F_2 (d) HF

43. Among the following molecules H-bond is present in

(a) NH_3 (b) PH_3

(c) H_2S (d) CH_4

44. The covalency of oxygen in hydronium ion is equal to number of

(a) covalent bonds

(b) coordinate bonds

(c) covalent bonds and coordinate bonds

(d) valence electrons

45. A solid compound "A" consists of simple ions.

Choose corresponding answers from the choices given below.

Nature of the bond present in A will be

(a) ionic (b) covalent

(c) molecular (d) hydrogen bond

Level 2

1. Both CH_4 and CCl_4 are non-polar molecules, but $CHCl_3$ is a polar molecule. Discuss.

2. Copper (I) and silver (I) halides are more covalent in nature compared to sodium and potassium halides although the charges on the ions are same. How do you account for this?

3. The orbitals p and d can form π bonds, but the s-orbital cannot form a π bond. Give reasons.

4. Compare the shapes of the meniscus of water in a glass tube and in wax coated glass tube. Give an appropriate reason.

5. Between CuO and CuS which is more covalent and why?

6. Why is the repulsion between two lone pairs of electrons more than that between a lone pair and a bonded pair or a bonded pair and a bonded pair of electrons?

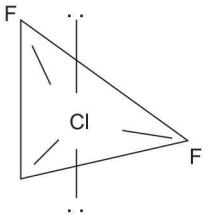
7. Between NF_3 and BF_3, which is the more polar molecule? Why?

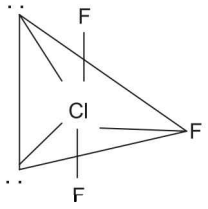
8. Noble gases do not usually form chemical bonds. But xenon forms a number of stable compounds. Account for this.

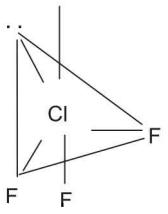
9. Just like H_2O, there are two lone pairs in Cl_2O molecule. But bond angle in Cl_2O is 111°. Explain.

10. Though sulphur has only two unpaired electrons it exhibits covalency of 2, 4, 6. Explain.

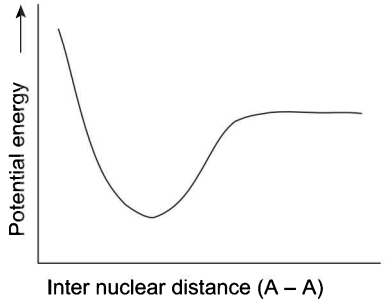
11. Phosphorous can form PCl_5 molecule in the excited state of phosphorous atom. But the formation of PH_5 is not possible in the same state. Account for this.
12. Between LiF and LiI, which has the higher lattice energy and why?
13. Which among the following geometries is most preferred with respect to ClF_3 molecule and why?

(a) 

(b) 

(c) 

14. Explain and give reasons for the changes in potential energy after the bond formation in a diatomic molecule from the given graph.



15. In comparison with sodium salts, ammonium salts are more soluble in water. Explain.

***Directions for questions from 16 to 25*: Application-Based Questions**

16. Compare NaCl and CsCl with respect to ease of formation and also strength of ionic bond.
17. Comment on the intensity of charge of an electric field when HF and dry air are placed between two charged parallel plates.
18. Phosphorous can form PCl_5 molecule in the excited state of phosphorous atom. But the formation of PH_5 is not possible in the same state. How do you account for this?
19. Predict hybridization and shape of SF_4 molecule.
20. All halides of sodium are ionic. Fluorides and chlorides of magnesium are ionic. But among halides of aluminum, only AlF_3 is ionic. How do you account for this variation?
21. The nitrogen atom of NH_3 acts as a donor during the formation of a coordinate covalent bond while the central nitrogen atom in NO_2 cannot act as a donor. Explain.
22. Increase in temperature decreases the conductivity of metallic conductors. Give a reason.
23. Why are metals malleable and ductile?
24. Explain how chlorine exhibits a maximum covalency of 7.
25. Both helium and beryllium have ns^2 valence electronic configuration. But berylium forms compounds and helium cannot form compounds. Explain.

Level 3

1. CO_2 exists in the gaseous state, whereas SiO_2 is a hard solid though both carbon and silicon belong to the same group. Give reasons.
2. A molecule has 3 bonded pairs and 2 lone pairs on the central atom. Explain the shape of the molecule with an example.
3. XeF_2 is also a linear molecule like $BeCl_2$. But they differ in their formation and structural aspects. How can you justify this?
4. A molecule has an octahedral geometry. So how many number of valence electrons should the central atom possess and are the number of valence electrons is the same if one, two bond pairs are successively replaced by lone pairs? What are the geometries of the molecules with one and two lone pairs? Explain with the help of hybridization.
5. Thallous compounds are more common and stable than thallic compounds. Justify this statement.

***Directions for questions from 6 to 10*: Application-Based Questions**

6. Lattice energies of fluoride, chloride, bromide and iodide compounds are 766.5, 597.5, 537.5 and

PRACTICE QUESTIONS

437.03 k J/mole, respectively. Compare the oxidizing capacities of the halogens on the basis of the lattice energies of these compounds with an appropriate reason.

7. A molecule "AB_5" has five bond pairs around the central atom "A." If the bond pair of electrons are successively replaced by one, two and three lone pair of electrons, then what would be the preferred shapes of the molecules and how do they differ from actual geometry of AB_5?

8. Though covalent character increases from lithium fluoride to lithium iodide, lithium fluoride is insoluble in water while lithium iodide is soluble. Justify the above statement.

9. Between NF_3 and BF_3, which is the more polar molecule? Why?

10. The atomic number of tin is 50 and chlorine is 17. What should be the shape of $SnCl_2$ molecule in its vapour state?

CONCEPT APPLICATION

Level 3

True or false

1. False
2. False
3. True
4. False
5. True
6. False
7. False

Fill in the blanks

8. two
9. stronger
10. sigma
11. 109°28`
12. HF
13. linear
14. ammonia

Match the following

15. A : e
    B : g
    C : b
    D : c
    E : a
    F : d
    G : f

Multiple choice questions

16. b
17. a
18. a
19. d
20. a
21. d
22. b
23. c
24. a
25. b
26. d
27. c
28. b
29. c
30. c

Solutions for questions from 31 to 45:

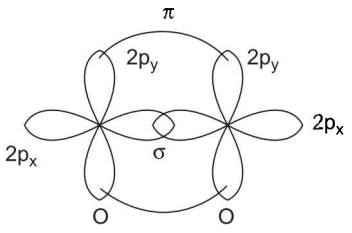
31. (i) Aqueous solutions of both ionic compounds and polar covalent compounds conduct electricity because of the presence of free ions.

(ii) All the ionic compounds are solids and most of the nonpolar covalent molecules are gases or solids at room temperature. Polar covalent compounds are liquids or gases.

(iii) As aqueous solution of X doesn't conduct electricity and moreover it is a gas at room temperature. It should be a non-polar molecule. Hence, it is a covalent molecule.

(iv) Y is a solid at room temperature in which its aqueous solution conducts electricity shows that it is an ionic compound.

32. (i) The electronic configuration of oxygen is O: $1s^2$ $2s^2$ $2px^2$ $2py^1$ $2pz^1$.



(ii) All the three 2p orbitals are perpendicular to each other.

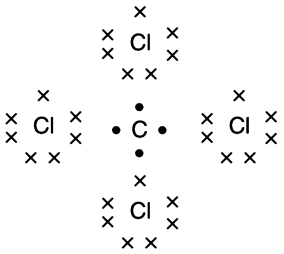
Hence 2pz orbitals of each oxygen atom overlap end to end to form a strong sigma bond.

(iii) 2py orbitals of each oxygen atom overlap laterally/sidewise to form a weak pi bond.

(iv) Thus double bond between two oxygen atoms in which one p_y–p_y pi bond is formed.

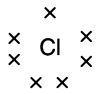
33. (i) Write the symbol of carbon and represent its valence electrons with the help of dots, i.e.,

HINTS AND EXPLANATION



(ii) Write the symbol of chlorine and represent its valence electrons with the help of crosses, i.e.,

(iii) When carbon combines with four chlorine atoms, the carbon atom contributes four electrons for sharing, whereas each chlorine atom contributes only one electron. Thus, both the atoms in CCl_4 attain an octet.

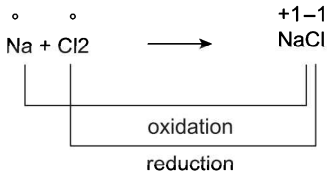


(iv) Lewis electron dot diagram for CCl_4. Thus, an electron pair is shared between C and Cl.

34. Since glucose does not ionize in water, it does not conduct electricity in its aqueous solution sate.

35. The ease of formation of ionic bond is directly proportional to the size of metal atom and inversely proportional to the size of non-metallic atom. Hence the ease of formation of ionic bond is maximum in CaCl.

36.



During the formation of NaCl, Na undergoes oxidation and Cl undergoes reduction. Hence Na is the reducing agent and Cl is the oxidizing agent.

37. The two elements are potassium and chlorine, respectively. Hence the bond formed between them is an ionic bond.

38. In a water molecule, oxygen has sp^3 hybridization. Two of these hybrid orbitals have lone pair of electrons, and the other two overlap with s-orbital of hydrogen to form sigma bonds. The expected shape is tetrahedral. But due to lone pair–lone pair repulsions, the shape becomes angular.

39.

Elements	Atomic numbers	Electronic configurations
A	11	2, 8, 1
B	12	2, 8, 2
C	13	2, 8, 3
D	19	2, 8, 8, 1

A and D can lose one electron and become stable, B loses two electrons and C loses 3. Strength of metallic bond depends on the charges on metal kernels and radii. As C has the maximum charge and is the smallest in size among the given elements, the metallic bond is the strongest in C.

40. CsCl is a compound in which the bond shows maximum ionic character. According to Fajan's rule, caesium has large size and lesser charge and hence shows maximum ionic character.

41. Ionic bond formation is favourable between metals having low IP values and nonmetals having high EA values.

42. Electronic configuration of fluorine is $1s^2 2s^2 2p^5$ and has a half-filled p-orbital for overlapping.

43. Since the electronegativity of N is greater than P, S and C, H-bond is present in NH_3 gas.

44. In hydronium ion both coordinate and covalent bonds are present. Hence the covalency of oxygen in hydronium ion is equal to number of covalent bonds and coordinate bonds.

45. As the solid compound A consists of simple ions, A is ionic in nature.

Level 2

1. (i) bonds present in the molecule of CH_4, CCl_4 and $CHCl_3$ and their polarity
(ii) bond moments of C–H and C–Cl bonds
(iii) shapes of the respective molecules
(iv) influence of the shape on the molecule of the net dipole moment

2. (i) size of the cation
(ii) comparison of the size of the alkali metals and transition metals belonging to the same group
(iii) effect of size on the polarizing power of the cation
(iv) relation between the polarizing power of the cation and the covalent character of the compound

3. (i) shape of orbitals
(ii) shapes of p- and d-orbitals in contrast to the shape of "s-" orbitals
(iii) type of overlapping in π bond

4. (i) composition and nature of glass and wax
(ii) comparison of types of forces existing between the molecules of water, glass and water and wax
(iii) relation between type of force and meniscus

5. (i) comparison of size of the anions
(ii) comparison between anionic sizes of O^{-2} and S^{-2} ions
(iii) effect of anionic size on the polarizing power of Cu^{+2} ion

6. (i) difference between lone pair and bond pair
(ii) comparative study of nuclear force of attraction on the lone pairs and bond pairs
(iii) comparison of spreading of electron clouds of lone pairs and bond pairs

7. (i) comparison of shape of $BF_3$and NF_3
(ii) number of lone pairs and bond pairs present in the valence shell of the central atom of respective molecules
(iii) shapes of the respective molecules
(iv) influence of shape on the polarity of the molecule

8. (i) comparison of atomic size of xenon with other noble gases
(ii) electronic configuration of xenon and atomic size of xenon
(iii) scope for excited state configurations
(iv) types of hybridizations possible

9. (i) comparison of electrons present in the valence shell in Cl in Cl_2O and H in H_2O
(ii) comparison of size between chlorine and hydrogen
(iii) comparison of the valence electronic configuration between hydrogen and chlorine

10. (i) valence shell of "S."
(ii) number and type of orbitals present in the valence shell
(iii) number of unpaired and paired electrons present in valence shell in ground state
(iv) number of unpaired electrons possible in different exited states
(v) relation between number of unpaired electrons and covalency

11. (i) valence electronic configuration of hydrogen and chlorine
(ii) type of hybridization in PCl_5
(iii) comparison of electronegativities between hydrogen and chlorine
(iv) the difference between the energies of overlapping orbitals

12. (i) comparison of the size of the anions
(ii) factors affecting the lattice energy

13. (i) order or intensity of repulsions between different electron pairs
(ii) preferred positions of an electron pair which causes more repulsion
(iii) geometry based on arrangement of different electron pairs

14. (i) relation between the energy of the system and its stability
(ii) kind of force exerted on the atoms when they approach each other after bond formation
(iii) interrelation among work, force and energy
(iv) effect of the amount of force on the rate of change of energy

15. (i) requisite of a substance to be soluble in water
(ii) type of forces of attraction in between the compounds of NaCl and NH_4Cl
(iii) effect of this on solubility

Solutions for questions from 16 to 25: **Application-Based Questions**

16. Ionic compounds are formed easily between larger cation and smaller anion. This is because an atom whose atomic radius is large can form a cation easily and an atom which has a small atomic radius can form an anion easily. Cs^+ ion can be formed more easily than Na^+ ion. Formation of CsCl is easier than the formation of NaCl. Between NaCl and CsCl, as the anion is the same, i.e., Cl^-, the sizes of the cations are compared. Cs^+ has a larger ionic radius than Na^+. Thus the strength of ionic bond is more in NaCl than CsCl.

17. When a polar molecule like HF is placed between charged parallel plates, the molecule orients in such a way that the positive end of the molecule is

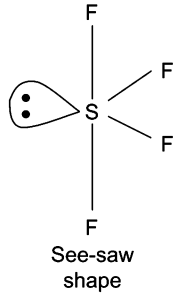
directed towards the negatively charged plate and the negative end of the molecule is directed towards the positively charged plate. As a result of this, the intensity of the charge on each plate is diminished. However, when dry air (nitrogen, oxygen) which is nonpolar in nature is placed, there would be no change in the intensity of the charge.

18. The valence electronic configurations of phosphorous is $3s^23p^3$. Though there are only 3 half-filled orbitals for bonding, in the excited state five half-filled orbitals are available for bond formation. Among these five orbitals, three are "p-" orbitals and two are "d-" orbitals. These orbitals overlap with the half-filled "3p" orbitals of five chlorine atoms forming PCl_5 molecule. Such a situation is not possible with hydrogen atoms since there is wide variation in energies between "3d" orbitals of phosphorous and "1s" orbitals of hydrogen.

19. electronic configuration of sulphur is $[Ne]3s^23p^43d^0$

electronic configuration of excited state of sulphur is $[Ne]3s^23p^33d^1$

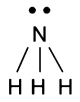
SF_4 is formed when four half-filled spd^3 dhybrid orbitals of sulphur atom overlap with half-filled "p" orbitals of fluorine atoms. Hence there exist four bond pairs and one lone pair in SF_4 molecule. According to the VSEPR theory expected structure of SF_4 is trigonal bipyramidal but as the lone pair and two bond pairs of the molecule lie on the plane and other two bond pairs present above and below the plane and the structure of SF_4 is "seesaw" structure. This deviation is due to the lone pair of electrons.



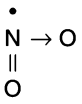
See-saw shape

20. Polarizing power of the cation depends on its size and the charge present on it. The smaller the size and the higher the charge of the cation, the greater the polarizing power. Among Na^+, Mg^{+2} and Al^{+3}, Al^{+3} has least ionic size and the charge present on it is maximum. Hence, polarizing power of Al^{+3} is maximum. Among the halides AlF_3 is ionic, but other halides of aluminium are covalent. Polarizing power of magnesium is less than aluminium. Hence, chloride and fluoride of magnesium are ionic. But Na^+ has the least polarizing power. Hence, all the halides of sodium are ionic.

21. The central nitrogen atom of ammonia has lone pair of electrons on it which can be donated to form coordinate covalent bond, which is obvious from the nature of bonding present in NH_3. Thus, the central N atom of NH_3 acts as a donor.



The central "N" atom of NO_2 doesn't participate in coordinate covalent bond formation due to the lack of lone electron pair on nitrogen. The central "N" participates in coordinate covalent bond formation with oxygen during the formation of NO_2 and thus it cannot further act as donor and forms coordinate covalent bond with other species which is obvious from the nature of bonding present in NO_2.



22. Being more electropositive in nature, metals have a tendency to lose their valence electrons. Due to the presence of these free electrons metals act as good conductors. But increase in temperature increases the vibrations of metal kernels in the metal lattice. Increase in the vibrations obstructs the path of the electrons which in turn increases the resistance of the metal. Therefore, the conductivity decreases.

23. When a large amount of shearing force is applied to a metal, the metal kernels of one layer slide over the other. After getting displaced, the metal kernels again get stabilized there due to the uniform distribution of free electrons throughout the metal. Hence metals can be permanently deformed without breaking and exhibit malleability and ductility.

24. Electronic configuration of Cl is [Ne] $3s^23p^5$. In the 3rd shell, there are vacant d-orbitals. The paired electrons of 3s and 3p orbitals can be excited to 3d orbitals. Therefore, the number of unpaired electrons increases. As a result, covalency corresponding to the number of unpaired electrons is exhibited. In the fully excited state of Cl atom, there are 7 half-filled orbitals giving covalency of 7. As there is

no scope for further excitation, it is the maximum covalency that chlorine can show.

Ground state : ⇅ | ⇅ | ⇅ | 1 | | | | | ⇒ Covalency of 1

1st excited state : ⇅ | ⇅ | 1 | 1 | 1 | | | | ⇒ Covalency of 3

2nd excited state : ⇅ | 1 | 1 | 1 | 1 | 1 | | | ⇒ Covalency of 5

3rd excited state : 1 | 1 | 1 | 1 | 1 | 1 | 1 | | ⇒ Covalency of 7

25. Both helium and beryllium have ns^2 valence electronic configuration. Berylium has an electron pair in 2s orbital and all three 2p orbitals are vacant. The paired electron of 2s orbital can be excited to 2p orbital thereby giving a covalency of 2. Helium has an electron pair in "1s" orbital and there is no scope for excitation of electrons in the 1st shell. Hence, helium cannot form any compounds.

Level 3

1. (i) comparison of size of carbon and silicon
(ii) effect of size of carbon and silicon on the nature of bond present in CO_2 and SiO_2
(iii) influence of nature of bonds on the structure of the molecules
(iv) relation between the structure of the substance and physical state of matter

2. (i) expected shape with 5 bond pairs
(ii) determination of number of hybrid orbitals
(iii) the expected shape of the molecule
(iv) distortion due to lone pairs and resultant shape of the molecule

3. (i) comparison of electronic configuration of beryllium and xenon
(ii) type of hybridization in XeF_2 and $BeCl_2$
(iii) the number of lone pairs and bond pairs present in the valence shell of the central atom

4. (i) relation between number of valence electron pairs (bond pairs and lone pairs) and geometry
(ii) number of valence electrons around central atom for octahedral geometry

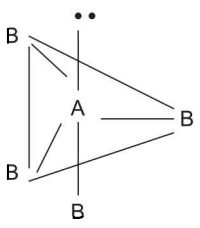
5. (i) valence electronic configuration of thallium
(ii) difference in the electronic configuration of thallous and thallic ions
(iii) comparison of the ease of formation of thallous and thallic ions
(iv) relation between the ease of formation of ion and availability of the compound in nature containing that ion

Solutions for questions from 6 to 10: **Application-Based Questions**

6. The more the lattice energy, the stronger the ionic bond which in turn depends on the ease of formation of anion if the cation is the same. The easier the formation of the anion, the more the oxidizing capacity. Hence, from the given lattice energies it can be concluded that the increasing order of the oxidizing capacities of halogens is

$$I_2 < Br_2 < Cl_2 < F_2$$

7. In AB_5 molecule, central atom A is surrounded by five electron pairs and no lone pairs. Hence the structure is a trigonal bipyramid and as there are no lone pairs, so the structure is not distorted. Here in this structure three bonded atoms occupy equatorial positions of the triangle and other two axial positions (top and bottom) of the equilateral triangle. When one of the bond pairs is replaced by a lone pair, the preferred position of the lone pair is equatorial and the geometry is distorted trigonal bipyramid because in this structure it experiences less number of repulsions and hence stable.



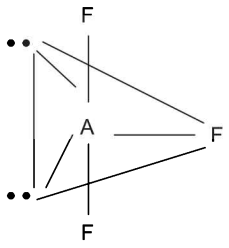
(i) Wrong structure (ii) Right structure

When two bond pairs are replaced by lone pair of electrons, then the preferred geometry will be the one of lowest energy with minimum repulsions.

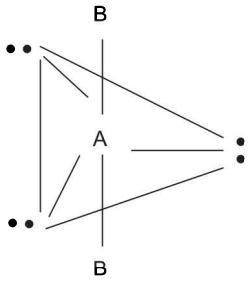
When two lone pairs are present among five electron pairs allowed the central atom then the molecule experiences three types of repulsions and their order is

1. p - l.p > l.p - b.p > b.p - b.p. The structure which has lesser repulsions is

HINTS AND EXPLANATION



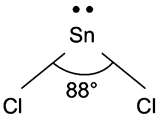
The two lone pairs are separated by maximum bond angle of 120° and hence the above structure is most preferred geometry which is T-shape with minimum repulsions. When three bond pairs are replaced by a lone pair, then the preferred geometry is the one where three lone pairs occupy equatorial positions with maximum separation of bond angle and hence shape is linear.



8. Since the size of halide ion increases down the group, the ease of getting polarized by a cation also increases. Thus Li^+ ion can polarize I^- ion to a greater extent and thus from LiF to LiI covalent character increases. Hence we expect that LiF is more soluble in water and LiI is less soluble or not soluble in water. The solubility of an ionic compound in water depends on the relative values of lattice energy and hydration energy. The substance becomes soluble in water if hydration energy exceeds lattice energy. From LiF to LiI, lattice energy decreases while hydration energy increases. Since lattice energy of LiF is much greater than hydration energy, it is insoluble in water and thus solubility in water increases from LiF to LiI.

9. Between NF_3 and BF_3, NF_3 is polar but BF_3 is non-polar. In the BF_3 molecule there is no lone pair of electrons on the central atom. The shape of this molecule is trigonal planar which is symmetrical. NF_3 has three bond pairs and one lone pair. But due to the presence of a lone pair on nitrogen the polarities are not cancelled. Hence, the NF_3 molecule is polar.

10. The electronic configuration of Sn is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2$ and chlorine is $1s^22s^22p^63s^23p^5$. Hence in $SnCl_2$ molecule in vapour state, there is one lone pair of electrons and two bond pairs of electrons in the valence shell of tin. Therefore, the expected shape is trigonal planar. But due to presence of the lone pair, its shape is bent and bond angle is 88°.



Chapter

6

Acids, Bases and Salts

Remember

Before beginning this chapter, you should be able to:

- review the methods of preparation, properties, and uses of acids and bases
- review the types of salts, their methods of preparation, properties and uses
- know neutralization method

Key Ideas

After completing this chapter, you should be able to:

- classify the acids and bases based on different properties and to calculate the equivalent masses of acids and bases
- learn about the preparation of standard solution and estimation of volumes of solutions (volumetric analysis)
- study the self ionization of water and the ionic product of water
- know about pH (the hydrogen ion concentration of solutions), calculation of pH and it's importance in daily life
- identify the classification of salts based on the characteristics
- know about the laboratory preparation of specific soluble and insoluble salts
- understand the application of the concepts of acids and bases in qualitative analysis of simple salts.

INTRODUCTION

Acids and bases are two important classes of compounds which we come across in chemistry. Initially, the substances which are sour to taste were termed acids. In fact, the name acid was derived from a Latin word "acidum" meaning "sour." Similarly, bases or alkalies were characterized by their bitter taste and their slippery touch.

The earliest idea regarding acids was that all acids necessarily contain oxygen as one of the elements. Later further researches proved that the acids are of two categories. The first category of acids called hydracids contains only hydrogen and a nonmetal. E.g., HCl. The second category of acids that contain oxygen in addition to hydrogen and a nonmetal are called oxyacids. E.g., H_2SO_4. These two types of acids are together called mineral acids since they originate from mineral sources in contrast to the organic acids which have their origin from plant and animal sources.

Acids and bases were basically distinguished by their response to litmus test. Acids turn blue litmus red and bases turn red litmus blue. "Salts" is another important category of chemical compounds. The term salt is generally used in our daily life for common salt which is an important component of our diet. In the language of chemistry, however, the term "salts" covers all electrovalent compounds having positive and negative radicals formed by the reactions of corresponding acids and bases. Therefore, the study of salts is invariably associated with the study of acids and bases.

THEORIES OF ACIDS AND BASES

Svante Arrhenius, for the first time in 1884, proposed a systematic theory to explain the nature of acids and bases.

Arrhenius Theory of Acids and Bases

Postulates

(i) An acid is a substance which contains hydrogen and produces H^+ ions in an aqueous solution.

Examples

$HCl \rightarrow H^+ + Cl^-$

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

$HSO_4^- \rightarrow H^+ + SO_4^{-2}$

(ii) A base is a substance which produces OH^- ions in the aqueous solution.

Examples

$NaOH \rightarrow Na^+ + OH^-$

$KOH \rightarrow K^+ + OH^-$

$Mg(OH)_2 \rightarrow Mg^{+2} + 2OH^-$

(iii) All acids which ionize completely and hence produce more concentration of H^+ ions are called **strong acids**. All acids which ionize partially and hence produce less concentration of H^+ ions are called **weak acids**.

Examples

$HNO_3 \rightarrow H^+ + NO_3^-$ (100% ionization, strong acid)

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ (partial ionization, weak acid)

(iv) All bases which ionize completely and hence produce more concentration of OH^- ions in their aqueous solutions are called **strong bases**. All bases which ionize partially and produce less concentration of OH^- ions are called **weak bases**.

Examples

$KOH \rightarrow K^+ + OH^-$ (100% ionization, strong base)

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (partial ionization, weak base)

(v) Neutralization is defined as the reaction between an acid and a base to give salt and water.

Example

$HCl + NaOH \rightarrow NaCl + H_2O$

Since the strong acid and the strong base are completely ionized in aqueous solutions, they will be present in the form of ions. During the reaction, the anion of acid and cation of the base do not undergo any net change.

Therefore, the net reaction would be formation of water by the combination of H^+ and OH^- ions. The other ions which remain unchanged during the reaction are called spectator ions.

Examples

$HCl + NaOH \rightarrow NaCl + H_2O$

$H^+ Cl^- + Na^+ OH^- \rightarrow Na^+ + Cl^- + H_2O$

The net reaction of neutralization becomes $H^+ + OH^- \rightarrow H_2O$

After proposing his theory of electrolytic dissociation, Arrhenius himself gave a modified version of his theory.

According to this version, the acid is defined as a substance which increases the concentration of H^+ ions or hydronium ions in aqueous solutions. The base is defined as a substance which increases the concentrations of OH^- ions in their aqueous solutions.

Examples

$CO_2 + 3H_2O \rightarrow SO_4^{-2} + 2H_3O^+$

$NH_3 + H_2O \rightarrow SO_4^{-2} + OH^-$

Limitations of Arrhenius Theory

(i) Arrhenius theory could not explain the acidic nature of substances which do not contain hydrogen. For example, non-metal oxides are generally acidic, but they do not contain hydrogen.

Examples: CO_2, SO_3, etc.

(ii) Bases which do not contain OH^- ions also could not be explained by Arrhenius concept. For example, metal oxides are generally basic, but they do not contain OH^- ions.

Examples: CaO, MgO, etc.

(iii) Arrhenius theory was confined only to aqueous solutions. It could not explain the nature of acidic and basic substances in gas phase or in non-aqueous solutions.

(iv) Arrhenius theory failed to explain the neutralization reactions which do not involve formation of water.

Example: $CaO + CO_2 \rightarrow CaCO_3$

(v) Later studies on solutions have revealed that H^+ ions have no independent existence in aqueous solutions. They exist as hydronium ions (H_3O^+). This is in contradiction to Arrhenius theory.

In order to account for these drawbacks, a more advanced theory was proposed which introduced the protonic concept of acids and bases.

Lowry–Bronsted Theory of Acids and Bases

In 1923, J.N. Bronsted and J.M. Lowry independently proposed a broader concept of acids and bases in order to overcome some of the drawbacks of Arrhenius theory.

Postulates

(i) The acid is a substance which donates protons to any other substance(s).

Example

HCl acts as a proton donor and hence is called an acid.

$HCl \rightarrow H^+ + Cl^-$

(ii) The base is a substance which accepts protons from any other proton donors.

Example

NH_3 acts as a base as it is a proton acceptor.

$NH_3 + H^+ \rightarrow NH_4^+$

(iii) An acid on losing a proton produces a species which has proton accepting tendency that means the tendency of a base. The base so formed is called conjugate base of the acid.

Example

$HCl \rightarrow H^+ + Cl^-$
Acid Conjugate base

(iv) The base on accepting a proton produces a species which has proton donating tendency that means the tendency of an acid. The acid so formed is called conjugate acid of the base.

Example

$NH_3 + H^+ \rightarrow NH_4^+$
Base Conjugate acid

(v) Neutralization is defined as the transfer of a proton from the acid to the base to form a conjugate acid–base pair. Since this theory mainly focuses on proton transfer, this is also known as protonic concept of acids and bases.

Example

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NH_3} \rightarrow \underset{\text{Conjugate acid}}{NH_4^+} + \underset{\text{Conjugate base}}{Cl^-}$$

Merits

(i) The acidic and basic nature of substances in gas phase could be convincingly explained by this theory which could overcome the major limitations of Arrhenius theory.

(ii) It involves a broader coverage of acids and bases in comparison to Arrhenius theory. This is because it is not confined to aqueous solutions alone.

(iii) The basic nature of substances which do not contain OH^- ions could also be explained on the basis of protonic concept.

Limitations

(i) The acidic nature of substances which do not contain hydrogen cannot be explained.

Examples: CO_2, SO_2, etc.

(ii) This theory mainly involves proton transfer. Proton donation or acceptance being a relative tendency of substances, cannot give the absolute acidity or basicity of substances.

In order to explain the nature of acids and bases in cases where there is no role for protons, a more advanced theory was proposed which introduced the electronic concept of acids and bases.

Lewis Theory of Acids and Bases

In 1930, G.N. Lewis introduced another theory of acids and bases which could successfully explain the cases where there is no role for protons.

Postulates

(i) The acid is a substance which can act as an electron pair acceptor. The molecule or ion should be associated with shortage of electrons to act as the acid.

Examples: BF_3, H^+, etc.

(ii) The base is a substance which can act as an electron pair donor. The molecule or ion should be associated with one or more lone pairs of electrons to act as the base.

Examples: NH_3, OH^-, etc.

(iii) Acid–base neutralization can be defined as the transfer of an electron pair from the base to the acid.

$H^+ + NH_3 \rightarrow [H^+ \leftarrow NH_3]^+$

Formation of a hydronium ion and an ammonium ion can be explained by means of Lewis theory of acids.

Formation of Hydronium ions (H_3O^+)

$H^+ + H_2O \rightarrow H_3O^+$

Formation of ammonium ion

$NH_3 + H^+ \rightarrow NH_4^+$

Merits

(i) This theory could explain the acidic nature of those substances which do not contain hydrogen molecules.

(ii) It could explain the neutralization reactions which do not involve any transfer of protons.

Limitations

(i) This theory failed to explain the acidic and basic nature of general acids and bases.

(ii) This theory could not explain the general neutralization reactions involving the formation of salt and water.

(iii) Generally, the acid–base reactions are fast reactions. But the formation of a coordinate bond is a slow process.

(iv) This theory cannot explain the relative strengths of acids and bases.

The three different theories of acids and bases explain the nature of various acids and bases in different perceptions. However, none of the theories could convincingly explain all the properties of acids and bases and hence cannot be universally applicable. Depending on the nature and conditions of a reaction, an appropriate theory is made applicable. Thus all the three theories put together can cover the entire range of acids and bases.

Acids and bases can be further classified on the basis of certain properties as discussed hereunder.

CLASSIFICATION OF ACIDS

(i) *On the basis of strength*

(a) **Strong acids**: The acids which undergo nearly 100% ionization in aqueous solutions are called strong acids. These produce a high concentration of H^+ ions in the solution.

Example

$HCl \rightarrow H^+ + Cl^-$ (~100% ionized)
(aq)

(b) **Weak acids**: Acids which undergo partial ionization in aqueous solutions are called weak acids. These produce low concentration of H^+ ions in the solution.

Example

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

(ii) *On the basis of basicity*

Number of H^+ or H_3O^+ ions produced by ionization of one molecule of an acid in aqueous solution is called its basicity.

(a) **Monobasic acids**: The acids which dissociate in aqueous solutions to produce one hydronium ion per molecule of the acid are called monobasic acids.

Examples

HCl, HBr, HNO_3, HI, CH_3COOH

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

(b) **Dibasic acids**: The acids which dissociate in aqueous solutions to produce two hydronium ions per molecule of the acid are called dibasic acids.

Examples

H_2SO_4, $H_2C_2O_4$, H_2SO_3, H_2CO_3

$H_2SO_4 + H_2O \rightleftharpoons H_3O + + HSO_4^-$

$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

(c) **Tribasic acids**: The acids which dissociate in aqueous solution to produce three hydronium ions per molecule of the acid are called tribasic acids.

Examples

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$

(iii) *On the basis of concentration*

(a) **Concentrated acid**: An aqueous solution that has a high percentage of acid and a low percentage of water is said to be a concentrated acid.

(b) **Dilute acid**: An aqueous solution that has a low percentage of acid and a high percentage of water is said to be a dilute acid.

(iv) *On the basis of volatility*

Acids which vaporize easily below 100°C are volatile acids.

Examples

HCl, HNO_3, H_2SO_3, H_2CO_3

Acids which do not vaporize even on strong heating are non-volatile acids.

Examples

H_2SO_4, H_3PO_4, etc.

CLASSIFICATION OF BASES

(i) *On the basis of strength*

(a) **Strong bases**: Bases which undergo nearly 100% (complete) ionization in aqueous solutions. These produce high concentration of OH^- ions in the solution.

Examples

$$Ba(OH)_2 \rightarrow \underset{(aq)}{Ba^{+2}} + \underset{(aq)}{2OH^-} \quad (\sim 100\%\ \text{ionized})$$

$$NaOH \rightarrow Na^+ + OH^-$$

(b) **Weak bases**: Bases which undergo partial ionization in aqueous solutions. It produces low concentration of OH^- ions in the solution.

Example

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

(ii) *On the basis of acidity*

Number of OH^- ions produced by the ionization of one molecule of the base in the aqueous solution is called its acidity.

(a) **Monoacidic bases**: The bases which dissociate in the aqueous solution to produce one hydroxyl ion per molecule of the base are called monoacidic bases.

Examples

$NaOH$, KOH, NH_4OH, etc.

$NaOH \rightleftharpoons Na^+ + OH^-$

(b) **Diacidic bases**: The bases which dissociate in aqueous solutions to produce two hydroxyl ions per molecule of the base are called diacidic bases.

Examples

$Ca(OH)_2$, $Cu(OH)_2$, $Mg(OH)_2$, etc.

$Ca(OH)_2 \rightleftharpoons Ca^{+2} + 2OH^-$

(c) Triacidic bases: Triacidic bases are those which dissociate in the aqueous solutions to produce three hydroxyl ions per molecule of the base.

Examples

$Al(OH)_3$, $Fe(OH)_3$, etc.

$Fe(OH)_3 \rightleftharpoons Fe^{+3} + 3OH^-$

General Preparation Methods of Acids

(i) By synthesis/direct combination (for hydracids and binary acids)

Hydrogen + Nonmetal → Acid

$H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$

$H_2 + Br_2 \xrightarrow[\text{discharge}]{\text{electric}}$

$H_2 + I_2 \rightarrow 2HI$

(Vapour)

(ii) By the reaction of non-metallic (acidic) oxides with water.

Non-metallic oxide + Water → Acid

$SO_3 + H_2O \rightarrow H_2SO_4$

$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$

$N_2O_5 + H_2O \rightarrow 2HNO_3$

(iii) By the oxidation of nonmetals with oxyacids

Non-metal + Acid → Acid + Water + Oxide

$S + 6HNO_3 \xrightarrow{\Delta} H_2SO_4 + 2H_2O + 6NO_2$

$2P + 5H_2SO_4 \xrightarrow{\Delta} 2H_3PO_4 + 5SO_2 + 2H_2O$

(iv) By the displacement of salts of more volatile acids with less volatile acid.

Salt + Less volatile acid → Salt + More volatile acid

$NaCl + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HCl$

$NaNO_3 + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HNO_3$

General Preparation Methods of Bases

(i) By the action of water on metals

Water + Metal → Base/Alkali + Hydrogen↑
(cold)

$2H_2O + 2Na \rightarrow 2NaOH + H_2\uparrow$

$\underset{\text{(steam)}}{H_2O} + Mg \rightarrow MgO + H_2\uparrow$

$\underset{\text{(steam)}}{4H_2O} + 3Fe \rightleftharpoons Fe_3O_4 + 4H_2\uparrow$

(ii) By the action of metallic oxides on water

Metallic oxide + Water → Base

$K_2O + H_2O \rightarrow 2KOH$

$MgO + H_2O \rightarrow Mg(OH)_2$

(iii) By the action of oxygen on metals

Metal + Oxygen → Metallic oxides

$2Mg + O_2 \rightarrow 2MgO$

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$

(iv) By the decomposition of metal carbonates

Metal carbonate $\xrightarrow{\Delta}$ Basic oxide + Carbon dioxide

$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$

$CuCO_3 \xrightarrow{\Delta} CuO + CO_2\uparrow$

(v) Using soluble metal salts and NaOH/KOH

Soluble metal salt + NaOH/KOH → Salt + Insoluble metal hydroxide

$AlCl_3 + 3NaOH \rightarrow 3NaCl + Al(OH)_3\uparrow$

$Zn(NO_3)_2 + 2KOH \rightarrow 2KNO_3 + Zn(OH)_2\downarrow$

(vi) Strong heating of metal nitrates

Metal nitrate $\xrightarrow{\Delta}$ Metal oxide + NO_2 + $O_2\uparrow$

$2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + 4NO_2\uparrow + O_2\uparrow$

$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2\uparrow + O_2\uparrow$

(vii) By the action of oxygen on metal sulphides

Metal sulphide + Oxygen → Metal oxide + Sulphur dioxide

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$

(viii) Dissolution of NH_3 in H_2O

$NH_3 + H_2O \rightarrow NH_4OH$
(weak alkali)

Chemical Properties of Acids

(i) *Action with metallic oxides*

Metal oxide + dilute acid → Salt + Water

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$

(ii) *Action with metallic carbonates and bicarbonates*

Carbonate or bicarbonate + Acid → Salt + H_2O + $CO_2\uparrow$

$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2\uparrow$

(iii) *Action with metallic sulphite and bisulphite*

Metal sulphite/bisulphite + Acid → Salt + H_2O + $SO_2\uparrow$

$CaSO_3 + 2HCl \rightarrow CaCl_2 + H_2O + SO_2\uparrow$

$NaHSO_3 + HCl \rightarrow NaCl + H_2O + SO_2\uparrow$

(iv) *Action with metallic sulphide and bisulphide*

Metal sulphide/bisulphide + acid → Salt + H_2S

$FeS + 2HCl \rightarrow FeCl_2 + H_2S$

$NaHS + HCl \rightarrow NaCl + H_2S$

(v) *Action of active metals with dilute acids*

Active metal + dil acid → Salt + $H_2\uparrow$

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$

$Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow$

(vi) *Reaction with chlorides*

Metal chloride + acid → Salt + acid

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$

$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl\uparrow$

(vii) *Reaction with nitrates*

$KNO_3 + H_2SO_4 \xrightarrow[200°C]{\text{over}} KHSO_4 + HNO_3$

$KHSO_4 + KNO_3 \xrightarrow[200°C]{\text{over}} K_2SO_4 + HNO_3$

Chemical Properties of Bases

(i) *Action with non-metallic oxides*

Alkali + CO_2 → Metal carbonate + H_2O

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O$

(ii) *Action with ammonium salt*

Ammonium salt + Alkali → Metal salt + H_2O + $NH_3\uparrow$

$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_3\uparrow$

$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + 2NH_3\uparrow$

(iii) *Action with soluble salts of metals other than that of Na, K and Ca*

Soluble metallic salt + Base → Soluble salt + Insoluble hydroxide

$CuSO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + Cu(OH)_2\uparrow$

Uses of Acids and Bases

Some important acids	Uses
(i) Sulphuric acid	Manufacture of fertilizers, dyes, drugs, explosives, paints, chemicals, artificial fabrics, etc.
(ii) Hydrochloric acid	Printing, tanning and tinning industries
(iii) Nitric acid	Manufacture of dyes, explosives, drugs, fertilizers and chemicals
(iv) Acetic acid	Preservation of food and as a flavouring agent
(v) Citric acid	Curdling of milk, flavouring of soft drinks and as a (source of vitamin C) medicine
(vi) Carbonic acid	Used in soft drink
(vii) Oxalic acid	Used as a ink stain remover
(viii) Boric acid	Preservation of grains, to wash eyes
(ix) Benzoic acid	As a food preservative
(x) Tartaric acid	Constituent of baking powder

Some important acids	Uses
(i) NaOH	Manufacture of soap
(ii) KOH	Manufacture of soft soap and in alkaline batteries
(iii) NH_4OH	Used to remove grease stains from woollen clothes
(iv) $Ca(OH)_2$	Manufacture of mortar, softening temporary hard water, neutralizing acidity of soil and as a general germicide
(v) $Mg(OH)_2$	Used as an antacid for neutralizing gastric acidity
(vi) $Al(OH)_3$	Used as a foaming agent in fire extinguishers

Neutralization

It is the reaction of the acid and the base to form the salt and water and is associated with the liberation of heat. The relative quantities of acid and base undergoing neutralization reaction and hence the heat liberated depends upon the concentration of H^+ ions and OH^- ions produced by the dissociation of the acid or the base in a given reaction. Since the acids and bases differ in their basicities and acidities, the concentration of H^+ and OH^- ions furnished by them also differs. Therefore, the quantities of acids and bases are expressed in terms of equivalents which represent quantities of substances which has same combining capacities in chemical reactions.

In a neutralization reaction, one equivalent of the acid is the quantity of the acid which furnished one mole of H^+ ions and for the base one mole of OH^- ions.

Example

$H_2SO_4 \rightarrow 2H^+ + SO_4^{-2}$

1 mole $H_2SO_4 \rightarrow$ 2 moles of H^+ ions

1 mole of H^+ ions $\rightarrow \frac{1}{2}$ mole H_2SO_4

= 1 equivalent H_2SO_4

For all monobasic acids and monoacidic bases, the equivalent weight is equal to the molecular weight.

Example

Molecular weight of HCl = Equivalent weight = 36.5

For the acids and bases that have their basicity or acidity greater than one, the equivalent weight must be calculated by taking the reaction into consideration.

$$\text{Equivalent weight of the acid} = \frac{\text{Molecular weight}}{\text{Number of replaceable hydrogen in the given reaction}}$$

$$\text{Equivalent weight of the base} = \frac{\text{Molecular weight}}{\text{Number of replaceable } OH^- \text{ ions in the given reaction}}$$

H_2SO_4.

$H_2SO_4 + NaOH \rightarrow NaHSO_4 + H_2O$

Example

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{1} = 98$$

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{2} = 49.$$

$Ca(OH)_2$

$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{2} = \frac{74}{2} = 37\,g$$

$$\text{Equivalent weight of salt} = \frac{\text{Molecular weight}}{\text{Net charge on ion}}$$

Na_2SO_4

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{2} = \frac{142}{2} = 71\,g.$$

Neutralization Reaction

Reaction between the acid and the base to form the salt and water liberating heat in the process.

Acid + Base $\longrightarrow$ Salt + Water + Heat

$HCl + NaOH \longrightarrow NaCl + H_2O + Heat$

$HNO_3 + KOH \longrightarrow KNO_3 + 2H_2O + Heat$

$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O + Heat$

Heat of Neutralization

The amount of heat liberated when one equivalent of the acid reacts with one equivalent of the base. For any strong acid–strong base reaction, the heat of neutralization has the same value, i.e., 13.7 kcal/mole since the acid and base involved are completely ionized.

Example

$HCl + NaOH \rightarrow NaCl + H_2O + 13.7$ kcal/mole

When the weak acid or the weak base is involved in the reaction, some amount of heat is utilized to ionize the acid or base to furnish ions. This is called heat of ionization. Therefore the net heat released is less than the heat of neutralization for strong acid–strong base reaction.

Example

Weak acid + strong base $\rightarrow$ salt + H_2O + 13.4 kcal/mole

Heat of ionization = 13.7 – net heat liberated

= 13.7 – 13.4 = 0.3 kcal/mole

$NaOH \rightarrow Na^+ + OH^-$

$CH_3COOH \rightarrow CH_3COO^- + H^+$ (consume 0.3 kcal)

$H^+ + OH^- \rightarrow H_2O$ (liberates 13.7 kcal)

$CH_3COOH + NaOH \rightarrow Na^+ + CH_3COO^- + H_2O$ + 13.4 kcal/mole

Uses of Neutralization

(i) Slaked lime ($Ca(OH)_2$) is added to reduce the acidity of soil.

(ii) Antacid tablets with $Mg(OH)_2$ or cold milk are used to treat acidity by neutralizing HCl in stomach.

(iii) Sting of ants/bees containing HCOOH (formic acid) can be neutralized by rubbing soap (NaOH).

(iv) Sting of wasps that contains an alkali can be treated by neutralizing it with CH_3COOH.

(v) Lithium hydroxide is used to neutralize CO_2 exhaled by astronauts in spaceships or submariners in submarines.

The concept of equivalent helps in determining the number of moles of the acid needed to neutralize the base and vice versa. This also plays a major role in determining the concentration of a solution in terms of normality.

Normality

The number of equivalents of a solute present in one litre of the solution is called normality. It is denoted by "N."

$$\text{Normality} = \frac{\text{Number of equivalents}}{\text{Volume of solution in litres}}$$

$$= \text{Number of equivalents} \times \frac{1000}{\text{V in ml}}$$

$$= \frac{\text{weight}}{\text{Equivalent weight}} \times \frac{1}{\text{V in } \ell} = \frac{\text{weight}}{\text{Equivalent weight}} \times \frac{1000}{\text{V in ml}}$$

The normality of the solution is helpful in expressing the concentration of the solution. However, in case of the acids and bases the concentration can also be expressed in terms of pH. The pH of the solution represents the hydrogen ion concentration in it. This is a single factor which represents not only the concentration but also helps in determining whether a solution is acidic or basic. To calculate the pH of a solution, the concept of ionic product of water should be well understood.

Ionic Product of Water

Water molecules ionize partially to give H^+ and OH^- ions. Equilibrium exists between the ionized and unionized molecules:

$$H_2O \rightleftharpoons H^+ + OH^-$$

Applying the law of mass action to the above equilibrium, $K = \frac{[H^+][OH^-]}{[H_2O]}$

Since $[H_2O]$ is constant (Molar concentration of water in its pure sample is $= \frac{1000}{18} = 55.55\,M$)

$K[H_2O] = K_w = [H^+]\,[OH^-]$

where K_w is called the ionic product of water.

At normal temperature (25°C), the concentration of H^+ and OH^- ions remains equal, i.e., 10^{-7} M

$\therefore [H^+] = [OH^-] = 10^{-7}$ moles/ℓ

$$K_w = [H^+]\,[OH^-] = 10^{-7} \times 10^{-7}$$
$$= 10^{-14}\ \text{mole}^2/\ell^2$$

On adding a base, $[OH^-]$ increases and $[H^+]$ decreases but K_w remains constant at constant temperature.

Example

$[H^+]$ mole ion/l	$[OH^-]$ mole ion/l	K_w (mol. ion)^2/l^2
1×10^0	1×10^{-14}	1×10^{-14}
1×10^{-3}	1×10^{-11}	1×10^{-14}

At 25°C,

Neutral solution → $[H^+] = [OH^-] = 10^{-7}$ mole ion/l

Acidic solution → $[H^+] > [OH^-] < 10^{-7}$ mole ion/l

Basic solution → $[H^+] < [OH^-] > 10^{-7}$ mole ion/l

In all the cases, the product of $[H^+]$ and $[OH^-]$ remains constant and is equal to 10^{-14} at 25°C.

Thus, at a given temperature the value of ionic product of water remains constant. Addition of the acid or the base does not change the value of K_w. On the addition of the acid, when $[H^+]$ increases a corresponding decrease in $[OH^-]$ keeps the K_w value constant.

pH

The concept of pH was introduced by Sørensen in order to avoid the use of negative exponents in expressing the concentration of acids and bases.

In pH, p means potentz and "H" stands for hydrogen.

pH is defined as the negative logarithm to base 10 of H^+ ion concentration (or) logarithmic reciprocal of H^+ ion concentration.

$$pH = -\log_{10}[H^+] \text{ or } \log_{10}\frac{1}{[H^+]}$$

Similarly,

$$pOH = -\log_{10}[OH^-] \text{ or } \log_{10}\frac{1}{[OH^-]}$$

At 25°C, for a neutral solution, $[H^+] = [OH^-] = 10^{-7}$ mole ion/l

$$\text{The pH} = -\log_{10}\frac{1}{[H^+]} = -\log_{10}\frac{1}{10^{-7}} = -\log_{10}10^7 = 7$$

For the acidic solution: $[H^+] > [OH^-] < 10^{-7}$ mole ion/l

$$\text{pH} = -\log_{10}\frac{1}{>10^{-7}} = < 7.$$

Lower the pH value, greater will be the acidic strength of the solution.

For the basic solution: $[H^+] < [OH^-] > 10^{-7}$ mole ion/l

$$\text{pH} = -\log_{10}\frac{1}{>10^{-7}} = > 7$$

Greater the pH value, greater will be the basic strength of the solution.

Relation between pH and concentration of H^+ ions

$[H^+]$	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Acid
←Acidity increases

Base
Basicity increases→

pH of Some Common Substances

Substances	pH values
HCl (gastric juice in stomach)	1.0
H_2SO_4	1.2
Citric acid	2.3
Lime juice	2.4
Acetic acid	2.9
Carbonic acid	3.0
Orange	3.5
Boric acid	5.2
Milk (lactic acid)	6.6
Pure water	7.0
Human blood	7.3
Albumin (egg)	7.9
$NaHCO_3$ solution	8.4
Sea water	8.5
Milk of magnesia	10.5
Ammonium hydroxide	11.1
Na_2CO_3 solution	11.6
NaOH	13

Uses of pH Value

(i) In brewing, pH values are strictly controlled for wines of desired flavour.

(ii) pH value of soils is tested to enhance growth of crops in acidic/alkaline soils.

(iii) pH value of milk is controlled in dairies.

(iv) Depending on pH values of skin secretion, different soaps for oily/dry skin are prepared.

(v) In medicine, for diagnosis of certain diseases, pH of blood and urine are determined.

By mathematically calculating the pH the nature of a solution can be determined. In a lab, however, certain chemicals are used as indicators to determine whether a solution is acidic or basic.

Indicators

Indicators are organic dyes that have one colour in acidic solutions and another colour in basic solutions. There are two types of indicators as listed hereunder:

(i) common indicator and

(ii) universal indicator.

Common Indicators

These are specific and work only in a specified pH range. Using these, it is possible to identify the acidic, basic and neutral solutions and the pH range of the solution. However, it is not possible to know the exact pH value of the solution.

Indicators	Colour in acidic solution	Colours in basic solution
Litmus	Red	Blue
Methyl orange	Red	Yellow
Phenolphthalein	Colourless	Pink

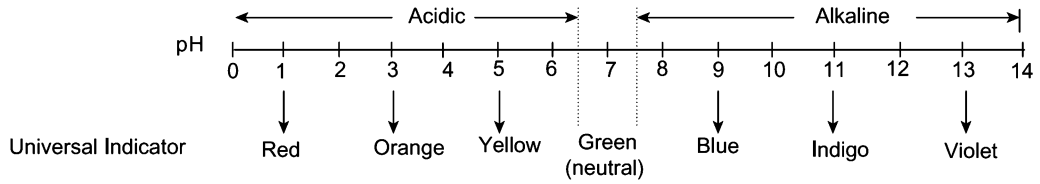
Determination of pH using indicators

Name of the indicators	Acid Colours	pH range of colour change	Base colours
Methyl violet	Yellow	0.0–1.6	Blue
Thymol blue	Red	1.2–2.8	Yellow
Methyl orange	Red	3.2–4.4	Yellow
Bromocresol green	Yellow	3.8–5.4	Blue
Methyl red	Red	4.8–6.0	Yellow
Litmus	Red	5.0–8.0	Blue
Bromothymol blue	Yellow	6.0–7.6	Blue
Thymol blue	Yellow	8.0–9.6	Blue
Phenolphthalein	Colourless	8.2–10.0	Pink
Thymolphthalein	Colourless	9.4–10.6	Blue
Alizarin yellow R	Yellow	10.1–12.0	Red

Universal Indicator

It is a mixture of organic dyes which gives different colours with solutions of different pH values. This is more sensitive than other common indicators.

Determination of pH using universal indicators



EXAMPLE

How does the concentration of hydronium ions change during dilution of an acid?

SOLUTION

Dilution of an acid decreases the concentration of hydronium ions per unit volume.

EXAMPLE

Give reasons for the following.

(a) Metal oxides generally react with acids. But zinc oxide reacts even with sodium hydroxide.

(b) Heat of neutralization value for the reaction of HCl and NH_4OH is less than 13.7 kcal/mole

(c) All indicators are not suitable for all titrations.

SOLUTION

(a) Zinc oxide is amphoteric in nature. Hence, it can react both with acids as well as bases.

(b) NH_4OH is a weak base and hence some heat is utilised to ionise the weak base.

(c) Indicator which underegoes colour change in the pH range of the titration is only suitable for a particular titration.

EXAMPLE

Explain the action of phenolphthalein indicator in the titration of acetic acid versus sodium hydroxide.

SOLUTION

Acetic acid is a weak acid having a pH value of more than 6. Sodium hydroxide is a strong base and addition of OH^- ions neutralizes the H^+ ions formed by the dissociation of acetic acid. Since H^+ ion concentration is very low, the addition of further OH^- ions increases the pH value abruptly. Therefore, the titration range of this reaction lies between 6.5 to 10.0.

The pH range of phenolphthalein is 8.2 to 10.0 and hence it undergoes colour change in this range. Hence it acts as a suitable indicator for this titration.

EXAMPLE

Is a solution with pH 6 acidic, basic or neutral? Justify.

SOLUTION

A solution with pH 6 will be acidic when the ionic product of water is 1×10^{-14} $mole^2$ / $litre^2$. In such a case, a solution with pH less than 7 is acidic in nature. On increasing the temperature, the ionic product of water increases due to increase in the ionization of water. When the ionic

product of water increases to 1×10^{-12} mole^2 / litre^2, a solution with pH 6 will be neutral and below 6 will be acidic in nature.

SALTS

All salts are basically ionic compounds and are electrically neutral as the total positive charge on positive radicals is equal to the total negative charge on negative radicals. These oppositely charged ions are held together by strong electrostatic forces of attraction when the salts are in the solid state. In fused state or in aqueous solutions, these forces of attraction are broken and the salts are dissociated into ions. This accounts for the electrical conductivity of their solutions. Thus all salts are electrolytes in their molten states as well as in their aqueous solutions.

Formation of Salts

Salts are the compounds formed during the neutralization reaction between the acid and the base. Therefore, salts can also be defined as the compounds formed by either partial or complete replacement of ionizable hydrogen atoms of the acid by one or more metal ions or ammonium ions of a base.

$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O$ (partial neutralization)

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$ (complete neutralization)

Ionic definition of salt can be given as the ionic compound which on dissociation in water yields one or more positive ions other than H^+ ions and one or more negative ions other than OH^- ions.

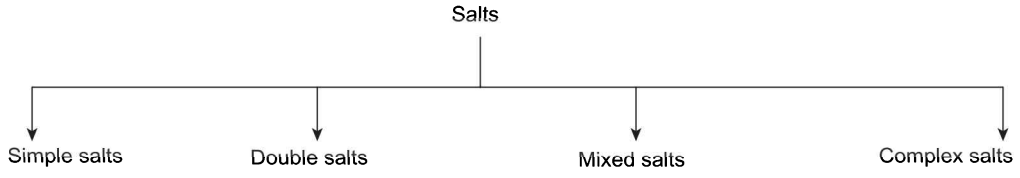
Examples

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

$(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^{-2}$

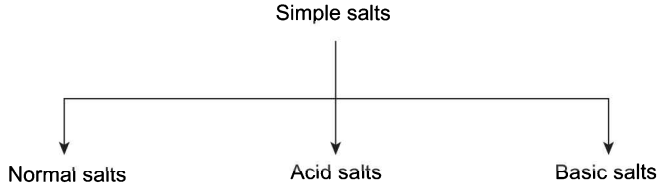
There are a large number of salts present. To make the study of salts easier they are classified into four different categories on the basis of their composition.

Classification of Salts



Simple Salts

The salts which contain only one type of positive ion and one type of negative ion are called simple salts. These are further classified into three types based on their chemical nature.



Comparative Study of Normal, Acid and Basic Salts

	Normal Salts	Acid Salts	Basic Salts
Definition	The salts which do not contain any replaceable hydrogen or "OH" groups.	The salts which contain one or more replaceable hydrogen groups.	The salts which contain one or more replaceable "OH" groups.
Formation	By complete neutralization of acids and bases. E.g. $2NH_4OH + H_2SO_4 \downarrow (NH_4)_2SO_4 + H_2O$	By incomplete neutralization of acids and bases. E.g. $NaOH + H_2SO_4 \downarrow NaHSO_4 + H_2O$	By incomplete neutralization of acids and bases. E.g. $Cu(OH)_2 + HNO_3 \downarrow Cu(OH)NO_3 + H_2O$
Composition	All ionizable hydrogens are replaced by a metal or NH_4^+ ion.	Partial replacement of ionizable hydrogen by a metal or NH_4^+ ion.	Partial replacement of ionizable hydroxyl groups by non-metal ions or negative radicals
Properties	Neutral in nature. Do not react with acids or bases.	Acidic in nature. Reacts with bases.	Basic in nature. Reacts with acids.
Examples	NaCl, $(NH_4)_2SO_4$, $Al_2(SO_4)_3$	$NaHSO_4$, NH_4HSO_4	$Cu(OH)NO_3$, Cu(OH) Cl

Double Salts

The salts which contain more than one simple salt are called double salts. These salts are formed by the crystallization and union of two simple salts dissolved in water. Double salts undergo complete dissociation in aqueous solutions. They give reactions of all ions present in both the simple salts. These salts are usually associated with water of crystallization.

Examples

Potash alum: $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Mohr's salt: $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Dolomite: $CaCO_3 \cdot MgCO_3$

Mixed Salts

The salts which contain more than one basic or acidic radicals are called mixed salts. These are formed by multi-step reactions involving corresponding acids and bases. Mixed salts undergo complete dissociation in aqueous solutions. They give the reactions of all the ions produced in aqueous solutions.

Examples

Sodium potassium carbonate ($NaKCO_3$) (Na^+, K^+ and CO_3^{-2} radicals)

Bleaching powder ($CaOCl_2$) (Ca^{+2}, OCl^-, Cl^- radicals)

Disodium potassium phosphate Na_2KPO_4 (Na^+, K^+, PO_4^{-3} radicals)

Complex Salts

The salts which contain one complex ion and one or more simple ions are called complex salts. These salts are formed by mixing saturated solutions of simple salts followed by crystallization.

Examples

Sodium argentocyanide $Na[Ag(CN)_2]$

Potassium ferrocyanide $K_4[Fe(CN)_6]$

A complex salt dissociates into complex ion and simple ions. Simple ions react individually, while the complex ions react as one unit.

Example

$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{-4}$

It gives reactions of potassium ions and ferrocyanide ions. But it cannot give reactions of ferrous ions and cyanide ions separately.

Preparation of Salts

(i) Preparation of Soluble Salts

(a) By direct combination (synthesis): Heating a metal and a nonmetal together. The nonmetal is over the surface of the hot metal to get the salt.

Examples

$2Al + 3Cl_2 \rightarrow 2AlCl_3$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

(b) By the action of dilute acids on metals: Active metals like sodium and potassium are treated with acids like HCl, H_2SO_4 and HNO_3 to give their respective salts.

Examples

$Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$

$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2\uparrow$

(c) By the action of dilute mineral acids on oxides: Metal oxides are generally insoluble and basic in nature. When these oxides are treated with dilute acids, displacement takes place. Since metal oxides are basic in nature, neutralization takes place.

Examples

$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O$

$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + 2H_2O$

(d) Action of dilute mineral acids on hydroxides: Soluble salts are obtained by the titration of an acid with a soluble hydroxide.

Example

$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O$

(e) Action of dilute acids on carbonates: Soluble salts are obtained by the titration of a carbonate salt solution with an acid.

Example

$(NH_4)_2CO_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2O + CO_2$

(f) Action of dilute mineral acid on hydroxide: Soluble salts are obtained by the neutralization of an acid and its respective insoluble hydroxide.

Example: $Fe(OH)_2 + H_2SO_4 \rightarrow FeSO_4 + 2H_2O$

(g) Action of dilute acids on carbonates: Soluble salts are obtained by the neutralization of the acid with an insoluble carbonate.

Example: $PbCO_3 + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O + CO_2$

(ii) Preparation of Insoluble Salts

(a) By direct combination (synthesis): Heating the powdered metal with sulphur.

Example: $Fe + S \rightarrow FeS$

(b) Precipitation from soluble salts: In this method, when two soluble salt solutions are mixed, double decomposition takes place and the insoluble salt is precipitated. This is the most common method for the preparation of insoluble salts.

Example: $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

General Characteristics of Salts

(i) Physical state: Salts are nonvolatile crystalline solids.

(ii) Electrical conductivity: Salts being electrovalent (ionic) compounds conduct current in molten state as well as in aqueous state due to their dissociation into ions.

(iii) Solubility: The salts are ionic compounds. But all the salts are not soluble in water. Some salts remain insoluble.

Table Showing the Solubility of Salts

Solubility of salts in water	
Solubility of compounds	Exceptions
All NH^{4+}, Na^+, K^+ compounds are soluble	–
All nitrates and nitrites are soluble	–
All chlorides are soluble in water	Hg_2Cl_2, AgCl, $PbCl_2$ $PbCl_2$—Soluble in hot water
All sulphates are soluble	$CaSO_4$, $PbSO_4$, $BaSO_4$
All oxides and hydroxides are insoluble	Oxides of Na^+, K^+, Mg^{+2}
All carbonates are insoluble	K_2CO_3, Na_2CO_3, $(NH_4)_2CO_3$
All sulphides are insoluble	K_2S, Na_2S, $(NH_4)_2S$

Salt Hydrolysis

The phenomenon in which a simple salt on dissolution in water forms a parent acid and a parent alkali resulting in acidic, basic or neutral solution is called salt hydrolysis. It is the most important property of salts.

Depending on the nature of the salts, it is classified into the following four types.

(i) Hydrolysis of salts of strong acids and weak bases: This type of hydrolysis produces a strong acid which ionizes and a weak base which does not ionize. This increases the concentration of H^+ ion making the solution acidic.

Example

$(NH_4)_2SO_4$, $CuSO_4$, NH_4NO_3, $FeCl_3$, etc.

$Cu^{+2} + SO_4^{-2} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ + SO_4^{-2}$

As only the cation of the salt reacts with water it is also called cationic hydrolysis.

(ii) Hydrolysis of salts of weak acids and strong bases: This produces a weak acid which does not ionize and a strong base which ionizes and gives OH^- ions. This makes the solution basic and has a pH > 7.

Example

Na_2CO_3, CH_3OOK, CH_3COONa

$CH_3COO^- + Na^+ + H_2O \rightarrow CH_3COOH + Na^+ + OH^-$

As the anion of the salt reacts with water, it is also called anionic hydrolysis.

(iii) Hydrolysis of salts of strong acids and strong bases: This type of hydrolysis produces a strong acid and a strong base which are completely ionized giving equal number of H^+ and OH^- ions. Thus, this solution is neutral with a pH = 7.

Example

NaCl, K_2SO_4, KNO_3

$Na^+ + Cl^- + H_2O \rightarrow Na^+ + OH^- + H^+ + Cl^-$

(iv) Hydrolysis of salts of weak acids and weak bases: This produces a weak acid and weak base, which exist in the molecular form. Thus there are no free H^+ or OH^- ions and the solution is neutral with pH = 7.

Example

$(NH_4)_2CO_3$, CH_3COONH_4

$2NH_4^+ + CO_3^{-2} + 2H_2O \rightarrow 2NH_4OH + H_2CO_3$

Qualitative Analysis of Simple Salts

A simple salt contains an acidic radical (anion) and a basic radical (cation). The analysis of a simple salt involves identification of the constituent acidic and basic radicals of the salt.

Identification of Some Important Anions

Anions	Tests	Reactions involved	Observations and Inference
Carbonate	Action of dilute HCl	$CaCO_3 + 2HCl$ ↓ $CaCl_2 + H_2O + CO_2$	Colourless gas with brisk effervescence which puts off burning splinter and turns lime water milky. CO_2 gas is evolved.

Chloride	Action of conc. H_2SO_4	$BaCl_2 + H_2SO_4$ $\downarrow$ $BaSO_4 + 2HCl$ $HCl + NH_4OH$ $\downarrow$ $NH_4Cl + H_2O$	A colourless and pungent smelling gas is evolved (HCl). The gas when exposed to a glass rod dipped in NH_4OH forms white dense fumes.
Nitrate	Action of conc. H_2SO_4 + in the presence of copper turnings	$4NaNO_3 + 2H_2SO_4 + Cu$ $\downarrow$ $2Na_2SO_4 + 2NO_2 +$ $Cu(NO_3)_2 + 2H_2O$	A reddish brown pungent gas is evolved (NO_2) and the solution turns blue $(CuNO_3)_2$.

Confirmatory Tests for Anions

Anions	Tests	Reactions Involved	Observations
Carbonate	Reaction with $BaCl_2$ solution	$CaCO_3 + BaCl_2$ $\downarrow$ $BaCO_3 + CaCl_2$	A white precipitate which is insoluble in conc. HCl ($BaCO_3$).
Chloride	Reaction with $AgNO_3$ solution	$2BaCl_2 + 2AgNO_3$ $\downarrow$ $2AgCl + Ba(NO_3)_2$	White curdy precipitate (AgCl).
Nitrate	Brown ring test: Salt solution + Freshly prepared ferrous sulphate solution + conc. H_2SO_4		A reddish brown ring is formed at the junction of the two layers.

Identification of Some Important Cations

For the identification of cations in the salts, NaOH and NH_4OH are the generally used reagents. These form insoluble precipitates with characteristic colours.

Table Showing Different Characteristic Precipitations Given by Different Metal Ions

Cations of salts	Precipitates formed	
	NaOH	NH_4OH
Fe^{+2}	$Fe(OH)_2$ Dirty green Insoluble in excess NaOH	$Fe(OH)_2$ Dirty green Insoluble in excess NH_4OH
Fe^{+3}	$Fe(OH)_3$ Reddish Brown Insoluble in excess NaOH	$Fe(OH)_3$ Reddish Brown Insoluble in excess NH_4OH
Ca^{+2}	$Ca(OH)_2$ Milky white Insoluble in excess NaOH	No reaction – –
Zn^{+2}	$Zn(OH)_2$ White Soluble in excess NaOH (colourless solution)	$Zn(OH)_2$ White Soluble in excess NH_4OH (colourless solution)
Pb^{+2}	$Pb(OH)_2$ Chalky white Soluble in excess NaOH	$Pb(OH)_2$ Chalky white Insoluble in excess NH_4OH
Cu^{+2}	$Cu(OH)_2$ Pale blue Insoluble in excess NaOH	$Cu(OH)_2$ Pale blue Soluble in excess NH_4OH (deep blue solution)
Al^{+3}	$Al(OH)_3$ White gelatinous Soluble in excess NaOH	$Al(OH)_3$ White gelatinous Soluble in excess NH_4OH

EXAMPLE

Define salt hydrolysis. Explain the nature of aqueous solution of $CuSO_4$ on the basis of the above phenomenon.

SOLUTION

The phenomenon in which a simple salt on dissolution in water forms a parent acid and a parent alkali resulting in acidic, basic or neutral solution is called salt hydrolysis. It is the most important property of salts.

$CuSO_4$ on hydrolysis produces a strong acid which ionises and a weak base which does not ionise. This increases the concentration of H^+ ions making the solution acidic with pH < 7 (at 25 °C)

$$Cu^{+2} + SO_4^{-2} + 2H_2O \rightarrow Cu(OH)_2 + 2H^+ + SO_4^{-2}$$

As cation of the salt reacts with water, it is called cationic hydrolysis.

EXAMPLE

Explain the amphoteric nature of zinc oxide and aluminium oxide.

SOLUTION

Amphoteric nature of zinc oxide and aluminium oxide:

On warming zinc oxide with dilute sulphuric acid, the zinc oxide dissolves rapidly and forms clear solution of zinc sulphate.

Similarly, when aluminium oxide is warmed with dilute sulphuric acid forms aluminium sulphate.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$
(dil)

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O$$
(dil)

On warming zinc oxide with concentrated sodium hydroxide or potassium hydroxide, the zinc oxide rapidly dissolves to form clear solution of sodium zincate or potassium zincate.

Similarly, aluminium oxide reacts with concentrated sodium hydroxide to form sodium metaluminate.

$$ZnO + 2NaOH \rightarrow Na_2ZnO_2 + H_2O$$
$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

As the oxides of zinc and aluminium react with acids as well as alkali to form salt and water they are amphoteric in nature.

EXAMPLE

How do you identify the following cations in their aqueous solutions by using caustic soda solution?

(a) Fe^{+2} **(b)** Zn^{+2} **(c)** Al^{+3}

SOLUTION

(a) Fe^{+2} gives light green precipitate of ferrous hydroxide ($Fe(OH)_2$)

(b) Zn^{+2} gives white precipitate of zinc hydroxide ($Zn(OH)_2$)

(c) Al^{+3} gives white gelatinous precipitate of aluminium hydroxide ($Al(OH)_3$).

EXAMPLE

What is the use of an indicator in titration? Name the indicator used when sodium hydroxide is titrated against sulphuric acid.

SOLUTION

The neutralization point can be determined by the use of indicator. The indicator used when sodium hydroxide is titrated against sulphuric acid is phenolphthalein.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. What is meant by ionic product of water?
2. Give examples of some acidic substances without H^+ ions.
3. Which acids/bases are used for the following?
   (i) to neutralize sting of wasps
   (ii) in alkaline batteries
   (iii) manufacturing of soap
4. Define oxyacid. Give two examples.
5. According to Bronsted–Lowry theory neutralization reaction is the formation of _____.
6. Give one example of acid–base reaction without formation of water.
7. $X + H_2O \rightarrow Y$. Y is used to remove grease stains from woollen clothes. Identify X and Y.
8. How do neutral, acidic and basic salt solutions respond to litmus test?
9. Give examples of some basic substances without OH^- ions.
10. How does a complex salt dissociate in its aqueous solution?
11. What is the principle involved in the preparation of $FeCl_3$?
12. In the equation $X + HCl \rightarrow NaCl + H_2S$, what is X?
13. Mention any two methods of preparation of acids. Illustrate with equations.
14. How are basic salts formed?
15. How are soluble salts prepared by direct combination? Give an example.
16. Illustrate any one method of preparation of bases with equations.
17. What is the pH range in which phenolphthalein is colourless?
18. Name the insoluble salts which can be prepared by direct combination?
19. What are the pH values of the following solutions at 25°C?
    (i) 0.001 M of HCl
    (ii) 0.05 M of H_2SO_4
    (iii) 0.01 M of NaOH
20. The formula of the basic salt formed by treating calcium hydroxide with HCl is _____.
21. Which method is employed for the preparation of sulphate of Ba, Ca and Pb?
22. Define pH and give its mathematical representation.
23. What would be the nature of aqueous solutions of the following salts?
    (i) KNO_3
    (ii) Na_2CO_3
    (iii) CH_3COONa
24. Define basicity of an acid. Give an example each for monobasic, dibasic and tribasic acids.
25. Normality of 0.01M aluminium hydroxide is _____ (assuming complete ionization).
26. Write the equation for the action of a dilute acid on a metal oxide.
27. The hydroxyl ion concentration of sodium hydroxide having a pH value of 12, at 25°C is _____.
28. Mention the steps involved in ionization of phosphoric acid.
29. Non-metallic oxides are either _____ or _____ in nature.
30. The number of ions produced by one mole of $[Co(NH_3)_6]Cl_3$ in its aqueous solution is _____.

Short Answer Type Questions

31. What is meant by a universal indicator? State the colours given by a universal indicator to the solutions of following pH values.
    (i) pH = 1 (ii) pH = 8
    (iii) pH = 5 (iv) pH = 12
32. How is NH_4OH helpful as a reagent for the analysis of cations in the aqueous solutions of their salts? Give equations.

PRACTICE QUESTIONS

33. What is meant by acidity of a base? Give the acidities of the following bases.
(i) caustic potash (ii) slaked lime
(iii) aluminium hydroxide

34. Define indicator. Why are different indicators used in different pH ranges?

35. Define salt hydrolysis. Explain the hydrolysis of potassium carbonate by giving ionic equations.

36. Explain protonic concept of acids and bases with one example each.

37. How do bases react with the following? Write the equations.
(i) non-metallic oxide (ii) ammonium salt
(iii) soluble metallic salt

38. What is meant by neutralization? Give some examples identifying spectator ions in the reactions.

39. How do you identify the following cations in their aqueous solutions by using caustic soda solution?
(i) Fe^{+2} (ii) Zn^{+2}
(iii) Al^{+3}

40. What is the value of ionic product of water at 25°C? How does it change with temperature?

41. Give pH range for various solutions at 25°C.

42. Distinguish between acidic and basic salts giving examples.

43. Mention any four applications of pH.

44. Define basicity of an acid. Give an example each for monobasic, dibasic and tribasic acids.

45. What is the difference between mixed and complex salts with respect to chemical reactions? Explain with an example.

Essay Type Questions

46. State the postulates of Arrhenius theory. Explain with examples. What are the limitations of Arrhenius theory?

47. On the basis of ionization explain classification of acids and bases with suitable examples. Classify acids/bases on the basis of amount of water present in the solution.

48. Explain the formation of hydronium ion and ammonium ion.

49. Define salt hydrolysis. Explain the nature of aqueous solution of the following salts on the basis of salt hydrolysis.
(i) $(NH_4)_2CO_3$ (ii) $CuSO_4$
(iii) $NaNO_3$ (iv) $CaCl_2$

50. Explain with examples the use of NaOH and NH_4OH as reagents for the identification of cations in salts.

CONCEPT APPLICATION

Level 1

***Direction for questions from 1 to 7*: State whether the following statements are true or false.**

1. Formation of coordinate covalent bond between NH_3 and BF_3 is an example of neutralization reaction according to Bronsted theory.

2. A diacidic base has one replaceable hydroxide ion.

3. For a dibasic acid, normality is twice the molarity for a given solution.

4. S^{-2} is the conjugate base of HS^-.

5. Methyl orange exhibits yellow colour in basic medium.

6. Curd is sour in taste due to the presence of an acidic substance.

7. $K_2SO_4 \cdot Al_2(SO_4)_3\ 24H_2O$ gives reactions of both K^+ and Al^{+3} ions respectively.

***Direction for questions from 8 to 14*: Fill in the blanks.**

8. Phenolphthalein is a/an_____ indicator.

9. The salt obtained by partial neutralization of sodium hydroxide and sulphuric acid is _____ in nature.

10. Metallic oxides are either _____ or _____ in nature.

PRACTICE QUESTIONS

11. $[H^+]$ of nitric acid having a pH value of 6 is ____

12. The pH of aqueous solution of salt obtained by the reaction between NaOH and CH_3COOH is _____at 25°C.

13. A salt, X is prepared by the complete neutralization of $Cu(OH)_2$ with H_2SO_4. The nature of X is _____

14. The units of K_w are _____.

***Direction for question 15*: Match the entries given in column A with appropriate ones from column B.**

15.

Column A	Column B
A. Sodium chloride	( ) a. Baking powder
B. Tartaric acid	( ) b. Freezing mixture in ice creams
C. Potassium nitrate	( ) c. Antacid in medicine
D. Sodium bicarbonate	( ) d. Gun powder
E. Citric acid	( ) e. Bleaching powder
F. Calcium hydroxide	( ) f. Flavouring agent

***Direction for questions from 16 to 45*: For each of the questions, four choices have been provided.**

Select the correct alternative.

16. Which of the following is not a base according to any of the theories?

(a) $Mg(OH)_2$ (b) NH_3

(c) $H_2PO_4^-$ (d) BF_3

17. According to Lewis acid–base concept, which is a correct statement?

(a) Species in which central atom has completed octet cannot act as acid.

(b) All negatively charged ions are acids.

(c) Molecule in which the central atom has vacant "d" orbitals acts as acid.

(d) All positively changed ions are bases.

18. At a certain temperature, K_w was found to be 1×10^{-10} mole^2 ℓ^{-2}. At this temperature, a solution is taken and red litmus is added to this solution. The solution turned to blue. pH range of the solution could be

(a) between 5 and 7 (b) between 7 and 10

(c) less than 5 (d) both 1 and 2

19. Which of the following indicators is the best indicator for the detection of end point in the titration of CH_3COOH and KOH?

(a) methyl orange (b) phenolphthalein

(c) methyl red (d) none of these

20. According to Lewis theory, neutralization is the

(a) transfer of proton from acid to base

(b) transfer of proton from base to acid

(c) transfer of electron pair from acid to base

(d) transfer of electron pair from base to acid

21. The indicator which shows colour changes in the entire pH range is

(a) phenolphthalein (b) methyl orange

(c) universal indicator (d) thymol blue

22. Which of the following has the highest value of pH?

(a) HCl (b) NaOH

(c) $Ca(OH)_2$ (d) CH_3COOH

23. Heat of neutralization is less than 13.7 kcal/mole for the reaction

(a) $HCl + NaOH \rightarrow NaCl + H_2O$

(b) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

(c) $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

(d) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

24. Which among the following does not undergo hydrolysis?

(a) Na_2CO_3 (b) CH_3COOH

(c) CH_3COONH_4 (d) K_2SO_4

25. Which of the following acts as both Bronsted acid and Lewis acid?

(a) Cu^{+2} (b) SO_2

(c) Fe^{+3} (d) NH_4^+

26. Which among the following factors changes the value of ionic product of water?

(a) change in temperature

(b) addition of acid

(c) addition of base

(d) addition of either acid and base

27. Which of the following solutions has the same concentration of H+ ions as 0.1 N HCl?

(a) 0.1N H_2SO_4 (b) 0.3 N H_3PO_4

(c) 0.2 N HNO_3 (d) All of these

PRACTICE QUESTIONS

28. Which of the following cannot show acidic nature?
(a) H_2CO_3 (b) $CaCO_3$
(c) HCl (d) HSO_4^-

29. The spectator ions in the hydrolysis of $(NH_4)_2CO_3$ are
(a) NH_4^+, H^+, OH^-
(b) NH^+_4, CO_3^{2-}, H^+, OH^-
(c) CO_3^{2-}, H^+, OH^-
(d) no spectator ions

30. Disodium potassium phosphate is a/an _____ salt.
(a) acid (b) mixed
(c) complex (d) double

31. V_1 ml of x molar hydrochloric acid is mixed with V_2 ml of y molar sodium hydroxide. Arrange the following steps in correct sequence for calculation of pH of the mixture. ($y > x$ and $V_1 > V_2$)
(1) Calculation of the number of equivalents of acid and base.
(2) Calculation of the total volume of mixture.
(3) Calculation of the normality of acid and base.
(4) Calculation of the net OH^- ion concentration.
(5) Taking the negative logarithm of H^+ ion concentration.
(6) Dividing K_w by OH^- ion concentration.
(a) 1 3 2 6 4 5 (b) 3 1 2 4 5 6
(c) 3 1 2 6 4 5 (d) 1 2 3 4 5 6

32. A strongly acidic solution is taken and a base is slowly added to it drop by drop. Arrange the colours observed during the process of addition in proper sequence.
(1) green (2) indigo
(3) orange (4) red
(5) blue (6) violet
(7) yellow
(a) 3 4 1 7 2 5 6 (b) 4 3 7 1 5 2 6
(c) 4 3 1 7 5 2 6 (d) 3 4 7 1 6 2 5

33. A red litmus paper when dipped in an aqueous solution of potassium acetate turned blue. Arrange the following steps in proper sequence to explain the above observation.
(1) identification of spectator ions
(2) identification of free ions which caused the colour change of the litmus paper
(3) identification of positive and negative radicals
(4) writing the net reaction taking place
(5) writing ionic equation for the reaction of positive and negative radicals with water
(a) 3 5 1 4 2 (b) 3 1 5 4 2
(c) 5 1 4 3 2 (d) 5 3 1 4 2

34. Identify the species which can give both conjugate acid and conjugate base.
(a) NH_4^+ (b) $H_2PO_4^-$
(c) PO_4^{-3} (d) H_3O^+

35. The basicity of acetic acid is the same as the basicity of _____.
(a) HNO_3 (b) H_2SO_4
(c) H_3PO_4 (d) H_2CO_3

36. Which of the following species cannot have conjugate base?
(a) HSO_4^- (b) HPO_4^{-2}
(c) PO_4^{-3} (d) $H_2PO_2^-$

37. Which among the following pairs of acid and base are weak respectively?
(a) HCOOH and NH_4OH
(b) HCl and NaOH
(c) CH_3COOH and KOH
(d) $HClO_4$ and CsOH

38. The pH of 0.001 N sodium hydroxide solution at 25°C is
(a) 3 (b) 4
(c) 11 (d) 12

39. A solution turns methyl orange red. It can turn the universal indicator to _____
(a) violet (b) blue
(c) orange (d) green

40. Which of the following pH values at 25°C corresponds to the strongest acid?
(a) 2 (b) 4
(c) 6 (d) 8

41. Which of the following during hydrolysis gives an acidic solution in water?
(a) KNO_3 (b) NH_4Cl
(c) $(NH_4)_2CO_3$ (d) KCl

42. X is formed by the partial replacement of hydroxyl groups of a diacidic base by an acidic radical. The number of ionizable hydroxyl groups in X is _____.
    (a) 0 (b) 1
    (c) 2 (d) 3

43. In the reaction between silver nitrate and sodium chloride, the spectator ion is _____.
    (a) Ag^+ (b) Cl^-
    (c) NO_3^- (d) All of these

44. Which among the following statements is false?
    (a) Every protonic acid has its conjugate acid.
    (b) Pair of Bronsted acid and base that differ by a proton is conjugate acid–base pair.
    (c) A substance that accepts an electron pair to form coordinate covalent bond is an acid.
    (d) Arrhenius theory is confined to aqueous solutions.

45. Which of the following salts can produce only two types of radicals?
    (a) $NaKCO_3$
    (b) $CaOCl_2$
    (c) NH_4HSO_4
    (d) $Na(NH_4)HPO_4$

Level 2

1. Calculate the resultant pH of a solution when 20 ml of 0.1N NaOH is mixed with 20 ml of 0.05 M $Ca(OH)_2$ at 25°C.

2. The ionic product of water is found to be 1×10^{-12} $mole^2/\ell^2$ at 60°C. What would be the nature of solution with pH = 7? Explain giving reasons.

3. Explain why phosphorous acid is not a tribasic acid like phosphoric acid though both acids contain three hydrogen in their molecules.

4. What volume of 0.45 M H_3PO_4 is needed to neutralize 60 ml of 0.60 N NaOH solution? (Assume that there is a complete ionization of acid and base.)

5. Explain the nature of resultant solution when 20 ml of 0.05 M NaOH is mixed with 10 ml of 0.1N HCl solution at 25°C. When 10 ml of this solution is diluted 100 times what is the change in pH?

6. Account for the variation of acidic character with increase in the oxidation state of central atom.

7. Two salts are dissolved in water separately. When phenolphthalein is added to the two solutions, one solution turned pink and the other solution was colourless. How do you justify this?

8. How many moles of NaOH must be added to 200 ml of 0.1 M solution of HNO_3 to get a solution having pH value 2.00?

9. Explain the nature of the following salts:
    (a) NaH_2PO_2 (b) Na_2HPO_3
    (c) Na_2HPO_4

10. An aqueous solution of Mohr's salt can give a precipitate with NaOH or NH_4OH. But the aqueous solution of potassium ferrocyanide cannot give a precipitate with both reagents. How do you account for this?

11. Two coloured salt solutions of two metals A and B gave precipitates with NaOH and NH_4OH. On further addition of NH_4OH, the precipitate disappears, in the case of B. There is no such change in the case of "A" either with NaOH or NH_4OH. Identify A and B. Give equations.

12. Compare and contrast the nature of aqueous solutions of ammonium acetate and sodium sulphate.

13. Find the pH of resultant solution when 100 ml of 0.005 M H_2SO_4 at 25°C is diluted to 1000 ml. What is the amount of NaOH required to be dissolved in 500 ml to exactly neutralize the above solution?

14. A strong alkali forms an acidic salt with a dibasic acid. From the aqueous solution of the salt formed on the addition of dilute acid evolves a gas which turns lime water milky. Identify the salt and predict the reactions involved in it.

15. Explain the variation in basic strengths of hydrides of VA group elements.

***Direction for questions from 16 to 25*: Application-Based Questions**

16. 14.3 g of Na_2CO_3 xH_2O is dissolved in water and the volume is made up to 200 ml. 20 ml of this

PRACTICE QUESTIONS

solution required 40 ml of $\frac{N}{4}$ HNO_3 for complete neutralization. Calculate x.

17. 10 ml of 1 N HCl, 25 ml of 2 N H_2SO_4 and 40 ml of X N HNO_3 are mixed and made up to 2000 ml. 100 ml of this solution required 30 ml of NaOH taken from a solution containing 4 g of NaOH in 250 ml of solution. What is the value of X?

18. 8 g of mixture of $NaNO_3$ and Na_2CO_3 are dissolved and made into 500 ml of solution. 50 ml of this solution neutralizes completely 25 ml of N/5 HNO_3. Calculate the percentage composition of the mixture.

19. Do equimolar solutions of NaOH and $Ca(OH)_2$ possess same pH value at the same temperature? Justify.

20. Explain why no indicator can be used for the titration between formic acid and ammonium hydroxide.

21. Sodium bicarbonate can be manufactured by Solvay process where addition of brine solution to ammonium bicarbonate solution gives precipitation of sodium bicarbonate. But, its analogue, potassium bicarbonate cannot be prepared by the above process. Explain with respect to the concept of solubility product.

22. Explain the acidic and basic nature of the following substances on the basis of protonic concept.
    (a) H_2SO_4 (b) HPO_4^{-2}
    (c) NH_3 (d) NH_4^+

23. "All Lewis bases are Bronsted bases. But all Lewis acids are not Bronsted acids." Comment on the statement.

24. Find the pH of resultant solution when 100 ml of 0.005M H_2SO_4 at 25°C is diluted to 1000 ml. What is the amount of NaOH required to be dissolved in 500 ml to exactly neutralize the above solution?

25. Explain the strengths of conjugate acid base pairs of the following species:
    (a) HSO_4^- (b) NH_3
    (c) HS^- (d) ClO_4^-

Level 3

1. Acetic acid contains four hydrogen atoms in each molecule. Explain why it is not a tetrabasic acid?

2. How do you account for the acidic nature of 10^{-8} M nitric acid? Justify by mathematical calculation (log 1.1 = 0.041).

3. Though zinc and manganese get precipitated as their sulphides, they do not get precipitated along with lead or copper when H_2S is passed through acidified solutions of their salts. Justify and also explain how the precipitation of Zn^{+2} and Mn^{+2} ions takes place.

4. Explain the action of phenolphthalein indicator in the titration of acetic acid versus sodium hydroxide.

5. How does the acidic character vary among the trihalides of boron? Give a reason in support of your answer.

***Direction for questions from 6 to 10*: Application-Based Questions**

6. Among H_3PO_2, H_3PO_3 and H_3PO_4 which is having maximum acidic strength? Explain.

7. Calculate the pH value of the 10^{-6} M HCl solution when diluted by 100 times. Justify (log 1.1 = 0.041).

8. Why do both acidic indicator and basic indicator show different colours in acidic and basic solutions?

9. A complex, salt with formula $[Co(NH_3)_6]Cl_3$ can form a white curdy precipitate with silver nitrate solution. Another complex with same ligands cannot form precipitate with $AgNO_3$ solution. What would be the probable formula of that complex? Give reasons in support of your answer.

10. Explain why the strengths of strong acids and strong bases cannot be determined in water. How is it possible to compare the acidic strengths in acetic acid?

CONCEPT APPLICATION

Level 1

True or false

1. False
2. False
3. True
4. True
5. False
6. True
7. True

Fill in the blanks

8. acidic
9. acidic
10. basic, amphoteric
11. 0.000001 mole ion/ℓ
12. greater than 7
13. normal salt
14. mol.ion^2/l^2

Match the following

15. A : b
    B : a
    C : d
    D : c
    E : f
    F : e

Multiple Choice Questions

16. d
17. c
18. d
19. b
20. d
21. c
22. b
23. a
24. d
25. d
26. a
27. a
28. b
29. d
30. b

Solutions for questions from 31 to 45:

31. (i) calculation of the normality of acid and base
    (ii) calculation of the number of equivalents of acid and base
    (iii) calculation of the total volume of the mixture
    (iv) calculation of the net OH^- ion concentration
    (v) dividing K_w by OH^- ion concentration
    (vi) taking the negative logarithm of H^+ ion concentration

32. (i) red (ii) orange (iii) yellow
    (iv) green (v) blue (vi) indigo
    (vii) violet

33. (i) identification of positive and negative radicals
    (ii) writing ionic equations for the reaction of positive and negative radicals with water
    (iii) identification of spectator ions
    (iv) writing the net reaction taking place
    (v) identification of free ions which caused the colour change of litmus paper

34. $H_2PO_4^-$ can form conjugate base $HPO4^{-}{}_2$ and conjugate acid H_3PO_4

35. Basicity of acetic acid = 1 since it ionizes as $CH_3COOH \Rightarrow CH_3\,COO^- + H^+$ and gives only one H^+ ion. HNO_3 also possesses only one replaceable hydrogen and has basicity = 1.

36. PO_4^{-3} has only conjugate acid, i.e., HPO_4^{-2}. It has no conjugate base as it does not possess any replaceable H^+ ion.

37. HCOOH is a weak acid and NH_4OH is a weak base.

38. $[OH^-]$ of sodium hydroxide = $0.001 = 10^{-3}$
    pOH = 3, pH = 14 – 3 = 11

39. Methyl orange shows red colour in acidic medium and universal indicator shows orange colour in the same pH range.

40. The lower is the pH value, the stronger is the acid. Therefore pH value of 2 corresponds to the strongest acid.

HINTS AND EXPLANATION

41. In the aqueous solution of NH_4Cl, NH_4^+ ion undergoes hydrolysis forming NH_4OH and HCl. Since HCl is a strong acid, the solution is acidic in nature.

42. Diacidic base contains two $-OH^-$ groups in a molecule. If one $-OH^-$ group is replaced by an acidic radical, the number of ionizable hydroxyl radicals in the salt "X" is one.

43. In the given reaction, Na^+ and NO_3^- ions are spectator ions.

44. Every protonic acid has a conjugate base.

45. $NaKCO_3 \rightarrow Na^+ + K^+ + CO_3^{-2}$

$CaOCl_2 \rightarrow Ca^{+2} + OCl^- + Cl^-$

$NH_4HSO_4 \rightarrow NH_4^+ + HSO_4^-$
(two types of radicals)

$Na(NH_4)\ HPO_4 \rightarrow Na^+ + NH_4^+ + HPO_4^-$

Level 1

Solutions for questions from 16 to 25:

1. (i) calculation of net H^+ ion concentration in the mixture
(ii) calculation of the total number of OH^- ions generated from the given volume of NaOH and $Ca(OH)_2$
(iii) calculation of concentration of OH^- ions in the resultant solution
(iv) calculation of pOH
(v) calculation of pH from the value of pOH at 25°C
(vi) 3

2. (i) concentration of H^+ and OH^-
(ii) $[H^+]/[OH^-]$ from the given ionic product of water
(iii) calculation of pH from $[H^+]$ (or) pOH from $[OH^-]$
(iv) relation between pH value and nature of the solution
(v) relation between given pH and nature of the solution

3. (i) comparison of the structures of two acids
(ii) condition required for a substance to behave like an acid in its aqueous solution
(iii) comparison of positions of hydrogen atoms present in phosphorus acid to that present in phosphoric acid
(iv) relation between the position of hydrogen in the respective molecules and its replaceability
(v) relation between the number of replaceable hydrogen and the basicity of the acid

4. (i) balanced equation and comparison of equivalents
(ii) basicity of acid
(iii) calculation of normality of H_3PO_4
(iv) calculation of number of equivalents of base
(v) calculation of volume of acid required based on normality of acid and number of equivalents of base
(vi) 26.6 ml

5. (i) calculation of net H^+ ions concentration in the mixture
(ii) calculation of the difference of number of H^+ and OH^- ions generated from the given amount of respective acid and base
(iii) determination of the pH of the given mixture at 25°C
(iv) relation between the pH of the solution and its nature
(v) relation between the nature of the solution and the effect of dilution

6. (i) effect of electronegative atom on the O–H bond strength
(ii) effect of oxidation state of the central atom on the position of electron cloud present between oxygen atom and the central atom
(iii) relation between the position of the above electron cloud and the charge separation between hydrogen and oxygen atom of the hydroxyl radical attached to the central atom
(iv) relation between the above charge separation and ease of formation of hydrogen ion
(v) relation between ease of formation of hydrogen ion with the acidic character of the respective acids

7. (i) nature of solution where phenolphthalein is pink and colourless
(ii) nature of the components produced on hydrolysis of salts
(iii) relation between the components produced and the colour change of indicator

8. (i) pH of initial solution
(ii) calculation of normality of the solution after neutralization
(iii) calculation of number of equivalents of HNO_3 neutralized
(iv) calculation of number of moles of NaOH required to neutralize this HNO_3 in 200 ml
(v) 0.018

9. (i) identification of parent acid from which the respective salts are formed
(ii) structures of the given salts
(iii) number of hydroxyl radical present in the respective acid
(iv) number of replaceable hydrogen in the respective acid
(v) identification of the negative radical(s) that can be formed from the given acids
(vi) determination of the number of replaceable hydrogen(s) present in the given salts based on the composition of the above negative radicals
(vii) relation between the number of replaceable hydrogen(s) present in the salt and its nature

10. (i) characteristics of double salts
(ii) type of salts
(iii) comparison of ions present in their salt solutions
(iv) requisite of a salt to give a precipitate

11. (i) metals giving coloured salts
(ii) coloured salts which give precipitates with NaOH and NH_4OH
(iii) comparison between the reactions of the precipitates obtained with excess NaOH and NH_4OH
(iv) solubility of the product formed

12. (i) identification of species undergoing hydrolysis in the respective salts
(ii) nature of constituent ions of the given salts
(iii) comparison of reactions that take place in the respective solutions
(iv) comparison of the concentration of hydrogen and hydroxyl ions in the respective solution

13. (i) calculation of H^+ ion concentration in the diluted solution
(ii) calculation of the number of moles of hydrogen ions present in 100 ml of 0.005 M H_2SO_4
(iii) calculation of the concentration of the hydrogen ions of H_2SO_4 solution after dilution
(iv) calculation of the number of moles of NaOH required to neutralize the above solution
(v) calculation of the amount of NaOH required
(vi) 4×10^{-2} g

14. (i) gas which turns lime water milky
(ii) identification of gas
(iii) dibasic acid responsible to produce this gas
(iv) acidity of the alkali
(v) requisite for acidic salt

15. (i) requisite for basic nature according to Lewis theory
(ii) elements present in group VA
(iii) number of lone pairs present in the valence shell of the elements of group VA
(iv) concept of base according to Bronsted–Lowry theory
(v) comparison of the size of the above elements
(vi) relation between the size of the element and tendency of accepting the proton
(vii) comparison of stability of the respective hydrides of the elements of group VA

16. $V_1N_1 = N_2V_2$

$20\ (N_1) = 40 \times 0.25$

$N_1 = 0.5$ N

Normality of $Na_2CO_3\ XH_2O$ solution is 0.5

$$0.5 = \frac{14.3}{\text{Eq.wt}} \times \frac{1000}{200}$$

$$\text{Eq. Wt} = \frac{14.3 \times 5}{0.5}$$

$$\text{Eq.Wt} = 143$$

But equivalent weight $Na_2CO_3\ XH_2O$ is

$$\frac{106 + x(18)}{2} = 143.$$

$$\therefore x = \frac{286 - 106}{18}$$

$$x = 10$$

$$\therefore Na_2CO_3 \cdot 10H_2O$$

17. Normality of NaOH

$$N_1 = \frac{4}{10} \times \frac{1000}{250}$$

$$N_1 = 0.4N$$

$$\therefore N_1V_1 = N_{mix}V_{mix}$$

$$0.4 \times 30 = N_{mix} \times 100$$

$$N_{mix} = 0.12N$$

$$\frac{(10 \times 1) + (25 \times 2) + (40 \times x)}{2000} = 0.12N$$

$$240 = 60 + 40x$$

$$180 = 40x$$

$$x = \frac{180}{40} = 4.5$$

$$N_{HNO_3} = 4.5N$$

18. $Na_2CO_3 + 2HNO_3 \rightarrow 2NaNO_3 + H_2CO_3$

Only sodium carbonate reacts with acid (HNO_3)

$N_1V_1 = N_2V_2$

Normality of Na_2CO_3 is $\frac{0.2 \times 25}{50} = 0.1N$

$$\therefore 0.1 = \frac{\text{wt of } Na_2CO_3}{53} \times \frac{1000}{500}$$

$$\therefore \text{wt of } Na_2CO_3 = \frac{0.1 \times 53 \times 500}{1000} = 2.65g$$

$$\therefore \text{wt of } NaNO_3 \text{ is} = 8 - 2.65 = 5.35g$$

$$\% \text{ of } NaNO_3 = \frac{5.35}{8} \times 100 = 66.8\%$$

$$\% \text{ of } Na_2CO_3 = \frac{2.65}{8} \times 100 = 33.2\%$$

19. Sodium hydroxide being a strong base than calcium hydroxide furnishes more number of OH^- as it undergoes complete dissociation. Greater the OH^- concentration greater will be the basic character. A stronger base will have pH value greater than a weak base. Hence NaOH which is a strong base has higher pH value than $Ca(OH)_2$.

20. In acid–base titrations, the end point is detected by the use of a substance called acid–base indicator. Acid–base indicator exhibits a sharp change in its colour at the end point. The experimentally determined point of completion of an acid–base titration is called end point. For the titration between a weak acid and weak base, there is no sharp change in pH. Hence no indicator can be used.

21. Sodium bicarbonate has low value of solubility product. Addition of sodium chloride solution to ammonium carbonate solution results in the double displacement reaction which results in the precipitation of sodium bicarbonate, as ionic product easily exceeds the low value of solubility product. Potassium bicarbonate has high value of solubility product and is highly soluble. In this case, though double displacement takes place, ionic product cannot exceed the high value of solubility product of $KHCO_3$. Therefore, precipitation cannot take place. Hence, this method cannot be employed for the preparation of potassium bicarbonate.

22. (a) H_2SO_4 is a proton donor and hence can act as an acid according to protonic concept.

(b) HPO_4^{-2} can act as a proton donor and form PO_4^{-3} ion. Therefore, it acts as an acid. HPO_4^{-2} ion can also accept proton and form $H_2PO_4^-$ Therefore, it acts as a base.

(c) NH_3 can act as a proton donor to form NH_2^- and can act as an acid. NH_3 can act as a proton acceptor to form NH_4^+ ion and can act as a base.

(d) NH_4^+ can act as a proton donor to form NH_3 and it can act as an acid only.

23. A Lewis base is an electron pair donor. A molecule which has excess electron pair can only act as an electron pair donor. As it has an excess electron pair, it invariably accepts a proton. Therefore, it can act as a proton acceptor which is a Bronsted base. However, this is not the case with Lewis acids. A Lewis acid is an electron pair acceptor and hence should be deficient in electrons. It need not necessarily be a proton donor as it may or may not possess hydrogen.

24. Normality of H_2SO_4 = Molarity × 2 = 0.005 × 2 = 0.01

According to dilution law

$100 \times 0.01 = 1000 \times x$

$$= \frac{100 \times 0.01}{1000} = 0.001 = 1 \times 10^{-3}$$

$$pH = -\log 1 \times 10^{-3} = 3$$

If this solution neutralized by 500 ml of NaOH solution

$1000 \times 10^{-3} = 500 \times c$

$c = 2 \times 10^{-3}$

Amount of NaOH required

$$2\times10^{-3} = \frac{x}{40} \times \frac{1000}{500}$$

$2\times10^{-3} \times 40 / 2 = 4\times10^{-2}$ g.

25. (a) $HSO_4^- \rightarrow SO_4^{-2}$

H_2SO_4 is a strong acid, HSO_4^- is a strong weak conjugate base. So, HSO_4^- is a strong acid; so, its conjugate base SO_4^{-2} is weak.

(b) $NH_3 + H^+ \rightarrow NH_4^+$

As ammonia is a weak base its conjugate acid is strong.

(c) $HS^- \rightarrow S^{-2}$

H_2S is a weak acid. HS^- is a strong conjugate base So, HS^- is weak acid so its conjugate base 5^{-2} is strong.

(d) $ClO_4^- \rightarrow HClO_4$

ClO_4^- is the conjugate base of strong acid $HClO_4$.

As ClO_4^- is the conjugate base of strong acid it has to be weak.

Level 2

1. (i) replaceable hydrogens in acetic acid
(ii) structure and bonding in acetic acid
(iii) comparison of the position of the hydrogen atoms present in the molecule of acetic acid
(iv) relation between the position of hydrogen atom and the effect of strong alkali on it

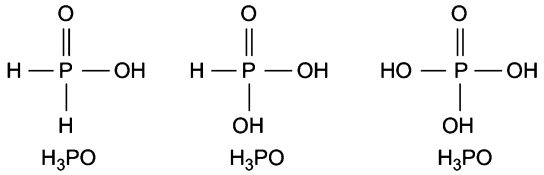
2. (i) pH range of acidic solutions
(ii) number of hydrogen ions furnished by nitric acid, present in the solution
(iii) determination of concentration of the hydrogen ions furnished by nitric acid
(iv) influence of the concentration of hydrogen ions furnished by the acid on the degree of dissociation of water
(v) concentration of hydrogen ions furnished by water
(vi) total concentration of hydrogen ions present in the solution
(vii) calculation of pH

3. (i) requisite for precipitation of the respective sulphides
(ii) difference in the types of ions present in an acidified salt solution and normal salt solution
(iii) ions present in the solution when H_2S is passed through it
(iv) influence of extra ions present in the acidified solution on the degree of dissociation of H_2S
(v) relation between the degree of dissociation of H_2S and the availability of sulphide ions in the solution
(vi) relation between the number of sulphide ions and the precipitation of the selective salts

4. (i) titration range of reaction and pH range of indicator
(ii) strength of acid and base
(iii) pH range of the solution at end point
(iv) nature of indicator
(v) pH range of indicator

5. (i) comparison of electronegativities of halogens attached to boron in various trihalides
(ii) reason for the trihalides of boron to act as an acid
(iii) comparison of valence electronic configuration of fluorine, chlorine, bromine, iodine with that of boron
(iv) orbitals in which the lone pairs of electrons of halogens are present
(v) identification of vacant orbital of boron
(vi) comparison of energy of vacant orbital of boron with the orbitals containing lone pairs of electrons in halogens
(vii) comparison of tendency of donating the electron pair to the vacant orbital of boron among the halogens
(viii) relation between the tendency of formation of the above kind of bond and availability of vacant orbital of boron for accepting the lone pairs of electrons from other species
(ix) comparison of acidic characters of trihalides of boron according to Lewis concept

6. Generally the acidic strength of oxyacids of an element with different oxidation states increases with the increase in oxidation state of central atom. So the expected order of acidic strength should be $H_3PO_4 > H_3PO_3 > H_3PO_2$. But actual order is $H_3PO_2 > H_3PO_3 > H_3PO_4$. This can be explained based on the number of OH^- groups attached to central P-atom. With increasing number of OH groups on central P-atom the acidic strength decreases. Hence H_3PO_4 is having minimum acidic strength and H_3PO_2 is having maximum acidic strength.



With the increases in number of −OH groups, the strength of conjugate base formed increases due to greater proton accepting tendency. Therefore, the strengths of corresponding acids decrease accordingly.

7. 10^{-6} M HCl solution when diluted by 100 times, should become 10^{-8} M solution. Then the pH value should increase from 6 to 8. However, a solution having pH value of 6 is acidic and the solution having pH value of 8 indicates basic nature. An acidic solution can never become neutral or basic howsoever dilute it is. The pH value of the solution is slightly less than 7. This is because in very low concentrated solution, the dissociation of water also should be taken into consideration. H^+ ion concentration should be equal to the sum of H^+ ion concentration from HCl and H_2O.

$[H^+]$ from HCl = 10^{-8}

$[H^+]$ from H_2O = 10^{-7}

$[H^+] = 10^{-8} + 10^{-7} = 10^{-7}(10^{-1} + 1) = 1.1 \times 10^{-7}$

$pH = -\log(1.1 \times 10^{-7})$

$= 7 - \log 1.1 = 7 - 0.041 = 6.96$

8. Acid–base indicators are either weak organic acids or weak organic bases. These indicators show one colour in molecular form and another colour in ionic form. Acidic indicator is represented by HIn.

$$HIn \rightleftharpoons H^+ + In^-$$

In acidic solution, the equilibrium shifts towards left.

Hence an acidic indicator has the colour of HIn in acidic solutions. In basic solution, the equilibrium shifts towards right and shows colour of In– in alkaline solutions.

Basic indicator is represented by InOH. $InOH \rightleftharpoons In^+ + OH^-$

In acidic solution, the equilibrium shifts towards right. In basic solution, the equilibrium shifts towards left. Hence basic indicator is having colour of In^+ in acidic solutions, and shows colour of InOH in basic solutions.

9. In a complex salt, there are two parts namely coordination sphere and ionisation sphere. The part present in ionization sphere gives reactions of the respective ions. But the part present in coordination sphere gives the reactions of complex ions only and cannot give reactions of individual ions. In the complex of the formula $[Co(NH_3)_3]Cl_3$, chloride ions are present in the ionization sphere and give the reactions of Cl^- ions. The complex $[Co(NH_3)_3Cl_3]$ has no chloride ions in the ionization sphere and does not give the reactions of Cl^- ions because the components present within the sphere do not further undergo any hydrolysis and hence do not behave independently.

10. In presence of any strong acid, water acts as a proton acceptor. In presence of any strong base, water acts as a proton donor. Therefore, the ability of a strong acid to donate protons is determined by the proton accepting capacity of water and not on the acid. Hence, all strong acids show equal tendency to donate protons. Same thing happens with bases also. When strong acids are taken in acetic acid which is a very weak proton acceptor than water, the different acids donate protons to different extents. Therefore, the strengths of various strong acids can be compared in acetic acid.

Chapter

7

Electrochemistry

Remember

Before beginning this chapter, you should be able to:

- describe the types of metals and non-metals along with the
- knowledge of oxidation and reduction.

Key Ideas

After completing this chapter, you should be able to:

- understand the process of electrolytic conduction and mechanism of electrolysis on the basis of Arrhenius theory.
- Solve the numerical on relative amounts of electrolytic products in correlation with Faraday's laws
- understand the concept of galvanic cells and the discharge of substances at the electrodes as part of electrochemical series.
- understand the techniques of electroplating, its importance
- study the extraction and refining of metals with the concept of electrochemistry.

INTRODUCTION

The interconversion of electrical energy and chemical energy by means of oxidation–reduction reaction comes under the purview of electrochemistry. Electrochemistry finds application in industries for the extraction, refinement and protection of metals. A very common natural phenomenon like rusting of iron also comes under the study of electrochemistry. Starting from a small dry cell used in toys to microprocessors of computers electrochemical processes are involved.

ELECTRO CHEMICAL REACTION

Electrochemical reactions are basically of two types. First, the oxidation–reduction reactions which take place with the passage of electricity and is known as electrolysis and second, the oxidation–reduction reactions which result in the generation of electricity.

Since electric current is considered as flow of electrons or flow of electric charges, a conducting medium is required. The substances which allow the passage of electric current through them are called electrical conductors. They are of two types:

(i) metallic conductors and
(ii) electrolytic conductors.

In metallic conductors, conduction takes place due to the flow of free electrons and hence these are called electronic conductors. Some compounds like HCl, NaOH and KCl conduct electricity because of the movement of ions in their molten state or in aqueous solution. These types of conductors are called electrolytic conductors.

The electrochemical reactions involve the process of decomposition of an electrolyte either in fused state or in solution state by the passage of electricity.

Mostly, all the electrovalent compounds in their fused or molten state conduct electricity. The electrical conduction in these can be attributed to the presence of mobile ions.

Conduction in Electrovalent Compounds

The electrovalent compounds contain an aggregate of oppositely charged ions in the solid state. The ions in the solid state are held in their positions by strong electrostatic forces of attraction. Hence, they are immobile. When they are melted or dissolved in a suitable solvent, the forces of attraction between their ions are weakened and the ions then move, thereby conducting electricity.

The process due to which an ionic solid dissociates into ions, in the fused state or in dissolved state is called electrolytic dissociation.

Examples: electrolytic dissociation of NaCl.

In fused state, the high temperature weakens the electrostatic force of attraction, between Na^+ and Cl^- ions, whereas in dissolved state of NaCl, they get separated due to the dielectric effect of the solvent and hence conducts electricity.

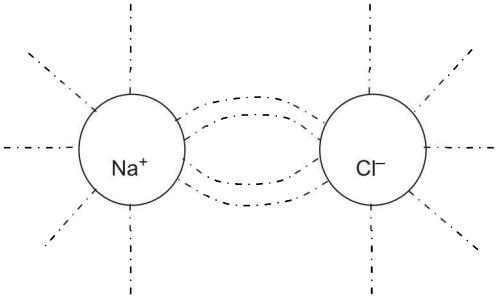


Figure 7.1 Dissociation of NaCl

The extent of electrolytic dissociation depends upon the nature of the solvent because the role of the solvent is to weaken the electrostatic forces of attraction between the ions.

Not only the ionic compounds but also the polar covalent compounds conduct electricity in solution state. Due to the polarity within the molecules of polar covalent compounds, charge separation takes place in solution state. The process of formation of oppositely charged ions from the molecules of polar covalent compound is called *ionization*.

Examples: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

In order to explain the process of electrolysis, Arrhenius in 1887 proposed a theory known as theory of electrolytic dissociation largely confined to aqueous solutions of the electrolytes.

Postulates of Arrhenius theory of electrolytic dissociation

(i) The molecules of the electrolyte when dissolved in water dissociate into two kinds of charged particles—positively charged particles and negatively charged particles or ions. This process is known as ionization or electrolytic dissociation.

(ii) When a voltage is applied, cations move towards the cathode and anions move towards the anode.

(iii) The number of positively charged ions and negatively charged ions may be different, but the total positive and total negative charges carried by anions and cations are same. Hence the electrolytic solution at any instant remains electrically neutral.

(iv) There is equilibrium between the ions and undissociated molecules of the electrolyte.

$$AB \because A^+ + B^-$$

(v) The fraction of the total number of molecules which are present as ions in the solution is called degree of dissociation of the electrolyte.

On the basis of degree of dissociation, electrolytes can be classified into two types. They are strong electrolytes and weak electrolytes.

Strong Electrolytes	Weak Electrolytes
These electrolytes are highly ionized in the solution and have high degree of ionization.	These electrolytes are feebly ionized and have low degree of ionization.
They conduct a good amount of electricity.	They conduct less amount of electricity.
These contain only freely moving ions in the solution or molten state.	These contain some ions and also molecules in the solution or molten state.
e.g., HCl, H_2SO_4, HNO_3, NaOH, KOH, KCl, NaCl, etc.	e.g., CH_3COOH, H_2CO_3, $Al(OH)_3$, NH_4OH, $BaSO_4$, etc.

With an increase in temperature, the conductivity of the electrolyte increases while conductivity of the electrolyte decreases with an increase in concentration.

Process of Electrolysis

The process of electrolysis takes place in an electrochemical cell called electrolytic cell or voltameter.

The electrolytic cell consists of a glass vessel in which an electrolyte is taken in a molten state or in an aqueous solution. Two conductors (metal plates or graphite rods) are dipped in the electrolyte and are known as electrodes. The electrode which is connected to the positive terminal of the battery (i.e., the source of electricity) is called anode and the one which is connected to the negative terminal of the battery is called cathode.

When an electric current is passed through an electrolyte, cations move towards the cathode and anions move towards the anode. Cations accept the electrons from the cathode and get neutralized, whereas anions give up their negative charge by releasing electrons at the anode and become neutral. Hence oxidation takes place at the anode and reduction takes place at the cathode. The number of electrons gained by the anode is equal to the number of electrons lost at the cathode. Generally, metals and H_2 are deposited/liberated at the cathode and nonmetals are liberated at the anode.

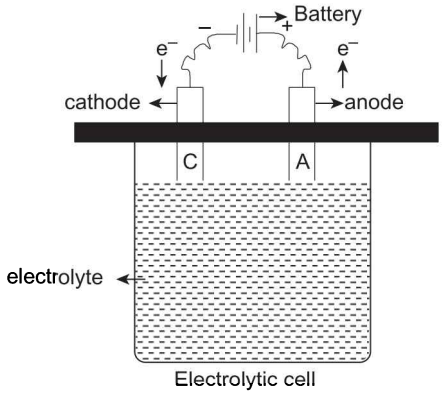


Figure 7.2 Electrolytic cell

Mechanism of Electrolysis

The process of electrolysis thus results in the decomposition of the electrolyte and subsequent deposition or liberation of the constituent products at the respective electrodes. However, the quantities of the electrolytic products at the respective electrodes are not same for all the electrolytes.

For the establishment of quantitative relationship between the electricity passed through the electrolyte and the products obtained at the electrodes, Michael Faraday conducted some experiments. The results were given out as Faraday's laws of electrolysis.

Faraday's Laws of Electrolysis

1st Law

The amount of substance deposited or liberated or dissolved at an electrode is directly proportional to the quantity of electricity passing through the electrolyte.

Mathematical Representation

$m \propto Q$ (m = mass of substance deposited at the electrode)

(Q = quantity of electricity passing through the electrolyte)

$Q = c \times t$ (c = current strength in amperes;

t = time of flow of current in seconds)

$m \propto ct$ or $m = ect$ (e = constant called electrochemical equivalent)

If c = 1 amp and t = 1 s (or Q = 1 coulomb), then m = e.

Electrochemical equivalent can be defined as the mass of substance which undergoes electrode reaction at an electrode by the passage of one coulomb of electricity through the electrolyte.

Since the charge of an electron is equal to 1.602×10^{-19} coulombs, passage of one mole of electrons through an electrolyte corresponds to passage of $(6.023 \times 10^{23} \times 1.602 \times 10^{-19})$ coulombs of electricity.

Charge of 1 mole of electrons = $6.023 \times 10^{23} \times 1.602 \times 10^{-19} = 96{,}496$ coulombs

≈96,500 coulombs, and is called one faraday.

The amount of substance which undergoes electrode reaction by the passage of one faraday (96,500 coulombs) of electricity is equal to the **equivalent weight** of the substance.

Calculation of Equivalent Weight

The equivalent weight of an element or radical is calculated by dividing its atomic weight/formula weight by its valency. The unit of equivalent weight is **atomic mass unit**.

$$\text{Equivalent weight of an element} = \frac{\text{Atomic weight}}{\text{valency}}$$

$$\text{Equivalent weight of a radical} = \frac{\text{Formula weight of the radical}}{\text{valency}}$$

$$\text{Equivalent weight of aluminium} = \frac{\text{Atomic weight of the aluminium}}{\text{valency of aluminium}} = \frac{27}{3} = 9$$

$$\text{Equivalent weight of oxygen} = \frac{\text{Atomic weight of oxygen}}{\text{valency}} = \frac{16}{2} = 8$$

$$\text{Equivalent weight of sulphate radical} = \frac{\text{Formula weight of sulphate radical}}{\text{valency}} = \frac{96}{2} = 48.$$

Therefore the number of equivalents of a substance deposited or liberated or dissolved at an electrode is equal to the number of faradays of electricity passed through the electrolyte.

Relation Between Equivalent Weight and Electrochemical Equivalent

$$\text{Electrochemical equivalent} = \frac{\text{Equivalent weight}}{96500} = \frac{\text{Atomic weight}}{z \times 96500}$$ (where z = valency of the element)

2nd Law

For the passage of same quantity of electricity through different electrolytes, the amounts of respective substances deposited at the electrodes are in the ratio of the equivalent weights of the substances.

If m_1, m_2 and m_3 are mass of different substances and E_1, E_2 and E_3 are the equivalent weights of the substances, then $m_1 : m_2 : m_3 = E_1 : E_2 : E_3$ (when quantity of electricity is constant).

Numerical Problem

A current of 9.65 amperes is passed through three different electrolytes NaCl, $AgNO_3$ and $CuSO_4$ for 30 min separately. Calculate the ratio of the metals deposited at the respective electrodes. Also find out the weights of various metals deposited at the respective electrodes.

Solution

Quantity of electricity passed through the electrolyte = current strength × time of flow = 9.65 × 30 × 60 coulombs

$$m_{Na} : m_{Ag} : m_{Cu} = E_{Na} : E_{Ag} : E_{Cu}$$

$$E_{Na} = \frac{23}{1} = 23 \qquad (Na^+ + e^- \rightarrow Na)$$

$$E_{Ag} = \frac{108}{1} = 108 \qquad (Ag^+ + e^- \rightarrow Ag)$$

$$E_{Cu} = \frac{63.5}{2} 31.75 \quad (Cu^{+2} + 2e^- \rightarrow Cu)$$

$$m_{Na} : m_{Ag} : m_{Cu} = 23 : 108 : 31.75$$

$$\text{Weight of sodium deposited} = \frac{23 \times 9.65 \times 30 \times 60}{96500} = 4.14\,g$$

$$\text{Weight of silver deposited} = \frac{108 \times 9.65 \times 30 \times 60}{96500} = 19.44\,g$$

$$\text{Weight of copper deposited} = \frac{31.75 \times 9.65 \times 30 \times 60}{96500} = 5.715\,g$$

EXAMPLE

Aqueous solution of electrolyte is a better conductor than fused electrolyte. Give reason.

SOLUTION

Due to the high dielectric constant of water, the dissociation of electrolyte into ions is greater in aqueous solution than in fused electrolyte. As a result, the concentration of free ions in aqueous solution is greater than in fused state. Therefore, conductivity of aqueous solution of electrolyte is greater than that of fused electrolyte.

EXAMPLE

Explain the mechanism of electrolysis of molten sodium hydroxide.

SOLUTION

Molten sodium hydroxide dissociates to give Na^+ and OH^- ions. Na^+ ions go towards cathode while OH^- ions go towards anode.

Reaction at anode : $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Reaction at cathode : $4Na^+ + 4e^- \rightarrow 4Na$

EXAMPLE

Distinguish between electrochemical equivalent and equivalent mass of a substance.

SOLUTION

Electrochemical equivalent is the amount of substance deposited or liberated at the electrode by the passage of one coulomb of electricity through the electrolyte. Equivalent mass is the amount of substance deposited or liberated at the electrode by the passage of 1 Faraday (96500 coulombs) of electricity through the electrolyte

EXAMPLE

When any strong electrolyte is subjected to electrolysis, are equal number of moles of products formed at cathode and anode for the passage of same quantity of electricity? Explain.

SOLUTION

When a strong electrolyte is subjected to electrolysis, it is not necessary that equal number of moles of cathodic and anodic products are formed. It depends on the relative charges of cation and anion in that electrolyte and the number of electrons involved in the respective cathodic and anodic reactions.

Galvanic Cells or Voltaic Cells

Based on the concept of electrolysis, it is obvious that chemical reactions can be carried out by making use of electrical energy. Similarly, it is possible to generate electrical energy by means of spontaneous redox reactions. The electrochemical cell used for this purpose of conversion of chemical energy into electrical energy is also known as a galvanic cell or voltaic cell.

The galvanic or voltaic cell consists of two half-cells viz., anodic half-cell where oxidation takes place and cathodic half-cell where reduction takes place.

Principle and Working of the Galvanic or Voltaic Cell

When a metal strip (e.g., zinc) is dipped in a solution of its own ions, equilibrium exists between the metal atoms and the metal ions. This is because, the metal atoms may have a tendency to lose electrons and enter into the solution as metal ions. The electrons so released remain on the rod. The region of solution which is very close to the metal strip becomes rich in positive charge.

Other metals like copper behave in a different way. The metal ions from the solution have a tendency to take out electrons from the metal atoms on the strip and become neutralized. In this case, the metal rod is left with positive charge and the part of the solution which is in contact with the metal rod becomes slightly negatively charged. These metal rods are called electrodes.

The equilibrium [$M^{n+}(aq) + ne^- \rightarrow M\ (s)$] is set up in both the cases and an electrical double layer is formed.

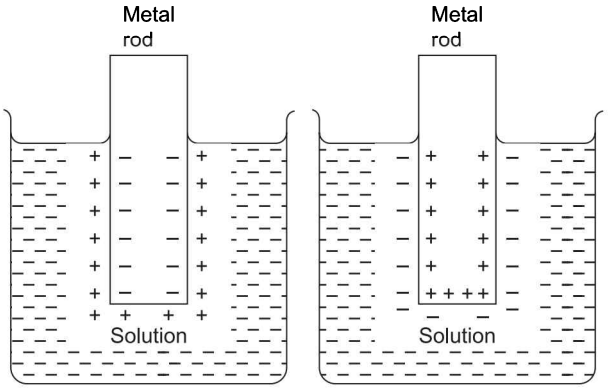


Figure 7.3 Schematic representation of Zinc and Copper Electrodes

In the first case, equilibrium lies to the left and in the second case it lies to the right.

Single Electrode Potential

Since the metal rod and the solution surrounding it differ in charge, a potential is developed between the metal rod and the salt solution. This potential developed at the interface of metal rod and the solution of its own ions is called *single electrode potential*. It is denoted by E.

Each electrode system (the metal rod in contact with its salt solution) is called a half-cell. If oxidation takes place in the half-cell it is called oxidation half-cell and if reduction takes place in the half-cell, it is called reduction half-cell. The electrode at which oxidation takes place is called anode

and the electrode at which reduction takes place is called cathode. Since measurement of single electrode potentials for any electrode is not possible it is absolutely necessary to combine it with an electrode whose potential is known. For this purpose, hydrogen electrode has been taken as a standard whose potential has been arbitrarily fixed as zero volts. This is known as standard hydrogen electrode.

Standard Hydrogen Electrode (SHE)

Hydrogen gas at 1 atm. pressure is taken in contact with platinum surface and HCl solution of 1 molar concentration at 25°C temperature. This is called standard hydrogen electrode. The electrode potential has been assigned a value of zero volts.

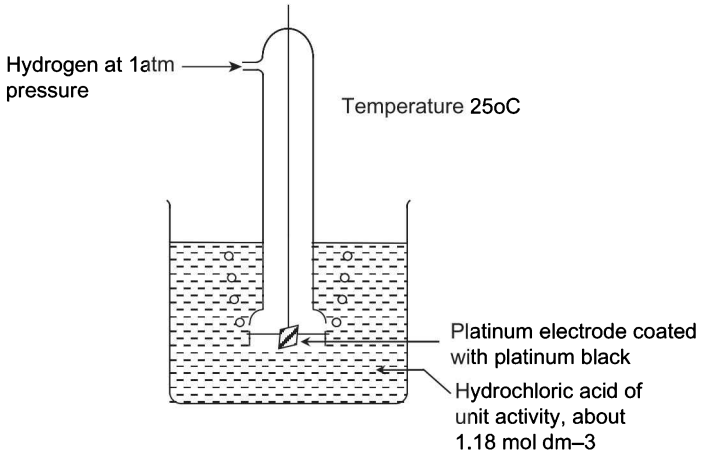


Figure 7.4 Standard Hydrogen Electrode

Standard Electrode Potential

Electrode potential depends upon the nature of electrode, concentration of the salt solution and the temperature. Therefore, certain standard conditions are considered. The salt solution of 1M concentration is taken at 25°C temperature. The electrode potential measured under these standard conditions is called standard electrode potential. It is denoted by E°.

When any electrode is connected to the SHE, the potential difference between the two electrodes is called **standard electrode potential** of that electrode.

The hydrogen electrode constitutes one half-cell and the other electrode system constitutes another half-cell. These two half-cells are separated by a salt bridge. A salt bridge is a U-shaped tube containing KCl solution in agar agar. This salt bridge serves the purpose of providing an electrical contact between the two half-cells. The two half-cells are connected through a voltmeter. The reading of the voltmeter gives the emf of the cell.

$$\textbf{EMF of the cell} = E^{\circ}_{RHE} - E^{\circ}_{LHE}$$

The half-cell in which oxidation takes place is taken on the left-hand side, whereas the half-cell in which reduction takes place is taken on the right-hand side.

When zinc electrode is coupled with SHE, zinc electrode is taken as RHE and SHE is taken as LHE.

$$H^{+} + e^{-} \rightarrow H_2(RHE)$$

$$Zn \rightarrow Zn^{+2} + 2e^{-} \text{ (LHE)}$$

$$E^{0}_{Zn^{+2}/Zn} = 0.76 \text{ volts}$$

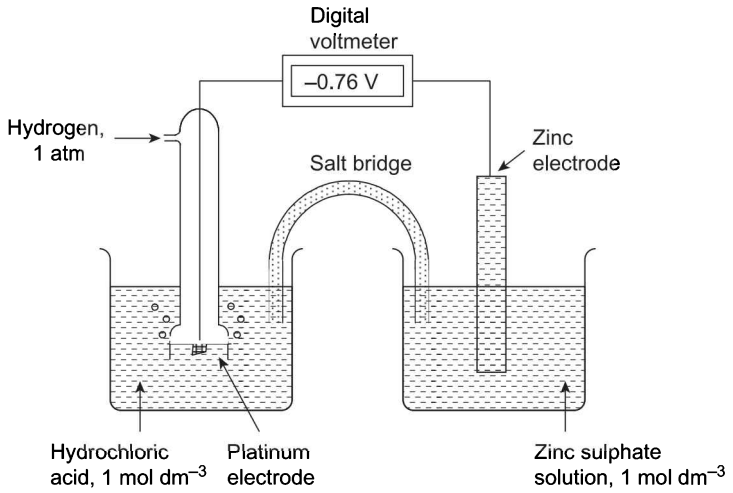


Figure 7.5 Voltaic cell with Zinc Electrode and Hydrogen Electrode

In the similar way, the standard electrode potentials of all the electrodes can be calculated by coupling with SHE.

Depending on whether the loss or gain of electrons takes place in the electrode system, the standard electrode potential may be oxidation potential or reduction potential. Oxidation potential and reduction potential for an electrode are equal in magnitude but with opposite sign.

However, according to IUPAC convention, usually, reduction potentials are considered for the various electrodes. Therefore, standard electrode potentials correspond to standard reduction potentials only.

Electrochemical Series

The arrangement of the electrodes in the order of their standard electrode potentials is called electrochemical series. A greater negative value indicates the greater ease of reduction and greater positive value indicates greater ease of oxidation.

Standard Reduction Potentials at 25°C

Half-reaction	E°, Volts
$F_2(g) + 2e^- \rightarrow 2F^-$	2.87
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$	1.23
$Br_2(\ell) + 2e^- \rightarrow 2Br^-$	1.07
$Ag^+ + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$I_2(s) + 2e^- \rightarrow 2I^-$	0.54
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$2H^+ + 2e^- \rightarrow H_2(g)$	0.00

Half-reaction	E°, Volts
$Fe^{3+} + 3e^- \rightarrow Fe(s)$	–0.04
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	–0.42
$Fe^{2+} + 2e^- \rightarrow Fe(s)$	–0.44
$Cr^{3+} + 3e^- \rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn(s)$	–0.76
$Cr^{2+} + 2e^- \rightarrow Cr(s)$	–0.90
$Al^{3+} + 3e^- \rightarrow Al(S)$	–1.67
$Mg^{2+} + 2e^- \rightarrow Mg(s)$	–2.36
$Na^+ + e^- \rightarrow Na(s)$	–2.71
$Ca^{2+} + 2^{e-} \rightarrow Ca(s)$	–2.84
$Sr^{2+} + 2e^- \rightarrow Sr(s)$	–2.87
$Ba^{2+} + 2e^- \rightarrow Ba(s)$	–2.92
$Cs^+ + e^- \rightarrow Cs(s)$	–2.92
$Rb^+ + e^- \rightarrow Rb(s)$	–2.93
$K^+ + e^- \rightarrow K(s)$	–2.93
$Li^+ + e^- \rightarrow Li(s)$	–3.05

A voltaic or galvanic cell is constructed by combining two electrode systems where the potential difference between the two electrode systems can be measured by means of an voltmeter and this potential difference of the given cell is called *cell emf or cell potential.*

An example of the voltaic cell is the Daniel cell.

Daniel Cell

Daniel cell can be constructed by connecting a Zn/Zn^{+2} half-cell with a Cu^{+2}/Cu half-cell with a wire. Zinc ions leave the surface of the electrode and move into the solution. Electrons from the zinc electrode move to the copper electrode through the wire. Copper (II) ions from the solution move to the copper electrode and get neutralized. A KCl salt bridge is used to connect the two half-cells. Negatively charged chloride ions from the salt bridge flow to the Zn/Zn^{+2} half-cell, whereas potassium ions flow to Cu/Cu^{+2} half-cell to maintain electrical neutrality.

The salt bridge allows the charge to move from one half-cell to the other half-cell, but prevents mixing of the solutions.

In Daniel cell, zinc electrode is called anode because oxidation takes place at the zinc electrode and copper electrode is called cathode because reduction takes place there.

Half-cell reactions

$$Zn \rightarrow Zn^{+2} + 2e^{-1}$$

$$Cu^{+2} + 2e^{-1} \rightarrow Cu$$

Net reaction

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

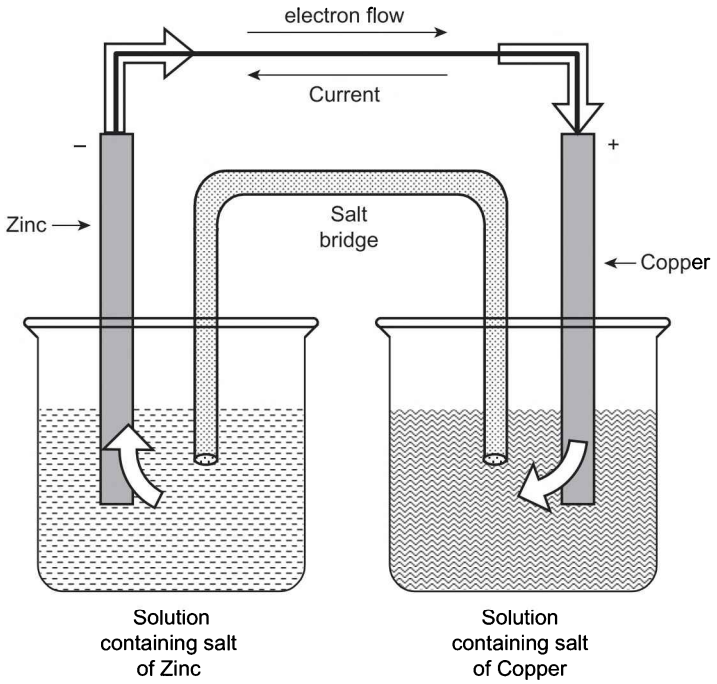


Figure 7.6 Schematic representation of Daniel cell

Representation of Cell

According to the IUPAC convention, oxidation half-cell is written first by writing metal followed by metal ion separated by a single vertical line. The reduction half-cell is written later by writing metal ion followed by metal. The two half-cells are separated by a double vertical line which indicates salt bridge.

Examples: Daniel cell

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

Applications of Electrochemical Series: Prediction of Cell Reaction

By coupling the standard electrodes whose potentials are known, the standard emf of the cell can be calculated. Since the emf of a cell is always positive, accordingly RHE and LHE are chosen. RHE involves oxidation half-reaction and LHE involves reduction half-reaction. Therefore, the cell reaction can be predicted from the relative positions of the electrodes in the electrochemical series.

Selective Discharge of Ions During Electrolysis

The cations with lower discharge potential get discharged at the cathode in preference to one with higher discharge potential.

Examples:

(i) If Cu^{+2} and H^{+1} are present in the solution, Cu^{+2} will be discharged due to its lower discharge potential.

(ii) If Na^{+1} and H^{+1} are present in the solution, H^{+1} will be discharged due its lower discharge potential.

Similarly, the anions with lower discharge potential get discharged at the anode due to increasing ease of oxidation from the top to bottom of the electronegative series.

Examples:

Between Cl^- and OH^-, OH^- gets discharged at the anode due to its lower discharge potential than that of Cl^-.

Electrolysis of Acidulated Water Using Platinum Electrodes

Electrolytic cell: Hoffmann's voltameter

Electrolyte: H_2O + dil H_2SO_4 (small amount)

Electrodes: Platinum electrodes as cathode and anode

Current: 12 V (from a battery)

Dissociation reaction: $2H_2O \rightarrow H_3O^+ + OH^-$

Ions present: OH^- and H_3O^+, SO_4^{-2}, H^+ (H_3O^+)

Electrode reaction:

At cathode: $H^+ + e^- \rightarrow H$

$$H + H \rightarrow H_2\uparrow$$

At anode: $4OH^- - 4e^- \rightarrow 2H_2O + O_2$

Products obtained: H_2 and O_2

(net reaction: $2H_2O \rightarrow 2H_2 + O_2$)

Volumetric Analysis

On electrolysis, water gives 2 volumes of H_2 and 1 volume of O_2. Hence ratio of H_2 and O_2 formed is 2 : 1.

Apart from the position of an electrode in the electrochemical series, other factors also affect the preferential discharge of ions at the respective electrodes.

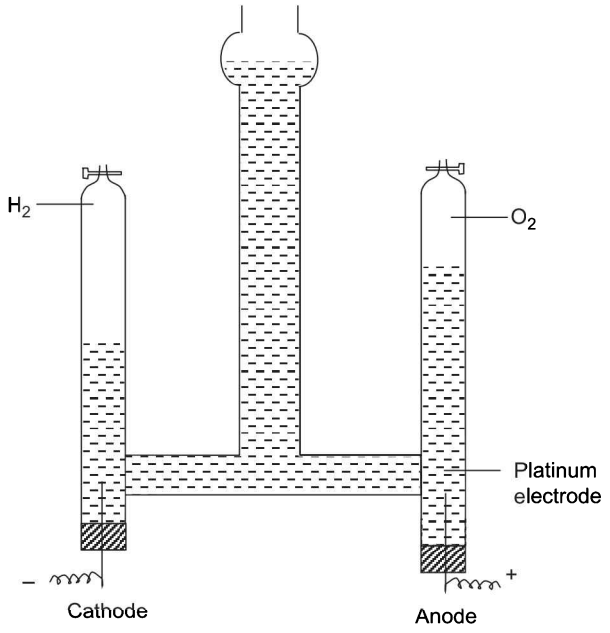
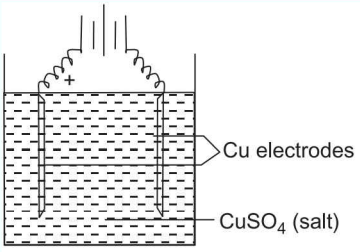
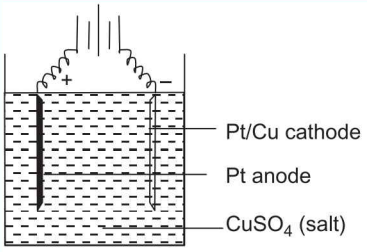


Figure 7.7 Hoffman's voltameter

	Electrolysis of $CuSO_4$ (aq) using active anode (Cu)	Electrolysis of $CuSO_4$ (aq) using inert anode (Pt)
Electrolytic cell	Iron crucible at normal temperature	Iron crucible at normal temperature
Electrolytic reactions	Electrolytic dissociation: $CuSO_4 \therefore Cu^{+2} + SO_4^{-2}$ $H_2O \therefore H^+ + OH^-$	Electrolytic dissociation: $CuSO_4 \therefore Cu^{+2} + SO_4^{-2}$ $H_2O \therefore H^+ + OH^-$
	At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$ At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$	At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$ At anode: $4[OH^- - e^- \rightarrow OH] \rightarrow 2H_2O + O_2$
Procedure	(i) Electric current is passed through $CuSO_4$ solution keeping copper as anode. (ii) Cu^{+2}, H^+, SO_4^{-2} and OH^- ions are formed. (iii) SO_4^{-2} and OH^- ions migrate towards the anode. An ionization potential of copper is less than the discharge potential of SO_4^{-2} and OH^- copper anode itself ionizes.	(i) Electric current is passed through $CuSO_4$ solutions keeping platinum as anode. (ii) Cu^{+2}, H^+, SO_4^{-2} and OH^- ions are formed. (iii) SO_4^{-2} and OH^- migrate towards the anode but OH^- is discharged in preference to SO_4^{-2} ions due to the low discharge potential.
Observation	Blue colour of $CuSO_4$ solutions does not fade as concentration of Cu^{+2} does not change.	Blue colour of $CuSO_4$ fades away as the concentration of $CuSO_4$ decreases.
Schematic Diagram		

EXAMPLE

How does aqueous and acidified $CuSO_4$ dissociate on the passage of current? Also write the electrode reactions at the respective electrodes

SOLUTION

Aqueous acidified copper sulphate, dissociates as shown below.

$CuSO_4 \rightarrow Cu^{2+} + SO_4^{-2}$; $H_2O \rightarrow H^+ + OH^-$; $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

Reaction at cathode: Copper gets discharged at the cathode because of lower discharge potential than that of hydrogen.

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

Reaction at anode

(a) If anode is platinum or graphite (inactive anode)

OH^- is discharged at the anode because its discharge potential is lower than that of SO_4^{2-} ion.

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

(b) If the anode is copper itself (active anode)

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

No product is formed at anode.

EXAMPLE

When concentrated solution of cupric chloride is taken, chlorine gets liberated at anode, in contrast to a dilute solution where oxygen is liberated. However, when aqueous solution of $CuSO_4$ is taken, only oxygen is liberated at anode irrespective of concentration. How do you account for this?

SOLUTION

An aqueous solution of cupric chloride contains Cl^- ions, OH^- ions, Cu^{+2} ions and H^+ ions. Due to lower discharge potential of OH^- than Cl^-, oxygen gas is liberated at anode in preference to chlorine. However, in the concentrated solution, as the concentration of OH^- ions is very low, only chlorine gets liberated at anode. This is possible because the difference between discharge potentials of Cl^- and OH^- is only marginal. An aqueous solution of $CuSO_4$ contains Cu^{+2}, H^+, OH^- and SO_4^{-2} ions. Due to large difference in discharge potentials between SO_4^{-2} and OH^-, only OH^- ions get discharged at anode irrespective of the concentration of the electrolyte.

EXAMPLE

Define discharge potential. Draw a comparison with the SRP values of elements in the electrochemical series.

SOLUTION

The actual potential required for the discharge of ion at the electrode is called discharge potential. In case of positive ions, higher SRP value indicates lower discharge potential as positive ions get discharged at the electrode by gaining electrons (reduction)

In case of negative ions, higher SOP value (lower SRP value) indicates lower discharge potential as negative ions get discharged at the electrode by losing electrons (oxidation).

Applications of Electrochemistry

The concept of electrolysis finds applications in various industries for various purposes.

The concept of electrochemical cells is made use in different types of batteries. The hydrogen oxygen fuel cells are also based on the same concept. The most important applications are listed hereunder:

(i) Electroplating of metals
(ii) Electrolytic refining of metals
(iii) Extraction of metals (electrometallurgy)

(i) Electroplating

It is an electrolytic process of depositing a thin film of a metal like gold, silver, nickel, etc., on other metals like iron, copper, etc., for different purposes.

Applications of Electroplating

(a) *For anti-corrosion*: To induce anti-corrosive properties by coating a metal with other metal.

(b) *For decorative purposes*: To give a pleasing appearance, less valuable metals are electroplated with costly ones. Example: gold over brass.

Conditions to be Maintained During Electroplating

(i) The article to be electroplated is always made the cathode in electrolysis since the metal is deposited at the cathode.

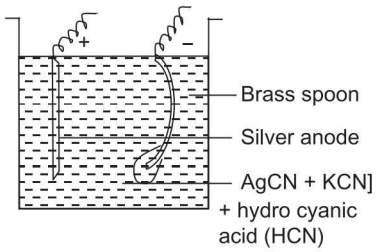
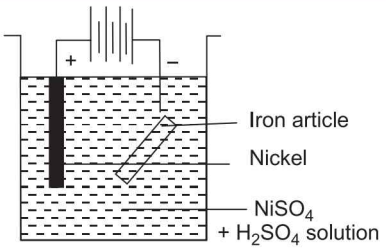
(ii) The metal (like Ni, Ag, Au, etc.), which is to be electroplated on the given metal is always placed at anode. Since the metal anode continuously dissolves in the solution, it has to be replaced periodically.

(iii) The electrolyte solution must contain the metal ions like Ag, Au, Ni, etc., since these ions travel towards cathode and get deposited on the metal placed at cathode.

(iv) Less amount of current is supplied for longer time. It helps to reduce the uneven deposition of metal.

(v) Only direct current is to be used because alternating current causes discharge or ionization on alternate electrode. No effective coating takes place on cathode.

	Electroplating of a brass spoon with silver	Electroplating of iron with nickel metal
Electrolyte	$AgCN + KCN + HCN$ Silver cyanide + Potassium cyanide + Hydrogen cyanide	$NiSO_4 + H_2SO_4$ Nickel sulphate + Sulphuric acid
Electrodes	Brass spoon (cathode) Pure silver (anode)	Iron article (cathode) Nickel metal (anode)
Electrolytic dissociation reaction	$AgCN \because Ag^+ + CN^-$ $KCN \because K + CN^-$ $HCN \because H^+ + CN^-$ $K^+ + Ag^+ + CN^- \because$ $KAg(CN)_2$ The formation of potassium argentocyanide controls the deposition of silver on the cathode so that the coating becomes thin, uniform and adheres properly over the cathode.	Electrolytic reaction $NiSO_4 \because Ni^{+2} + SO_4^{-2}$ $H_2SO_4 \because 2H^+ + SO_4^{-2}$ $H_2O \because H^+ + OH^-$
	At cathode: $Ag^+ + e^- \rightarrow Ag$ At anode: $Ag - e^- \rightarrow Ag^+$	At cathode: $Ni^{2+} + 2e^- \rightarrow Ni$ At anode: $Ni - 2e^- \rightarrow Ni^{+2}$
Procedure	(i) A highly cleaned brass spoon which has to be electroplated is taken. (ii) Due to electrolytic dissociation, Ag^+, K^+, H^+, OH^- and CN^- ions are formed. (iii) CN^- and OH^- ions are not discharged at the anode due to high reduction potential than Ag. (iv) Silver gets deposited on brass spoon. $AgNO_3$ is also used an electrolyte.	(i) Take a highly cleaned iron article which has to be electroplated. (ii) Due to electrolytic dissociation Ni^{+2}, SO_4^{-2}, H^+, SO_4^{-2} and OH^- are formed. (iii) SO_4^{-2} and OH^- are not discharged at the anode due to high reduction potential than Ni. (iv) Hence, Ni metal gets deposited on iron article.

	Electroplating of a brass spoon with silver	Electroplating of iron with nickel metal
Schematic diagram		

(ii) Electrolytic refining

(a) Electrolysis can also be used for refining metals containing impurities. They can be purified electrolytically.

(b) For example, purification of copper.

Electrolytic Refining of Copper Metal

Electrolyte: Acidified copper sulphate ($CuSO_4 + H_2SO_4$) solution

Electrodes: Impure copper rod as anode and thin strip of pure copper rod as cathode.

Dissociation of electrolyte takes place in the following ways:

$$CuSO_4 \rightleftharpoons Cu^{+2} + SO_4^{-2}$$

$$H_2SO_4 \rightleftharpoons 2H^{+1} + SO_4^{-2}$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Reaction at the cathode

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

The Cu^{+2} ions in the solution get attracted to cathode and are deposited there by reduction.

Reaction at the anode

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

The impure copper rod gets oxidized and hence forms Cu^{+2} ions and dissolves in the solution. These Cu^{+2} ions get deposited at the cathode. As a result, gradually the cathode increases in size. The copper obtained at the cathode is 99.9% pure.

Anode mud: The impurities like silver, gold, mercury, etc., settle down as anode mud (slime).

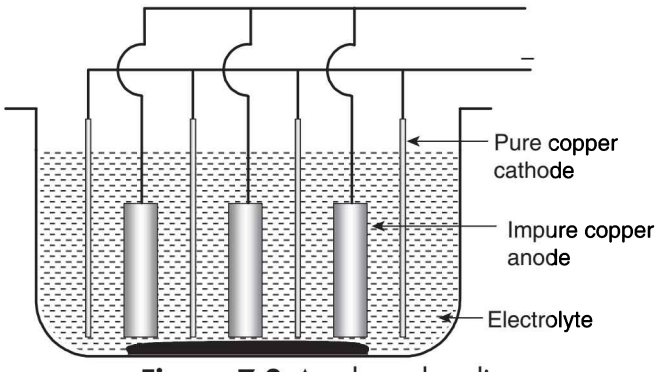


Figure 7.8 Anode mud or slime

(iii) Electrometallurgy

Electrolysis can also be used in the extraction of metals, which are at the top of electrochemical series. Examples: Na, K, Al, Ca, Mg, etc.

Electrometallurgy of Metals

Na, Mg and Ca are extracted by the electrolysis of their molten chlorides with iron as cathode and graphite as anode.

Anodic reaction is $2Cl^- - 2e^- \rightarrow Cl_2\uparrow$

Cathodic reaction is $M^{+n} + ne^- \rightarrow M$

where M is the metal.

Aluminium is extracted by the electrolysis of fused Al_2O_3 mixed with a small amount of cryolite. Gas carbon lining is made the cathode and thick carbon rods are made anodes in the electrolytic cell for extraction of aluminium.

Reactions

At cathode: $2Al^{+3} + 6e^- \rightarrow 2Al$

At anode: $3O^{-2} - 6e^- \rightarrow 3O_2\uparrow$

Batteries

Various types of batteries are used in watches, transistor radios, cars and other automobiles. Some batteries can be recharged and some cannot be recharged.

The most common type of battery consists of zinc rod dipped in a paste of zinc chloride and ammonium chloride. This entire set up is kept in contact with a graphite rod surrounded by a mixture of MnO_2 and graphite powder. Emf of this cell is around 1.5 volts.

Other type of batteries includes button-shaped cells having an emf of 1.6 volts. A common car battery consists of PbO_2 in contact with H_2SO_4.

Fuel Cell

Example: hydrogen–oxygen fuel cell.

In the hydrogen–oxygen fuel cell, platinum electrodes are placed in a solution of an alkali. Electricity is generated by means of the following cell reactions.

Cell reactions involved

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(\ell) + 4e^-$$

$$O_2(g) + 2H_2O(\ell) + 4e^-(aq) \rightarrow 4OH^-$$

Net reaction is $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$

EXAMPLE

Explain the electrometallurgical process for the extraction of potassium using fused potassium chloride.

SOLUTION

Electrolyte: Fused potassium chloride

Cathode: Iron

Anode: Graphite (inert anode)

Dissociation of electrolyte: $KCl \rightarrow K^+ + Cl^-$

Reactions at the cathode: $K^+ + e^- \rightarrow K$

Reactions at the anode: $[Cl^- - e^- \rightarrow Cl^-] \times 2$

$Cl + Cl \rightarrow Cl_2$

EXAMPLE

With reference to the position of various metals in the electrochemical series, identify and justify the method of extraction followed for the metals given below.

(a) Zinc **(b)** Copper **(c)** Magnesium

SOLUTION

(a) Zinc is a metal present in the middle of the electrochemical series. Zinc has negative SRP value that is why it can be reduced by normal reducing agents such as hydrogen, carbon monoxide and carb0on. This is because these reducing agents possess the ability to break ionic bonds between metal ion and oxide ion.

(b) Copper is a metal present above hydrogen in the electrochemical series. It has positive value for SRP which indicates the lesser thermal stability of its oxide. Thus it can be extracted by reduction with other metals which have lower SRP than Cu.

(c) Magnesium is a metal present at the bottom in the electrochemical series. It has very high value of negative SRP value. That means, it itself is a strong reducing agent and hence cannot be reduced by any other reducing agents. It is therefore extracted by the electrolytic reduction of its molten salt.

EXAMPLE

Why do platinum and gold occur in free state in nature?

SOLUTION

Platinum and gold have high negative values of oxidation potentials. They do not possess tendency to form positive ions at all. Therefore, they do not occur in combined state unlike other metals and hence they occur free in nature.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. What is meant by electrolysis?
2. What are batteries?
3. What do you mean by voltameter?
4. Current enters or leaves the electrolyte through _____.
5. Explain the principle involved in an electrochemical cell.
6. How does temperature affects the extent of dissociation of an electrolyte?
7. How do the impurities present in the electrolyte affect the conductivity?
8. _____ of electrolyte gets oxidized in electrolysis.
9. What is Daniel cell?
10. What is cell emf? Write down the cell reactions involved in Daniel cell.
11. What are the electrodes used in electrorefining of copper?
12. Define electrochemical equivalent.
13. What do you mean by standard hydrogen electrode?
14. Pure metal in electroplating gets deposited at _____.
15. Write the cell representation of Daniel cell.
16. Define standard electrode potential with an example.
17. What is the principle of fuel cells?
18. How many electrons constitute one Faraday?
19. _____ electrodes do not take part with deposited or liberated materials.
20. Write the cell reaction for the following cell representation.

$$Zn / Zn^{+2}_{(aq)} / / Ag^{+}_{(aq)} / Ag_{(s)}$$

21. What is the smallest possible charge existing?
22. Why do polar covalent molecules conduct electricity in aqueous solutions?
23. Why do anions move towards anode and cations move towards cathode in electrolysis?
24. Why are electrolytes in solid state not good conductors?
25. During electrolysis, the cations get discharged at cathode in _____ order of their discharge potential.
26. How many Faradays of charge are required to deposit 1 g atomic weight of Cu metal from Cu (II) solution of 1 mole concentration?
27. Write the electrolytic products of electrolysis of
    (i) aq $NaOH_{(conc)}$ (Pt electrodes)
    (ii) aq $NaCl_{(conc)}$ (Pt electrodes)
    (iii) aq $AgNO_{3(conc)}$ (Ag electrodes)
28. What happens when a bulb is connected in series with two electrolytic cells containing aqueous $CuSO_4$ and aqueous sucrose solution?
29. For uniform deposition of a metal during electroplating _____ amount of current is supplied for _____ time.
30. How much charge is required to deposit one equivalent of any substance?

Short Answer Type Questions

31. Differentiate strong and weak electrolytes.
32. List the differences between metallic and electrolytic conductors.
33. State the differences between ionization and electrolytic dissociation.
34. What is meant by 1 faraday of electricity? What happens when we supply 1 faraday to an electrolyte?
35. What is the difference between electrochemical and electrolytic cell?
36. Define the following terms with examples:
    (i) Electrolysis
    (ii) Electrolytic cell
    (iii) Electrochemical cell
    (iv) Ions and electrodes
    (v) 1 faraday

37. What is degree of ionization and ionization constant or dissociation constant?
38. What are the different types of electrolytes? Give examples for each.
39. On what factor does selectivity of ion to be discharged depends? Explain.
40. K^+ and H^+ ions are present in an electrolyte. Which would get discharged at cathode? Why?
41. What are noble electrodes? Explain their use.
42. Write down the procedure for electroplating iron.
43. The products obtained at electrodes vary as the electrodes used in electrolysis. Justify.
44. What do you mean by spectator ions? Give an example.
45. Write down applications of electrolysis with examples.

Essay Type Questions

46. State and explain Faraday's laws of electrolysis.
47. What is electrochemical series? Write down the properties of electrochemical series.
48. What is meant by electroplating? Explain the electroplating of brass spoon with silver with a neat sketch.
49. What is meant by electrometallurgy? Explain the extraction of Na, Mg and Al. State the reactions involved.
50. Explain the standard electrode potential of an electrode. How is it measured?

CONCEPT APPLICATION

Level 1

Direction for questions from 1 to 7: **State whether the following statements are true or false.**

1. Electrolysis brings about a chemical change.
2. Batteries are voltaic cells.
3. During electrolysis, cations move towards the positive terminal.
4. The negative sign of the reduction potential indicates that reduction occurs at that electrode when connected to the standard hydrogen electrode.
5. In the electrochemical series, ions are arranged in an increasing order of discharge potentials.
6. The salt bridge permits movement of charge and mixing of the solution.
7. The deposition of different ions at electrodes stops when the supply of electricity is stopped.

Direction for questions from 8 to 14: **Fill in the blanks.**

8. The extent to which an electrolyte can dissociate into ions is called _____.
9. Zn^{+2} and Ag^+ are present in a solution to be electrolysed. The metal that is deposited first at cathode is _____.
10. The thickness of _____ increases in the electrorefining of copper.
11. During electrolysis of molten $PbBr_2$, _____ fumes are liberated at the anode.
12. The electrode potential of standard hydrogen electrode is assigned a value of _____.
13. Thick sheets of pure copper are obtained at _____ in electrorefining.
14. In cell representation, oxidation half-cell is represented on the _____.

Direction for question 15: **Match the entries given in column A with the appropriate ones in column B.**

15.

Column A		Column B
A. Concentrated HCl solution	( )	a. Na and O_2
B. Fused alumina	( )	b. Na and Cl_2
C. Aqueous sodium hydroxide	( )	c. H_2 and Cl_2
D. Molten sodium chloride	( )	d. H_2 and O_2
E. Fused NaOH	( )	e. Al and O_2

PRACTICE QUESTIONS

Direction for questions from 16 to 45: **For each of the questions, four choices have been provided.**

Select the correct alternative.

16. On increasing temperature, conduction in metallic conductors_____.
(a) increases (b) decreases
(c) remains constant (d) none of these

17. The aqueous solution of non-electrolytes contains _____.
(a) atoms (b) ions
(c) electrons (d) molecules

18. The metal deposited first at the cathode when a solution containing Fe^{+2}, Cu^{+2} is electrolyzed is _____.
(a) Fe (b) Cu
(c) Fe^{+3} (d) both 1 and 2

19. Which of the following electrolytes exhibits maximum conductivity?
(a) 1 M NaCl (b) 1 M KCl
(c) 1 M $Ca(NO_3)_2$ (d) 1 M $Al_2(SO_4)_3$

20. Electrolysis of aqueous $CuSO_4$ with inert electrodes gives_____.
(a) Cu at cathode, anode gets dissolved
(b) Cu at cathode, O_2 at anode
(c) O_2 at anode, H_2 at cathode
(d) O_2 at anode, cathode gets dissolved

21. The amount of copper deposited by the passage of 1 mole of electrons during the electrolysis of aqueous $CuSO_4$ solution is
(a) 63.5 g (b) 31.75 g
(c) 159.5 g (d) 79.75 g

22. Negative sign in the standard electrode potential indicates
(a) greater ease of oxidation compared to that of hydrogen
(b) greater ease of reduction compared to that of hydrogen
(c) lesser ease of oxidation compared to that of hydrogen
(d) none of the above

23. The products of electrolysis of dilute aqueous solution of sodium hydride are
(a) Na at cathode and H_2 at anode
(b) H_2 at cathode and O_2 at cathode
(c) Na at cathode and O_2 at anode
(d) H_2 at both cathode and anode

24. In a Daniel cell, if A ($E_0 = -0.76$ v) and B ($= -2.36$ v) half-cells are taken then
(a) B acts as an anode (b) A acts as an anode
(c) B acts as a cathode (d) cannot be predicted

25. In the electroplating of iron by nickel, nickel sulphate solution is taken as an electrolyte. What is the acid that is added to the electrolyte during the process?
(a) HCl (b) HCN
(c) HNO_3 (d) H_2SO_4

26. Equimolar solutions of zinc sulphate and ferric sulphate are subjected to electrolysis. What is the ratio of Faradays of electricity required for deposition of one mole each of zinc and iron?
(a) 1 : 2 (b) 2 : 3
(c) 1 : 3 (d) 3 : 2

27. Emf of a voltaic cell can be given by_____.
(a) SRP of anode – SRP of cathode
(b) SRP of cathode + SRP of anode
(c) SOP of cathode – SOP of anode
(d) SOP of cathode + SOP of anode

28. The process used in purifying metals by electrolysis is called_____.
(a) electroplating (b) electrometallurgy
(c) electrorefining (d) electrodeposition

29. In a voltaic cell, if iron and silver electrodes are connected with each other then current flows
(a) from iron to silver outside the cell
(b) from silver to iron within the cell
(c) from silver to iron outside the cell
(d) current does not flow in this cell

30. The amount of sodium produced by passage of 2 moles of electrons in the electrolysis of fused NaCl is_____.
(a) 23 g (b) 46 g
(c) 11.5 g (d) 58.5 g

31. The standard electrode potentials of the electrodes are given below. Arrange them in decreasing order of ease of oxidation.
(1) Electrode – I, $E^\circ = -2.89$ V
(2) Electrode – II, $E^\circ = -0.16$ V
(3) Electrode – III, $E^\circ = 0.77$ V

(4) Electrode – IV, $E^\circ = -2.93$ V
(5) Electrode – V, $E^\circ = -1.67$ V
(a) 3 2 5 1 4 (b) 4 1 5 2 3
(c) 3 5 1 4 2 (d) 3 2 1 4 5

32. Pairs of electrodes and their corresponding standard electrode potentials are given. Arrange the cells constructed by these electrodes in increasing order of emf values.
(1) Electrode → A, $E^\circ = -2.92$ V and Electrode → B, $E^\circ = -2.71$ V
(2) Electrode → C, $E^\circ = -0.760$ V and Electrode → D, $E^\circ = -0.44$ V
(3) Electrode → B, $E^\circ = -2.71$ V and Electrode → D, $E^\circ = -0.44$ V
(4) Electrode → A, $E^\circ = -2.92$ V and Electrode → C, $E^\circ = -0.76$ V
(a) 2 1 4 3 (b) 1 2 4 3
(c) 2 4 1 3 (d) 2 4 3 1

33. 1 faraday = _____ coulombs.
(a) 10,000 (b) 95,000
(c) 96.5 (d) 96,500

34. Identify the set of metals which require same amount of charge for the deposition of one mole of metals:
(a) Na, Ag, Al (b) Zn, Cu, Ag
(c) Al, Cu, Zn (d) Mg, Zn, Cd

35. The amounts of metals deposited when 965 C of electricity is passed through NaCl and $AgNO_3$ solutions are _____ and _____ respectively.
(a) 23 g, 108 g (b) 11.5 g, 54 g
(c) 0.23 g, 1.08 g (d) 2.3 g, 10.8 g

36. The order of ease of oxidation of the ions F^-, OH^-, Br^-, SO_4^{2-} is _____.
(a) $SO_4^{2-} > F^- > Br^- > OH^-$
(b) $SO_4^{2-} < Br^- < OH^- < F^-$
(c) $SO_4^{2-} > F^- > Br^- > OH^-$
(d) $OH^- < Br^- < F^- < SO_4^{2-}$

37. The electrolytic process by which an oxide of a metal is coated over metal surface is called _____.
(a) electrolysis (b) electroplating
(c) anodising (d) electrorefining

38. The standard electrode potentials of four metals A, B, C and D are given below. Based on these values, arrange them in the descending order of ease of deposition of metals from their salt solutions when subjected to electrolysis under standard conditions.
(1) → –0.9 V (2) → –2.71 V
(3) → 0.77 V (4) → 0.8 V
(a) 4 3 2 1 (b) 2 1 3 4
(c) 3 4 1 2 (d) 4 3 1 2

39. Which of the following concentrations of the electrolyte corresponds to maximum conductivity?
(a) 1 M HCl (b) 1 M HNO_3
(c) 1 M $HClO_4$ (d) 1 M H_2SO_4

40. Identify the false statement among the following:
(a) Oxidation takes place at positive electrode in electrolytic cell, whereas reduction at negative electrode in voltaic cell.
(b) Deposition of metals takes place in both electrolytic and galvanic cells.
(c) Direction of flow of current is from cathode to anode in electrolytic cell.
(d) Both (a) and (b)

41. When an aqueous solution of zinc sulphate is subjected to electrolysis, 280 ml of oxygen gas at STP is liberated at anode. Calculate the quantity of electricity passed through the electrolyte.
(a) 0.05 F (b) 0.5 F
(c) 0.005 F (d) 5 F

42. Ratio of number of Faradays of electricity required to deposit magnesium, aluminium and sodium in equimolar ratio on electrolysis of their respective molten salts is _____
(a) 2 : 3 : 2 (b) 2 : 1 : 1
(c) 2 : 3 : 1 (d) 4 : 6 : 1

43. The ratio of volumes of H_2 and O_2 liberated on electrolysis of water is _____.
(a) 1 : 2 (b) 1 : 3
(c) 2 : 1 (d) 3 : 1

44. **Assertion (A)**: Passage of 48,250 coulombs of electricity through cupric sulphate and ferrous sulphate solutions result in the deposition 0.5 moles each of iron and copper at the respective cathodes.

Reason (R): Number of equivalents of a metal deposited at cathode is equal to the number of faradays of electricity passed through the electrolyte.

PRACTICE QUESTIONS

(a) Both "A" and "R" are true and "R" is the correct explanation of "A".
(b) Both "A" and "R" are true and "R" is not the correct explanation of "A".
(c) "A" is correct and "R" is wrong.
(d) "A" is wrong and "R" is correct.

45. 100 ml of 0.05 M aqueous $CuSO_4$ solution is subjected to electrolysis. Calculate the quantity of electricity required for the deposition of entire copper at the cathode.
(a) 0.005 F (b) 0.01 F
(c) 0.1 F (d) 0.05 F

Level 2

1. NaCl conducts electricity in water, but it cannot conduct electricity in benzene. Give a reason.

2. Iron is coated with two metals A and B separately. When the coating is partially worn away, it is still protected when coated with A and not by B. Explain with reference to electrochemical series.

3. What are the products of electrolysis of
(i) concentrated KBr and
(ii) dilute KBr solution?

Give reasons in support of your answer.

4. What happens when zinc pieces are added to aqueous copper sulphate solution and copper pieces are added to aqueous zinc sulphate solution? Justify.

5. Identify the cathode, anode and calculate cell emf when a cell is constructed with A (E^0 = –0.44 V) and B (E^0 = 0.337 V).

6. What is the role of moisture in rusting of iron?

7. An external voltage opposing the cell potential is applied to a Daniel cell with zinc and copper electrodes. What happens when the external emf is increased from 0.8 V to 1.1 V and then 1.54 V?

8. What should be used as the anode, cathode and electrolyte in the process of electroplating of iron by nickel and why?

9. During the electrolysis of silver nitrate using copper anode, the colour changes to blue and the intensity of the colour increases. Explain with the help of electrochemical series. What would you observe if $ZnSO_4$ is taken instead of $AgNO_3$?

10. How does galvanization of iron protect iron from rusting even when protective zinc coating is partially worn away?

11. If a metal is to be electroplated with silver, what would happen if a solution of silver nitrate alone is used as an electrolyte? What is the preferable electrolyte and why is it used?

12. A current 5.00 A liberates 0.252 g of hydrogen in certain time. How many grams of oxygen, aluminium and sodium can be liberated or deposited by the same current in the same time?

13. Two monovalent metals A and B are treated with dilute sulphuric acid. A liberates hydrogen and metal B does not. Predict the half-cell reactions and cell representation when these metals are coupled with H-electrode. Justify your answer with respect to standard electrode potential.

14. The standard oxidation potential of silver electrode is given as –0.799 V. The standard reduction potential of copper electrode is given as 0.337 V. Find out the emf of the cell constituted by these two electrodes. Also write the half-cell reactions involved in the cell and give cell representation.

15. Why is it not possible to measure the single electrode potential of any electrode? Justify.

16. Electrolysis of molten magnesium chloride results in the formation of 0.4 g magnesium. Calculate the volume of chlorine liberated during the reaction at STP. When an electrolytic cell consisting of molten $AlCl_3$ and molten NaCl are connected in series with the above cell, calculate the amount of aluminium and sodium deposited at cathode.

17. What is the amount of silver deposited by passing 2 A for 20 min through molten silver nitrate? If the same quantity of electricity is passed through a molten salt solution of gold, 1.6 g of gold is deposited at cathode, then find out its equivalent mass and oxidation state of gold in gold salt. (atomic weight of Au = 197, Ag = 108.)

18. A brass strip of dimensions 4 cm and 6 cm has to be coated with a silver layer of 2 mm thickness. Calculate the amount of charge required for the deposition

of silver and the amount of magnesium deposited in another electrolytic cell when same amount of charge is passed. (density of Ag = 10.5 g/cc.)

19. An aqueous solution of ferrous sulphate is taken and subjected to electrolysis. Calculate the number of electrons flowing through the circuit when 0.7 g of iron is deposited at cathode. (atomic mass of Fe = 56.)

20. Compare the conductivity of same amount of NaCl dissolved in water and in alcohol (assume that volumes of solvents are equal).

21. Why does conductivity of metallic conductor decrease with an increase in temperature, whereas in case of electrolytic conductors the conductivity increases with an increase in temperature?

22. Three electrolytic cells A, B and C are connected in series which consist of concentrated aqueous solution of sodium chloride (brine solution), fused zinc sulphate and aqueous silver nitrate solution. If 1.4 ℓ of chlorine is produced at STP in A at the anode, calculate the volumes of all gaseous products liberated in B and C at their respective electrodes at STP and the charge required for the deposition.

23. During electrolysis of aqueous copper sulphate solution using platinum electrodes, the blue colour of the electrolytic solution fades and towards the end of the process bubbles appear at the cathode. Why? Also comment on the change in pH of solution due to electrolysis.

24. Little litmus is placed in the cathode and the anode compartments of Hoffmann's voltameter containing acidulated water and then electrolysis is carried out. What do you observe and why?

25. An aqueous solution of copper sulphate is subjected to electrolysis using platinum electrodes. Calculate the number of electrons flowing through the circuit when 0.3175 g of copper is deposited. Also calculate the number of molecules present in anodic product (atomic mass of copper = 63.5).

Level 1

1. $AgNO_3$ is soluble salt of silver, but it is preferable to use (NaCN + AgCN) as an electrolyte for silver plating. Give a reason in support of your answer.

2. Lithium batteries are very expensive. Explain why they are still preferred.

3. Some batteries are rechargeable, whereas others must be thrown away after they get discharged. Justify with respect to the concept of electrochemical cells.

4. Explain the effect of change in temperature on the conductivity of the following conductors. Justify with appropriate reasons.

(a) copper rod

(b) aqueous solution of $CuSO_4$

(c) aqueous solution of acetic acid

5. Why does single electrode potential depend upon the concentration of the electrolyte?

6. Thermal stability of metal oxides can be compared using electrochemical series. Explain.

7. How does magnesium connected by a wire to buried iron pipeline protect it from corrosion?

8. How does dilution affect the conductivity of strong electrolytes and weak electrolytes?

9. What do you observe when electrolysis of copper sulphate is done using iron strip as anode? Give reasons.

10. Rusting is an electrochemical process. Justify. If two iron articles are coated with tin and zinc respectively, in which case will the rusting of iron be more rapid, if the coating is worn out in one place. Give a reason.

PRACTICE QUESTIONS

CONCEPT APPLICATION

Level 1

True or false

1. True
2. True
3. False
4. True
5. True
6. False
7. True

Fill in the blanks

8. degree of dissociation
9. zinc
10. cathode
11. bromine
12. 0 volt
13. cathode
14. left-hand side

Multiple choice questions

15. A →c B →e C →d D →b E →a

Multiple choice questions

16. b
17. d
18. b
19. d
20. b
21. b
22. a
23. d
24. a
25. d
26. b
27. a
28. c
29. c
30. b

Solutions for questions from 31 to 45:

31. The electrode with greater negative value of standard reduction potential acts as anode. The electrode with greater positive value of standard reduction potential acts as cathode. Oxidation takes place at anode and reduction takes place at cathode. X
    (i) Electrode – IV $E^\circ = -2.93$ V
    (ii) Electrode – I, $E^\circ = -2.89$ V
    (iii) Electrode – V $E^\circ = -1.67$ V
    (iv) Electrode – II, $E^\circ = -0.16$ V
    (v) Electrode – III $E^\circ = 0.77$ V

32. (i) Electrode – A, $E^\circ = -2.92$ V and Electrode – B, $E^\circ = -2.71$ V
    (ii) Electrode – C, $E^\circ = -0.760$ V and Electrode – D, $E^\circ = -0.44$ V
    (iii) Electrode – B, $E^\circ = -2.71$ V and Electrode – D, $E^\circ = -0.44$ V
    (iv) Electrode – A, $E^\circ = -2.92$ V and Electrode – C, $E^\circ = -0.76$ V

33. Charge of one mole of electrons is known as one faraday which is equal to 96,500 coulombs.

34. Since the valencies of Mg, Zn and Cd are same, i.e., 2 equal amounts of charge is required for the deposition of atomic masses of these metals.

35. $W = \frac{M.c.t}{n.96,500}$ or $\frac{MQ}{n96,500}$

$$W_{Na} = \frac{23 \times 965}{1 \times 96,500}\text{g},\ W_{Ag} = \frac{108 \times 965}{1 \times 96,500}\text{g}$$

$$W_{Na} = 0.23\text{g},\ W_{Ag} = 1.08\,\text{g}$$

36. $SO_4^{2-} < F^- < Br^- < OH^-$

    In an electronegative series, ease of oxidation increases from top to bottom.

37. The electrolytic process by which an oxide of metal is coated on the metal is called anodising.

38. dcab
    d → 0.8 v
    c → 0.77 v
    b → 2.71 v
    a → 0.9 v

39. 1M solution of H_2SO_4 dissociates to produce 3 moles of ions, whereas 1 M solution of other acids dissociate to produce 2 moles of ions. Therefore, 1M H_2SO_4 shows maximum conductivity.

40. In an electrolytic cell, the direction of flow of electrons is from cathode to anode and hence the flow of current is taken in opposite direction from anode to cathode.

41. 22.4 ℓ O_2 at STP require 4 Faradays.

$$0.28\ \ell\ O_2 \text{ at STP require } = \frac{4 \times 0.28}{22.4} = 0.05\,F$$

42. Electrode reactions involved are

$Mg^{+2} + 2e^- \rightarrow Mg$

$Al^{+3} + 3e^- \rightarrow Al$

$Na^+ + e^- \rightarrow Na$

1 mole of Mg requires 2 Faradays.

1 mole of Al requires 3 Faradays.

1 mole of sodium requires 1 Faraday.

Ratio of number of Faradays = 2 : 3 : 1.

43. $H_2O \rightarrow H^+ + OH^-$

Cathode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

Anode: $4H^+ + 4e^- \rightarrow 2H_2$

$\therefore$ The ratio of volumes of H_2 and O_2 is 2 : 1

44. 48,250 coulombs is equal to 0.5 Faraday. Number of equivalents of metal deposited is equal to the number of faradays of electricity passed through the electrolyte and that means 0.5 equivalents of copper and iron are deposited. Since they are bivalent ions, 0.5 equivalents correspond to 0.25 moles.

45. $\frac{W_{Cu}}{63.5} \times \frac{1000}{100} = 0.05\,M$

$$\Rightarrow W_{Cu} = \frac{0.05 \times 63.5}{10} = 0.3175\,g$$

$$\text{No. of equivalents} = \frac{0.3175}{31.75} = 0.01$$

$\therefore$ No. of Faradays is 0.01 F

Level 2

1. (i) Water is a polar solvent.
(ii) The particles responsible for conduction.
(iii) The characteristic of solvent responsible for generating these particles.
(iv) Comparison of characteristics of water and benzene.

2. (i) Comparison of electropositivity of A, B and Fe.
(ii) Comparison of standard reduction potential of A, B and iron.
(iii) Relation between standard reduction potential of an element and the tendency of getting oxidized.
(iv) Relation between the tendency of a metal to get oxidized and its ability to protect iron from corrosion.

3. (i) Preferential discharge of ions.
(ii) The various ions present in the respective solutions.
(iii) Factors responsible for the products obtained at the two electrodes.
(iv) The relative domination of various factors and their effect on the products produced.

4. (i) Electrochemical series
(ii) Comparison of standard electrode potentials of zinc and copper.
(iii) Comparison of reactivates of zinc and copper with respect to their dipositive ions.
(iv) Observable change in the solution corresponding to the reaction involved.

5. (i) Comparison of standard electrode potentials of A and B.
(ii) Relation between standard reduction potential of a metal and its tendency to get oxidized/reduced.
(iii) Identification of anode and cathode based on the relative tendency of getting oxidized/reduced.
(iv) Calculation of cell emf.

6. (i) Formation of Iron (II) hydroxide
(ii) Composition of rust.
(iii) Comparison of form in which iron is present in pure metal and rust.
(iv) Change undergone by iron during the rusting process.

(v) Requisite for an electrochemical cell.

(vi) Identification of electrode and electrolyte in the process of rusting.

(vii) Component of air which plays a significant role.

7. (i) Working principle of Daniel cell.

(ii) Calculation of cell emf.

(iii) Comparison of the cell emf with the external voltage applied.

(iv) Determination of direction of current depending on the magnitude of the external voltage.

8. Metal to be electroplated is taken as cathode.

9. (i) Comparison of electropositivity of copper and silver.

(ii) Identification of the product obtained at the electrode.

(iii) Nature of the anode.

(iv) Reaction that takes place between the anode and the electrolyte.

(v) Ions responsible for blue colour.

10. (i) Relative reactivity of zinc and iron.

(ii) Change undergone by iron during rusting.

(iii) Comparison of oxidation potentials of zinc and iron.

(iv) Mode of prevention of rusting by zinc if the coating is partially worn away.

11. (i) Purpose of silver plating.

(ii) Solubility of silver nitrate.

(iii) Quantity of ions present in the electrolyte.

(iv) Relation between the quantity of ions present in the electrolyte and the quality of coating.

(v) Soluble salt of silver which can form a complex with NaCN.

(vi) Ions produced from the complex.

(vii) Change in the concentration of ions due to the complex formation.

(viii) Effect of change in concentration of ions on quality of plating.

12. (i) The number of gram equivalents is same when the same amount of charge is passed through.

(ii) Calculation of total charge required to produce 0.252 g of hydrogen.

(iii) Calculation of the amounts of other products based on the quantity of charge passed through the respective electrolytes.

13. (i) Comparison of electropositivity of A and B with hydrogen.

(ii) Identification of anode and cathode of the electrochemical cells.

(iii) Half-reactions that take place at the electrodes of the respective cells.

14. (i) Difference in standard electrode potentials of the electrodes

(ii) Difference between oxidation and reduction potentials.

(iii) Comparison of standard electrode potentials of the respective metals.

(iv) Identification of anode and cathode in the electrochemical cell.

(v) Calculation of emf of the cell.

15. (i) Process of measurement of potential.

(ii) The particles present on metal rod and electrolyte.

(iii) The reason for origin of potential difference between the electrode and electrolyte.

(iv) The mode of measurement of single electrode potential.

(v) The changes associated with the system while carrying out the process.

16. $MgCl_2 \rightarrow Mg^{+2} + 2C^-$

For the deposition for 12 g of Mg (equivalent weight of magnesium) one faraday is required.

$\therefore$ 12 g requires 1 faraday

0.4 g requires?

$$= \frac{0.14}{12} = 0.03 \text{ faradays}$$

1 faraday gives 11.2 ℓ of Cl_2 at STP; therefore, 0.03 faradays gives?

= 0.336 l ℓ of Cl_2 at STP

1 faraday required to deposit 9 g of Al

$\therefore$ 0.03 faraday required to deposit? = 0.27 g

1 faraday required to deposit 23 g of Na

$\therefore$ 0.03 faraday required to deposit?

$= 0.03 \times 23 = 0.69$ g

17. Number of gram equivalents $= \frac{\text{current} \times \text{time}}{96500}$

$$= \frac{2 \times 20 \times 60}{96500} = 0.0248$$

Amount of silver deposited = 0.0248 × 108

= 2.68 g

Let the equivalent weight of Au be E_{Au}.

$$\therefore \frac{E_{Au}}{E_{Hg}} = \frac{W_{Au}}{W_{Ag}}$$

$$\Rightarrow \frac{E_{Au}}{108} = \frac{1.6}{2.68} \Rightarrow E_{Au} = 64.47$$

$\therefore$ Oxidation state of gold $= \frac{\text{Atomic weight}}{\text{Equivalent weight}}$

$$= \frac{197}{64.47}$$

$$= 3.05 \approx 3$$

Gold is present in Au^{+3} state in the salt

18. Density of Ag = 10.5 g/cc

Mass of silver required for coating brass spoon = 10.5 × 4 × 0.2 × 6 = 50.4 g

108 g of Ag requires 1 faraday of charge. Therefore, 50.4 g of Ag require -------?

$$= \frac{50.4}{108} = 0.466 \text{ faradays}$$

1 faraday of charge deposits 12 g of Mg. Therefore, 0.466 faradays charge deposits?

= 0.466 × 12 = 5.6 g

19. Equivalent mass of iron $= \frac{56}{2} = 28$

($Fe^{+2} + 2e^- \rightarrow Fe$)

1 faraday of electricity is required to deposit 28 g of iron.

1 faraday charge is required to deposit 6.023×10^{23} electrons.

$\therefore$ 28 g of Fe required to deposit 6.023×10^{23} electrons.

0.7 g of Fe required to deposit

$$= \frac{6.023 \times 10^{23} \times 0.7}{28} = 1.5 \times 10^{22} \text{ electrons}$$

20. The conductivity of an electrolyte depends on the nature of solvent. A solvent having high dielectric constant like water has greater ability to weaken the strong electrostatic force of attraction between Na^+ and Cl^- ions when it is dissolved in water. Therefore aqueous solution of NaCl contains free ions which conduct electricity. When the same substance is dissolved in alcohol which has low dielectric constant, the electrostatic forces cannot be weakened to a large extent. As a result, there are few mobile ions in the solution. Hence, it is a poor conductor of electricity.

21. With an increase in temperature the degree of dissociation of an electrolyte increases, thus more number of ions is produced and rate of migration of ions towards respective electrodes also increases due to increase in the mobility of ions. Therefore, conductivity increases. But conductivity decreases with decrease in temperature in case of metallic conductors because as temperature increases the vibration of positive kernels and free electrons increases but there is net increase in the KE of electrons, thereby the speed or flow of electrons is hindered or obstructed by increased movement of positive kernels. The obstruction caused by positive kernels to the flow of electrons is called resistance and due to the increase in resistance with increase in temperature, conductivity of a metal decreases.

22. $2Cl^- \rightarrow Cl_2 + 2e^-$

$\therefore$ 11.2 ℓ of chlorine is liberated by passing 96,500 C of electricity

11.2 l of Cl_2 is produced by 96,500 C

1.4 l of Cl_2 is produced by ?

$$= \frac{1.4 \times 96500}{11.2} = 12062.5 \text{ C of charge is required.}$$

Electrolytic cell A (aqueous NaCl)

$2H^+ + 2e^- \rightarrow H_2$

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

Cathodic product is H_2 and anodic product is Cl_2

11.2 l ℓ of H_2 is produced by 96,500 C

? is produced by 12,062.5 C

$$= \frac{12062.5 \times 11.2}{96500} = 1.4 \ \ell$$

Electrolytic cell B (fused $ZnSO_4$)

Cathode: Zn

Anode: $SO_4^{-2} \rightarrow SO_2 + O_2 + 2e^-$

2 × 96,500 C gives 22.4 ℓ of SO_2 and 22.4 ℓ of O_2 at STP

12,062.5 C gives ? of SO_2 and ? of O_2 at STP

$$= \frac{12062.5}{2 \times 96,500} \ell \text{ of } SO_2$$

and $\frac{22.4 \times 12.62.5}{2 \times 96,500} \ell$ of O_2

$= 1.4\ \ell$ of SO_2 and $1.4\ \ell$ of O_2

$V_{SO_2} + V_{O_2} = 2.8\ \ell$

Electrolytic cell C (Aq. $AgNO_3$)

Cathode: Ag; Anode: O_2

$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$

$4 \times 96,500$ C gives 22.4 ℓ of O_2 at STP; therefore, 12,062.5 C gives ? at STP

$$= \frac{12062.5 \times 22.4}{4 \times 96,500} = 0.7\ \ell \text{ of } O_2$$

23. Dissociation of electrolyte:

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$$

$$H_2O \rightarrow H^+ + OH^-$$

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

Anode: $4OH^- - 4e^- \rightarrow 2H_2O + O_2$

Cu^{2+} discharges in preference to H^+ due to low discharge potential. Due to this the blue colour of the solution fades as Cu^{2+} ions gradually migrate or discharge at cathode and as the electrolyte or whole Cu^{2+} ions are exhausted, H^+ ions get discharged and are liberated as H_2 gas at the cathode.

$\therefore$ Bubbles appear at cathode.

$H^+ + e^- \rightarrow H$

$H + H \rightarrow H_2$

In the beginning OH^- ions get discharged at anode and H^+ ions remain in the solution. Therefore, pH of the solution decreases. Once all Cu^{+2} ions are consumed, H^+ ions start getting discharged at cathode. Therefore, pH of the solution increases.

24. If blue litmus is added to the water in Hoffmann's voltameter, the colour of litmus is not changed in cathode compartment since the solution remains alkaline due to increase in OH^- ions in the solution due to the discharge of H^+ ions at the cathode to give H_2 gas. But blue litmus changes to red in the anode compartment since the OH^- ions get discharged at anode and the solution becomes rich in H^+ ions. Thus after electrolysis, in cathode compartment, the solution is blue and in anode compartment it is red.

25. $CuSO_4 \rightarrow Cu^{+2} + SO_4^{-2}$

$H_2O \rightarrow H^+ + OH^-$

Among the cations Cu^{+2} and H^+, Cu^{+2} requires lesser discharge potential compared to H^+ so Cu is discharged at cathode.

At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$

For the deposition of 63.5 g of Cu, $2 \times 6.023 \times 10^{23}$ e^- have to flow through the circuit; therefore, 0.3175 g of Cu requires ? electrons

$$= \frac{0.3175 \times 2 \times 6.023 \times 10^{23}}{63.5}$$

$= 6.023 \times 10^{21}$ electrons are required

At anode: $4OH^- \rightarrow 2H_2O + 4e^- + O_2$

For the formation of 1 mole of oxygen 4 moles of electrons are required.

$$96,500\,C = \frac{N}{4} \text{ moles of oxygen}$$

$$= \frac{6.023 \times 10^{23}}{4} \text{ molecule}$$

(6×10^{21} electrons = 965 C)

No. of molecules of oxygen liberated for 965 C

$$= \frac{965 \times 6.023 \times 10^{23}}{4 \times 96500} = 1.5 \times 10^{21} \text{ molecules}$$

Level 3

1. (i) Formation of complex

(ii) The characteristic of salt responsible for electrolysis.

(iii) Comparison of strengths of the two electrolytes given.

(iv) Effect of addition of NaCN to a solution of AgCN.

(v) Purpose of electroplating.

(vi) Effect of addition of NaCN on the quality of electroplating.

2. (i) Properties of lithium exploited in the battery.

(ii) Working principle of electrochemical cell.

(iii) Comparison of the oxidation potential of lithium with other metals.

(iv) Relation between the oxidation potential of the metal used in the electrode and cell emf.

(v) Comparison of density of lithium with other metals having relatively higher oxidation potential.
(vi) Comparison of oxidation potential to density ratio of lithium to that of other metals.
(vii) Area of application of lithium battery.

3. (i) Reversible cell reaction
(ii) Requisite for an electrochemical cell.
(iii) Change taking place in a battery as electrochemical cell.
(iv) Effect of this change on the working of battery.
(v) Requisite for the revival of the function.
(vi) Change that takes place during the above process.

4. (i) Mechanism of conduction of electricity in the given conductors.
(ii) Requisite for a solid substance to conduct electricity.
(iii) Type of bond present in metal.
(iv) Changes that take place in the movement of the constituent particles of metal due to the change in temperature.
(iv) Particles that conduct electricity in an electrolyte.
(v) Comparison of number of ions present in equimolar $CuSO_4$ solution and acetic acid solution.
(vi) Effect of change of temperature on the concentration of ions in the above solutions.
(vii) Relation between conductivity of an electrolyte and the concentration of ions in it.

5. (i) Effect of concentration on direction of equilibrium
(ii) The particles present on metal rod and electrolyte.
(iii) The reason for the origin of difference in potential between the electrode and electrolyte.
(iv) The factor responsible for the potential difference.
(v) Effect of concentration on the above factor.

6. Elements with higher standard reduction potential have lesser tendency of losing electrons. They are less electropositive and form oxides which are less stable towards heat. These metals are generally placed on the top in electrochemical series when they are arranged in decreasing order of reduction potential (+ve) values and form unstable oxides towards heat, i.e., these oxides are decomposed on heating. In case of weak electrolytes, degree of dissociation increases with dilution.

7. Magnesium preferentially gets reduced to Mg^{+2} ions over iron. Therefore, iron does not produce Fe^{+2} ions. Magnesium acts as cathode and iron acts as anode. Due to this reason iron is protected from corrosion when it is connected to magnesium.

8. In case of strong electrolytes, when the concentration of the solution is high, the number of solvent molecules is few and the oppositely charged ions are close to each other. This results in strong electrostatic forces of attraction between the ions and lesser mobility of the ions. This accounts for increase in conductivity with dilution. In case of weak electrolytes, degree of dissociation increases with dilution.

9. Electrolyte: $CuSO_4$

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

Cathode (reduction)	Anode (Fe) Oxidation
$Cu^{2+} + 2e^- \rightarrow Cu$	$Fe - 2e^- \rightarrow Fe^{2+}$ Compared to SO_4^{2+}, Fe ionizes to give Fe^{2+} due to low reduction potential

$\therefore$ Cu and Fe^{+2} are products at cathode and anode, respectively.

10. Iron when exposed to humid atmosphere gets converted to Fe^{2+} due to the formation of $Fe(OH)_2$ and this is in presence of air (O_2) to form rust. $Fe_2O_3 . XH_2O$.

When tin coating on iron is broken, iron gets exposed to atmosphere. Since iron has greater oxidation potential than tin, iron acts as anode and tin acts as cathode. Iron gets oxidized to Fe^{+2} ions in preference to tin. Consequently rusting becomes rapid when tin coating on iron is broken. Since Zn has greater oxidation potential than Fe, though Zinc is worn out, Zn present on the rest of the article gets oxidized in preference to Fe. Hence, rusting of Fe is slow.

Chapter

8

Metallurgy

Remember

Before beginning this chapter, you should be able to:

- understand the concept of chemical bonding for metals and non-metals
- know occurrence of metals in our surrounding

Key Ideas

After completing this chapter, you should be able to:

- understand the characteristic, properties of metals, nonmetals and metalloids
- know the processes of extraction of magnesium, zinc, aluminium, iron, and copper from their respective ore and their uses
- learn the composition, properties and uses of important alloys and amalgams
- study the properties of copper, aluminium, zinc, iron and magnesium

INTRODUCTION

The periodic table of elements comprises of 118 elements which have been discovered and authorized till now. All these elements are broadly categorized as metals and Non-metals. In addition to these, there is another category of elements known as metalloids. However, over 75% of the elements are metals as the left and middle portions of the periodic table are completely occupied by metals. Owing to the large number and also to their widespread use in day-to-day life ranging from tools to sophisticated electronic devices, the study of metals gained a lot of significance.

The history of the study of metals dates back to 6000 BC, a period when gold, silver and copper were the only metals known. These metals occurred in their native state in the sands and gravels of river beds. However, the metals which were discovered in the later period were found to exist in combined state in the form of minerals. Owing to the significant ornamental and utilitarian values attributed to these metals, attempts were made not only for the discovery of new metals but also for the development of methods for the extraction of these metals from their compounds.

Thus the branch of metallurgy, probably one of the oldest applied sciences contributed much to the cultural and technological development of human society. Metallurgy is treated as the art and science of extracting the metals from the ores in the most profitable way. The other aspects of metallurgy include the transformation of these metals into various usable forms and also understanding the physical and chemical nature of metals.

COMPARATIVE STUDY OF METALS AND NON-METALS

Generally metals are considered as elements possessing 1 to 3 electrons in their valence shells and Non-metals as the elements possessing 4 to 7 electrons in their valence shells. Due to the difference in the number of valence electrons, metals and Non-metals differ widely in their characteristic properties.

Physical Properties

Metals are characterized by certain prominent physical properties which are not present in Non-metals.

Owing to the presence of less number of electrons in the valence shells of metals and lower ionization potential values, metals lose electrons easily. Therefore, the metal lattices contain free electrons which surround the metal ions (metal kernels). A strong electrostatic force of attraction exists between the metal kernels which is known as metallic bond. The presence of metallic bonds in metals is responsible for the characteristic physical properties of metals.

Metals exist in solid state due to the presence of strong metallic bonds in metal lattices. However, mercury and gallium exist in liquid state unlike other metals. They have high density, high melting point and boiling point. The metals possessing comparatively weaker metallic bonds have lower density, low boiling points and melting points. Examples in this regard include Na, K, Hg, Ga, etc. Metallic bond being omnidirectional makes the metals highly malleable and ductile. The high thermal conductivity, electrical conductivity and lustre of metals are attributed to the presence of free electrons in the metal lattices.

Non-metals do not lose electrons easily due to more number of electrons in their shells and relatively higher ionization potential values. Therefore, in contrast to metals, Non-metals do not possess free electrons.

Only weak intermolecular forces exist in the Non-metals. Due to this reason, most of the Non-metals exist as gases having lower densities. Bromine is the only liquid nonmetal. Few Non-metals exist in solid state such as carbon, sulphur, phosphorous and iodine. Generally, solid Non-metals are brittle. Except for few allotropic forms of carbon such as graphite, all other Non-metals are bad conductors of electricity.

Chemical Properties

Properties	Metal	Nonmetal
Number of electrons in the valence shell	Have 1 to 3 electrons in the valence shell	Have 4 to 7 electrons in their valence shell Exceptions: Hydrogen and helium have 1 and 2 electrons, respectively in their valence shell because the first shell is their valence shell.
Formation of ions	Lose electrons from their valence shell to attain a stable structure and form cations	Accept electrons to attain a stable structure and form anions
Formation of oxides	Metals on heating in air/oxygen react to form either basic or amphoteric oxides $4Na + O_2 \rightarrow 2Na_2O$ (basic oxide) $4Al + 3O_2 \rightarrow 2Al_2O_3$ (amphoteric oxide) Exceptions: Metals like Au and Pt do not form oxides.	Non-metals on heating in air/oxygen form their oxides. The oxides are either acidic or neutral: $S + O_2 \rightarrow SO_2$ (acidic oxide) $2H_2 + O_2 \rightarrow 2H_2O$ (neutral oxide)
Reactions of oxide with water	Metallic oxides give bases on reaction with water: $Na_2O + H_2O \rightarrow 2NaOH$ $K_2O + H_2O \rightarrow 2KOH$ $CaO + H_2O \rightarrow Ca(OH)_2$	Acidic (nonmetallic) oxides give acids on reaction with water: $SO_2 + H_2O \rightarrow H_2SO_3$ $CO_2 + H_2O \rightarrow H_2CO_3$
Reactions of oxide with acid (for metallic oxide) or with base (for non-metallic oxide)	Metallic oxides react with acids to give their respective salts and water: $Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O$ $MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O$	Non-metallic (acidic) oxides react with bases to give their respective salts and water: $SO_2 + NaOH \rightarrow Na_2SO_3 + H_2O$ $CO_2 + NaOH \rightarrow Na_2CO_3 + H_2O$
Reaction with acid and water	Metals, which are more reactive than hydrogen, replace hydrogen from the acid as well as from water: $Zn + 2HCl \rightarrow ZnCl_2 + H_2$ $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$ Copper, tin and mercury which are less reactive than hydrogen do not replace hydrogen either from acid or from water.	Non-metals do not react with water. The majority of Non-metals do not react with acids. Since nitric acid is an oxidizing agent, it oxidizes Non-metals like sulphur, carbon, iodine and phosphorus to their respective acids: $S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$ $C + 4HNO_3 \rightarrow H_2CO_3 + 4NO_2 + H_2O$ $I_2 + 10HNO_3 \rightarrow 2HIO_3 + 10NO_2 + 4H_2O$ $P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$
Displacement reactions	More electropositive metals displace less electropositive metals from their salts: $Fe + CuSO_4 \rightarrow FeSO_4 + Cu$ $Mg + FeSO_4 \rightarrow MgSO_4 + Fe$	More electronegative halogens displace less electronegative ones from their compounds: $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$ $2NaI + Cl_2 \rightarrow 2NaCl + I_2$

Occurrence of Metals

Generally, most of the metals occur in the combined state in nature. The metals in the combined form are called minerals. The most common minerals and ores are in the form of oxides, hydrated oxides, carbonates, sulphides, chlorides, etc., of which a few are listed in the following table.

Occurrence of metals					
Lead	Magnesium	Calcium	Mercury	Sodium	Silver
Lead ochre (PbO)	Magnesite ($MgCO_3$)	Gypsum ($CaSO_4.2H_2O$)	Cinnabar (HgS)	Rock salt (NaCl)	Horn silver (AgCl)
Galena (PbS)	Dolomite ($CaCO_3.MgCO_3$)	Fluorspar (CaF_2)		Chile salt petre ($NaNO_3$)	
Anglesite ($PbSO_4$)	Epsom salt ($MgSO_4.7H_2O$) Carnallite ($KgCl.\ MgCl_2.6H_2O$)				

Each metal can exist in the form of various minerals. The mineral from which a metal can be extracted in an easy and cost-effective process is called an ore. The extraction of the metal from the ore involves various stages. Though the exact steps involved in the process of the extraction of the metal differ from metal to metal, the various stages of general metallurgical process can be broadly categorized into four stages.

General Metallurgical Processes

The metallurgical processes are broadly classified into four steps as listed hereunder:

(i) Dressing and concentration of ore

(ii) Conversion of ore to oxide or desired compound

(iii) Extraction of metal

(v) Refining of metal

(vi) Air is a mixture of nitrogen, oxygen, CO_2 and water vapour.

Dressing and Concentration of Ore

(i) Dressing of ore

Since ores are obtained in crude form from the earth's crust, they are invariably associated with huge amounts of earthy impurities such as sand, mud, etc. The earthy impurities associated with the ores are called gangue. The ores should be freed from gangue before they are subjected to the extraction of metals from them. The process of the removal of gangue from an ore is called the dressing of ore.

(a) **Hand-picking**: During this process, big lumps of rock are removed by hand. The ore is then subjected to crushing and grinding to make it into smaller pieces.

(b) **Crushing or grinding**: The ores are crushed in big jaw crushers to obtain small pieces which are further hammered in hammer mills to give very small pieces. The small pieces are then pulverized.

(c) **Pulverization**: In this process, the ore is ground to a fine powder in huge ball mills. In the fine powdered form, the ore is sent for concentration. This process is not mandatory for all the ores. The ore is pulverized only if the fine powdered form of the ore is required for further processes.

(ii) Concentration of ore

The removal of gangue from the dressed ore is called concentration of ore. Depending upon the type of impurities, type of metal various procedures are employed for the removal of gangue from the ore.

(a) Gravity separation: This method of separation is applicable to all types of ores except sulphide ores. The method involves the separation of ore and gangue based on the difference in their specific gravities. The pulverized ore is placed on a wide rocking, sloping top table with lateral groove on it and it is treated with a stream of running water. The water carries the ore along with it. The gangue being lighter is washed down the table while the denser ore settles in the grooves of the table. The ore collected in the grooves is thrown sideways by the rocking movement of the table.

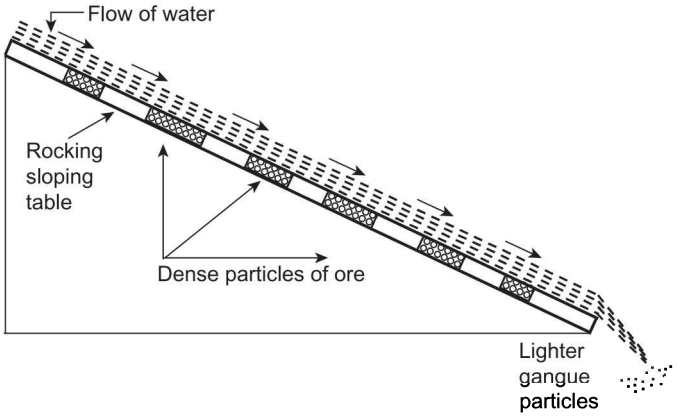


Figure 8.1 Concentration of ore by Gravity Process

(b) Froth flotation: This method is exclusively used for the concentration of sulphide ores. The basic principle involves the differential wetting characteristics of ore and gangue with oil and water, the ore being wet by oil and gangue by water.

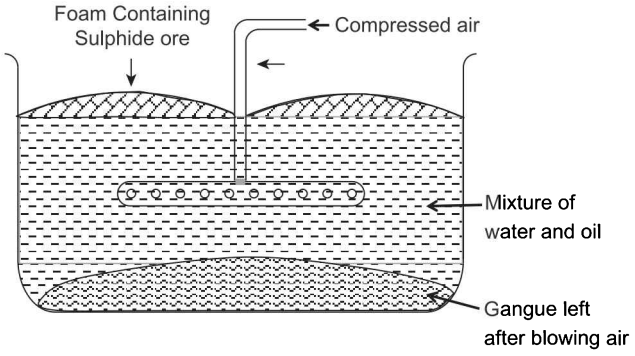


Figure 8.2 Froth floatation process

The ore is taken in a large tank called the flotation cell containing a mixture of pine oil and water.

This is then agitated by blowing a current of air into the tank. The oil along with the sulphide ore forms foam which floats on the tank and is removed. The sulphide ore is recovered from this.

(c) Magnetic separation: This method is employed for the concentration of ores in which either the ore or the gangue is attracted by a magnet and the other is not.

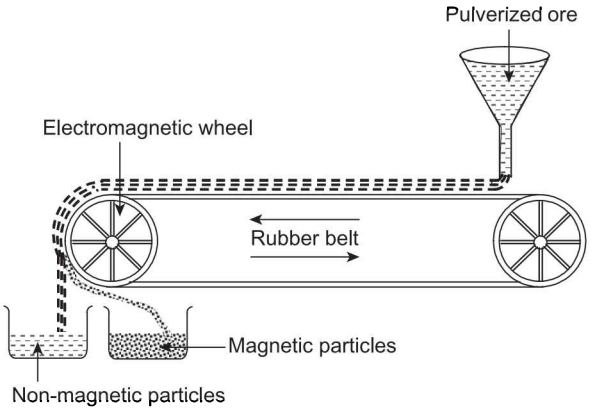


Figure 8.3 Electromagnetic separation

In this, a rubber belt is made to move horizontally over two pulleys of which one is a strong magnet. The powdered ore is made to fall on the moving rubber belt. As the ore is passed over the magnetic pulley, the one (either the ore or the gangue) which is magnetic is attracted towards the pulley and clings to the belt leaving behind the other. As the magnetic component moves away from the magnetic pulley, it falls down as a separate heap. Thus, the ore and gangue are separated based on these magnetic properties.

(d) Chemical separation: This is an exclusive method used for the concentration of aluminium ore (bauxite). The amphoteric nature of aluminium oxide is the basic principle involved in this method. In this, the ore is treated with the aqueous solution of caustic soda under pressure for a few hours resulting in the formation of sodium metaaluminate:

$$Al_2O_3 + 6NaOH \rightarrow 6NaAlO_2 + 2H_2O$$

Sodium metaaluminate so formed being soluble, the impurities are removed by filtration. The filtrate is then diluted, and aluminium hydroxide precipitates out:

$$3NaAlO_2 + 6H_2O \rightarrow 3Al(OH)_3 + 3NaOH$$

Aluminium hydroxide thus obtained is dried. The dried ore is strongly heated to 110°C till there is no further loss in weight. Aluminium hydroxide decomposes to alumina and water. This method of concentration of ore is called the Bayer's process.

Thus, in all the above ways, the gangue is removed and the metal is obtained in the form of its compound.

The metal ores so obtained after having undergone the process of concentration are then converted to their oxide form. The reduction of the oxide form can be carried out further to obtain pure metal.

Conversion of Ore to Oxide

The concentrated ore is converted to its oxide form. The further extraction of the metal from this oxide by reduction is easier than the extraction of metals from other forms. Two methods are used for the conversion of concentrated ore to its oxide form as listed hereunder:

(i) roasting and

(ii) calcination.

Comparison Between Roasting and Calcination

Roasting	Calcination
During roasting, the ore is strongly heated in the presence of excess air.	During calcination, the ore is strongly heated.
This is mainly performed on sulphide ores, during which sulphur is removed as sulphur dioxide: $4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$	Calcination is mainly performed for carbonate and hydroxide ores where the ores are decomposed to give oxides: $ZnCO_3 \xrightarrow{heat} ZnO + CO_2$
In addition to converting the ore to its oxide form, this process also results in the removal of moisture and the expulsion of volatile impurities from the ore. Moreover, the resultant ore remains porous.	Calcination is also associated with several other advantages like removal of moisture, increasing the porosity of the ore and the expulsion of the volatile impurities. Hydrated ores also get freed from the water of crystallization: $Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3 + 3H_2O.$

Extraction of Metal from Metal Oxide

The oxide ores obtained by the process of roasting or calcination are subjected to the reduction process. The reduction is, however, carried out by various methods.

Reduction by	Applied for the extraction of	Description
Coke	Zinc, iron, lead, copper	The metallic oxide is mixed with coke and heated in a huge furnace. The coke reduces metal oxide to metal: $ZnO + C \xrightarrow{\Delta} Zn + CO$
Carbon monoxide	Iron, lead, copper	Carbon monoxide gas and hydrogen gas are passed through the oxide at a high temperature. The metal oxide gets reduced to metal. Carbon monoxide gets converted to CO_2: $Fe_2O_3 + 3CO \xrightarrow{\Delta} 2Fe + 3CO_2$
Aluminium powder	Chromium, manganese	A mixture of metal oxide and aluminium powder are ignited. Aluminium, being a very strong reducing agent, reduces the metal oxide to the corresponding metal: $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr + \text{heat}$
Heating	Mercury, silver	Mercury and silver oxides on heating decompose to give metal and oxygen gas: $2HgO \xrightarrow{\Delta} 2Hg + O_2$
Electrolysis	Sodium, potassium, calcium, magnesium, aluminium	Electricity is passed through fused halides or oxide. The metal ions which are formed move towards the cathode, and get discharged there. $Al^{+3} + 3e^- \rightarrow Al$

The metal thus obtained by the reduction of oxide is not completely pure and is associated with certain impurities like other metals, Non-metals, other metal oxides and dissolved gases.

Therefore, the metals extracted are subjected to further purification. This is called the refining of the metal.

Purification or Refining of Metals

Different methods of the refining of metals are available for different metals. The method of refining generally depends upon the type of impurities present with the metal.

Processes of purification	Metals to be refined	Processes
Distillation	Iron, mercury	The metal is strongly heated above its boiling point in the absence of air. The metal vaporizes, leaving behind the impurities. The vapours are cooled in earthen retorts, to get the metal in solid or liquid form.
Liquation	Lead, tin (metals with low melting point)	The metal is taken on the upper part of sloping hearth and heated above its melting point. The metal melts, flows down the hearth and is collected at the bottom.

Processes of purification	Metals to be refined	Processes
Polling	Copper with cuprous oxide as an impurity	Molten copper is stirred with wooden poles. These poles emit wood gas (CO and H_2) which reduces copper oxide to copper.
Oxidation	Iron with oxidizable impurities	Oxygen is blown through molten metal where the impurities get converted to gaseous oxides and are removed: $C + O_2 \rightarrow CO_2\uparrow$ $S + O_2 \rightarrow SO_2\uparrow$
Electrolytic refining	Aluminium	A block of impure metal is taken as an anode and a thin strip of pure metal is taken as a cathode. The electrolyte is the soluble salt of the metal. On passing the current, the metal ions from the anode dissolve in the electrolyte, go towards the cathode and get discharged there. Electrolysis continues and the cathode becomes a thick block of pure metal.

Aluminium

Aluminium is a highly reactive metal belonging to the III A group of the periodic table. In nature, aluminium is found in the form of its oxide in its ores.

The important ores of aluminium are as follows:

Bauxite	$Al_2O_3.2H_2O$
Corundum	Al_2O_3
Cryolite	Na_3AlF_6

Metallurgy of Aluminium

Aluminium is mostly extracted from its bauxite ore.

Dressing of ore: The ore is crushed and pulverized.

Concentration of Ore

The bauxite ore contains ferric oxide and silica as impurities. It is first concentrated by gravity separation where silica is removed followed by the removal of ferric oxide impurities by the process of magnetic separation. The ore is then concentrated by chemical process. There are two chemical processes that are generally followed as listed hereunder:

(i) Bayer's process: In this process, aluminium ore is treated with concentrated sodium hydroxide. Soluble sodium aluminate is formed which is filtered off. The filtrate on heating with water gives aluminium hydroxide which gives alumina on strong heating.

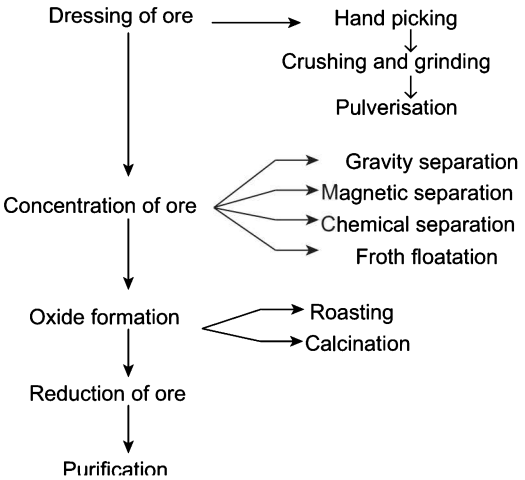


Figure 8.4 Flow sheet for common metallurgical processes

(ii) Hall's process: In this process, bauxite is made to react with sodium carbonate giving soluble sodium aluminate:

$$Al_2O_3 \cdot 2H_2O + Na_2CO_3 \rightarrow 2NaAlO_2 + 2H_2O + CO_2$$

This is dissolved in water and filtered. Carbon dioxide gas is passed through the filtrate which results in the formation of aluminium hydroxide:

$$2NaAlO_2 + 3H_2O + CO_2 \rightarrow Na_2CO_3 + 2Al(OH)_3$$

Conversion to Oxide

Aluminium hydroxide obtained by calcination gives alumina:

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O$$

Alumina so formed is highly stable and has very high thermal resistance. It is therefore subjected to electrolytic reduction.

Electrolytic Reduction

Electrolysis is carried out in fused state. Since alumina has very high thermal resistance, it doesn't melt easily. Hence, cryolite and fluorspar are added to alumina to decrease the melting point and increase the electrical conductivity.

The fused electrolyte is taken in an iron tank lined with gas carbon which acts as the cathode. A number of parallel carbon rods dipped in the electrolyte act as the anode. In order to prevent the loss of heat and burning of carbon electrodes, the electrolyte is covered with coke.

The fused electrolyte contains alumina, cryolite and fluorspar in their ionized states. On passage of current, the ions move towards their respective electrodes:

$$Al_2O_3 \rightarrow 2Al^{+3} + 3O^{-2}$$
$$Na_3AlF_6 \rightarrow 3Na^{+} + Al^{+3} + 6F^{-}$$
$$CaF_2 \rightarrow Ca^{+2} + 2F^{-}$$

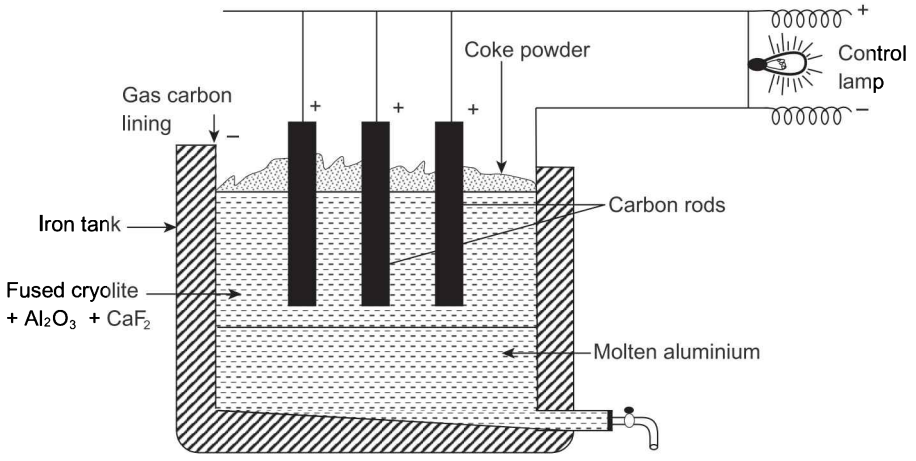


Figure 8.5 Electrolysis of fused alumina

The anions, O^{2-} and F^{-} move towards the anode. Oxide ion is oxidized to nascent oxygen which combines with carbon forming carbon dioxide:

At anode: $O^{-2} - 2e^{-} \rightarrow [O]$

$$C + 2[O] \rightarrow CO_2$$

The cations, Al^{+3}, $Ca^{+2}$and Na^{+}, move towards the cathode. Aluminium ion being the least electropositive metal gets reduced forming aluminium metal:

At cathode: $Al^{+3} + 3e^{-} \rightarrow Al$

The temperature in the tank being higher than the melting point of aluminium the aluminium formed is in the molten state, and settles at the bottom of the tank from where it is collected from time to time.

As the process of electrolysis continues, concentration of alumina decreases, thereby increasing the resistance of the electrolyte which is indicated by a control lamp. More alumina is added when required.

Aluminium extracted by the above process is 99·5% pure and is further refined by electrolytic refining (Hoope's electrolysis).

Electrolytic Refining (Hoope's Electrolysis)

This process is also called the three-layer process as the cell contains three layers of molten liquids. The cell is an iron tank lined internally with carbon. The electrolyte is composed of aluminium fluoride (36%), cryolite (18%) and calcium fluoride (16%) which forms the middle layer. The lower layer is the impure metal alloyed with copper and serves as the anode.

On passing the current, the aluminium ions from the middle layer go towards the cathode, get discharged there and form the upper layer of pure aluminium while an equivalent amount of aluminium passes into the middle layer from the bottom layer.

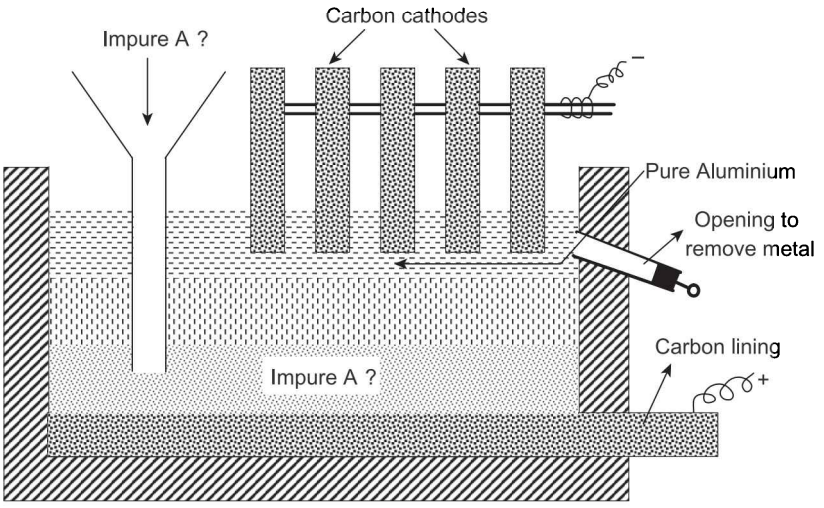


Figure 8.6 Refining of aluminium by Hoope's method

Pure aluminium is collected from the top layer.

Uses of Aluminium

(i) Aluminium being light is a good conductor of heat, corrosion resistant and cheap and hence used in making household appliances.

(ii) It is used in electric transmission as it is a good conductor of electricity.

(iii) As it can be made into thin sheets and foils, it is used in packing food stuffs.

(iv) As aluminium is a self-protective metal, when iron is coated with a layer of aluminium it can be prevented from rusting.

(v) Aluminium powder along with ammonium nitrate can be used as an explosive.

(vi) Aluminium being highly electropositive can replace metals like gold and silver from their salts, thus helping in the extraction of these metals.

(vii) Aluminium being a strong reducing agent is used in reducing many organic compounds.

(viii) Aluminium has a great affinity for oxygen. As a result, aluminium can displace metals from the metal oxides provided the metal is less electropositive than aluminium. The reaction being highly exothermic forms the basic principle of thermite welding.

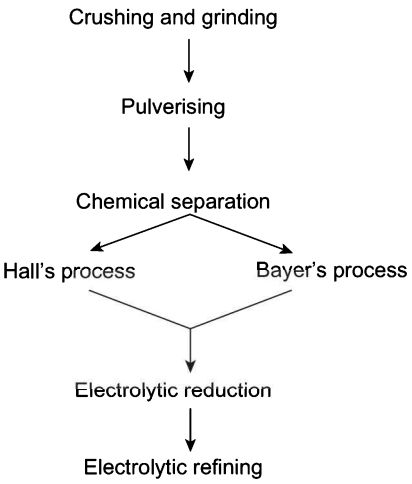


Figure 8.7 Process flow metallurgy of aluminium

Thermite Welding

A mixture of aluminium powder and ferric oxide in 1 : 3 ratio is called thermite. Thermite is taken in a funnel-shaped crucible which is lined inside with magnesite. A mixture of magnesium powder and barium oxide known as ignition mixture is placed on the surface of thermite. A magnesium ribbon is inserted into this mixture.

On lighting the magnesium ribbon, the ignition mixture catches fire. The heat produced by this process makes aluminium react with ferric oxide in which the latter gets reduced to iron. The enormous amount of heat released brings iron into a molten state. The molten iron when allowed to pour over the broken steel pieces solidifies and joins the broken pieces.

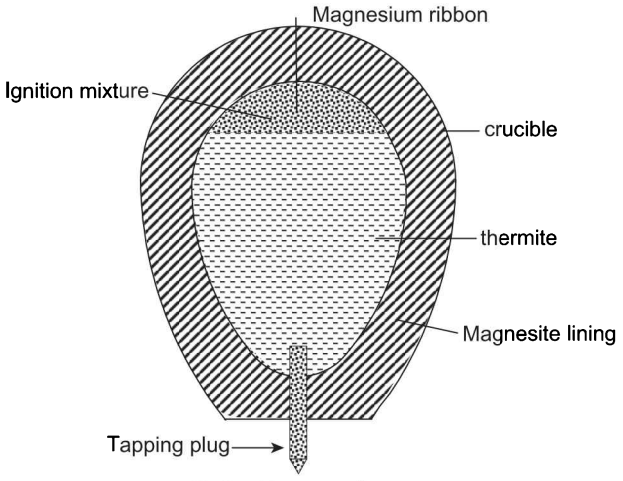


Figure 8.8 Alumino thermic process

The major advantage of this process is that welding can be carried out without disturbing the position of heavy broken parts which would otherwise involve a laborious process.

EXAMPLE

Extraction of metals always involves reduction processes. Explain.

SOLUTION

Metals are always available in nature in the form of ores, in which the metal remains as cation. Extraction of the metal from the ore is to get the metal in its elemental state. For this purpose any metal compound always require to be reduced.

EXAMPLE

Green wooden poles are used during the process of refining of copper. What purpose do they serve?

SOLUTION

Wooden poles are used to agitate molten impure copper. The heat of the molten metal decomposes green wooden poles and methane gas is emitted from the poles. This methane reduces cuprous oxide to copper.

EXAMPLE

Reduction of alumina which is obtained, either by Hall's process or Bayer's process to aluminium metal is carried out by electrolysis. During this process cryolite and fluorspar are added to alumina, the entire mixture is covered with coke powder.

(a) Why cannot alumina be directly electrolyzed?

(b) What is the role of addition of cryolite and fluorspar?

(c) What are the different cathodic and anodic reactions taking place during electrolysis?

SOLUTION

(a) Alumina cannot be directly electrolysed because alumina has high thermal stability and hence very high temperature is required for melting pure alumina.

(b) Cryolite and fluorspar are added to alumina in order to decrease the melting point of alumina and increase the electrical conductivity of the mixture.

(c) For the electrolysis of alumina, cryolite and fluorspar are added to it. The mixture undergoes electrolysis in the following way.

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

$Na_3AlF_6 \rightarrow 3Na^{+} + Al^{+3} + 6F^{-}$

$CaF_2 \rightarrow Ca^{+2} + 2F^{-}$

At anode: $O^{2-} - 2e^{-} \rightarrow [O]$ $\quad C + 2[O] \rightarrow CO_2$

At cathode: $Al^{+3} + 3e^{-} \rightarrow Al$

Metallurgy Physics and Chemical Properties of some Metals

Zinc

Zinc is a transition metal belonging to the II B group of the periodic table. It is highly reactive and found in a combined state in nature.

Ores of Zinc

Zinc blend	ZnS
Calamine	$ZnCO_3$
Zincite	ZnO

Metallurgy of Zinc

Zinc is generally extracted from zinc blend (ZnS) or calamine ($ZnCO_3$).

Crushing

The ore is crushed using ball mills and then pulverized. The pulverized ore is concentrated.

The concentration process depends upon the type of ore.

Concentration

Gravity separation process is followed for oxide ore (zincite) and carbonate ore (calamine) and froth flotation process is employed for sulphide ore (zinc blend).

If iron oxide is present as an impurity, it is separated by magnetic separation process.

Conversion to Oxide

In the case of sulphide ore, it is converted to oxide by roasting:

$$2ZnS + 3O_2 \xrightarrow{\text{heat}} 2ZnO + 2SO_2$$

The carbonate ore is subjected to calcination where it undergoes decomposition to oxide giving out carbon dioxide gas:

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

Reduction of Metal Oxide to Metal Using Coke

Zinc oxide is reduced to zinc by vertical retort process called smelting. The retort is a tall cylindrical structure lined internally with clay bricks. An automatic screw conveyer arranged at the bottom acts as an outlet for the waste residue. It is heated internally using producer gas as the fuel.

The powdered zinc oxide is mixed with charcoal and made into small briquettes by pressing. This is taken in the vertical retort where, due to the high temperature, carbon reduces zinc oxide to zinc and itself gets oxidized to carbon monoxide:

$$ZnO + C \xrightarrow{1400°C} Zn + CO$$

The zinc formed in the vapour state escapes out along with carbon monoxide. These vapours are collected in the condenser where zinc condenses and is collected from time to time while carbon monoxide remains as gas and is used for further heating of the retort.

The zinc obtained by this process is 97% pure and is called zinc spelter.

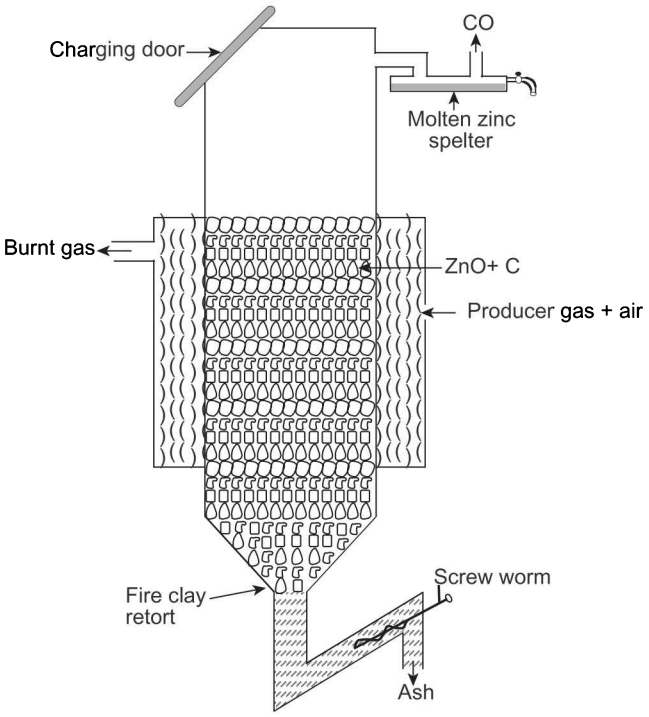


Figure 8.9 Smelting of Zinc ore

Refining or Purification

The spelter zinc obtained contains both volatile impurities (Cd and As) and non-volatile impurities (Fe and C) and can be refined by two methods, which we now discuss.

(i) Distillation under low pressure

The spelter is heated at a controlled temperature and the volatile impurities get vaporized. The metal is then strongly heated, when zinc changes to vapours. These vapours are condensed to obtain molten zinc which is poured into earthen moulds where it is cooled and solidified.

(ii) Electrolytic Method

A block of impure metal (spelter) is taken as anode and a thin strip of pure metal is taken as cathode. Acidified saturated zinc sulphate solution is taken as the electrolyte. On passing current, zinc from the anode dissolves in the electrolyte in the form of Zn^{+2} ions, goes towards the cathode, gets discharged there and is deposited on the cathode:

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

At cathode: $Zn^{+2} + 2e^- \longrightarrow Zn$

As electrolysis proceeds, the anode gets thinner and cathode (pure metal) thicker.

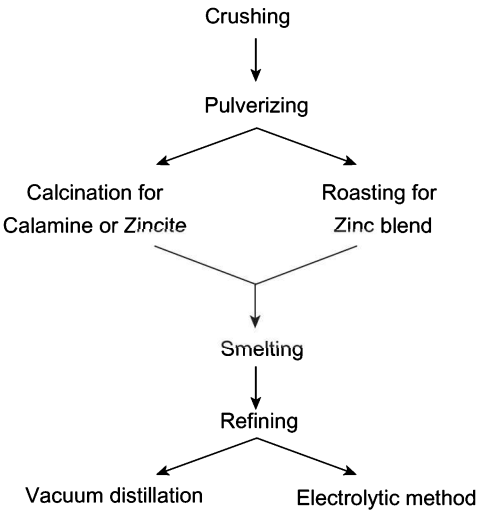


Figure 8.10 Process flow sheet for metallurgy of zinc

Uses of Zinc

(i) **Galvanization**: Zinc is mainly used for coating iron surfaces to prevent rusting of iron. The process of protecting iron surfaces from rusting by coating it with zinc metal is called galvanization.

(ii) **In dry cells**: Zinc is used to make the cathodes of dry cells.

(iii) **Reducing agent**: Because of the ability of zinc to act as a reducing agent, it is used in the extraction of metals.

(iv) **Alloys**: Used in the preparations of alloys like brass, bronze, etc.

Iron

Iron is the metal found in great abundance in nature. It is highly reactive and is hardly available in free state. Iron exists in the combined form in nature in various minerals among which oxide and sulphide ores are the most significant ones.

The most common ores of iron are the following:

Haematite	Fe_2O_3
Limonite	$2Fe_2O_3.3H_2O$
Magnetite	Fe_3O_4
Siderite	$FeCO_3$
Iron pyrites	FeS_2
Copper pyrites	$CuFeS_2$

Iron pyrite, however, is not used for the extraction and hence is not considered as an ore of iron. It is used as the source for the preparation of sulphuric acid.

Metallurgy of Iron

Iron is generally extracted from haematite, limonite and siderite. Among these haematite and limonite are the most preferred ores.

The manufacturing of pig iron is the first step in the metallurgy of iron. This pig iron is converted to cast iron which is further used for the manufacture of steel and wrought iron.

Dressing and Concentration of Ore

The ore is crushed to make small pieces from larger chunks.

The crushed ore is concentrated by the process of magnetic separation and further concentration is done by gravity separation process.

Conversion to Oxide

The concentrated ore is converted to oxide form by the process of roasting which involves heating the ore in the presence of excess air.

On roasting, the carbonate ore decomposes to oxide giving out carbon dioxide. This process is also associated with other advantages like

(i) the removal of moisture and other volatile impurities;

(ii) the removal of impurities like sulphur, phosphorous, arsenic, antimony in the form of gaseous oxides;

(iii) the conversion of ferrous oxide to ferric oxide and

(iv) inducing porosity in the mass, thus rendering easy reduction.

Reduction of Oxide to Metal

The reduction of oxide to metal is carried out with carbon in a blast furnace by the process called smelting.

Smelting in Blast Furnace

Blast furnace is a huge chimney-like structure about 30 m high and 8 m in diameter. It is made of iron plates and lined internally with refractory bricks. On the top, it has a double cup and cone arrangement. Below this, there is an outlet for waste gases. A hearth is present at the bottom to collect cast iron and slag, and has separate outlets for each. Hot compressed air is blown into the furnace through pipes called tuyeres which are placed above the hearth.

The ore is mixed with coke, and limestone approximately in the ratio of 8 : 4 : 1. This mixture is called charge.

The charge is lowered into the furnace from the top through the cup and cone arrangement and various reactions take place in the furnace at different levels.

(i) Lower region (1500°C–2000°C)

Coke combines with the heated air coming from the tuyeres and burns to form carbon dioxide. The reaction, being highly exothermic increases the temperature in this zone to 2000°C:

$$C + O_2 \rightarrow CO_2 + 97 \text{ kcal}$$

This region is also called the **combustion zone**.

(ii) Middle region or fusion zone (1500°C–1000°C)

The carbon dioxide formed in the lower layer moves to the middle layer where it is reduced to carbon monoxide:

$$CO_2 + C \rightarrow 2CO - 39 \text{ kcal}$$

At such a high temperature, the limestone added decomposes to calcium oxide and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2 - 43 \text{ kcal}$$

The calcium oxide (quick lime) formed reacts with impurities like sand in the ore and converts them to slag:

$$CaO + SiO_2 \rightarrow CaSiO_3$$

The slag, calcium silicate goes towards the hearth present at the bottom of the furnace.

As the reactions in the middle region are endothermic, the temperature of this zone decreases.

(iii) Upper region or reduction zone (1000°C–500°C)

The carbon monoxide formed in the middle region moves to the upper region where it reduces the iron oxide to iron.

$$FeO + CO \xrightarrow{600-400^\circ C} Fe + CO_2$$

$$Fe_2O_3 + 3CO \rightarrow \xrightarrow{600-400^\circ C} 2Fe + 3CO_2$$

The iron formed here melts due to the high temperature and then due to its high density settles down. Both the slag (calcium silicate) and iron settle down in the hearth. Iron being heavier forms the bottom layer with slag on top. From here, iron and slag are tapped through separate outlets. Iron thus obtained is called pig iron. Solid pig iron is remelted in a vertical furnace known as cupola and thereby gets refined. (Nowadays pig iron is directly poured in a laddle and sent to the converter for steel making process.)

Then it is poured into suitable moulds of required shape. This remelted pig iron is called cast iron.

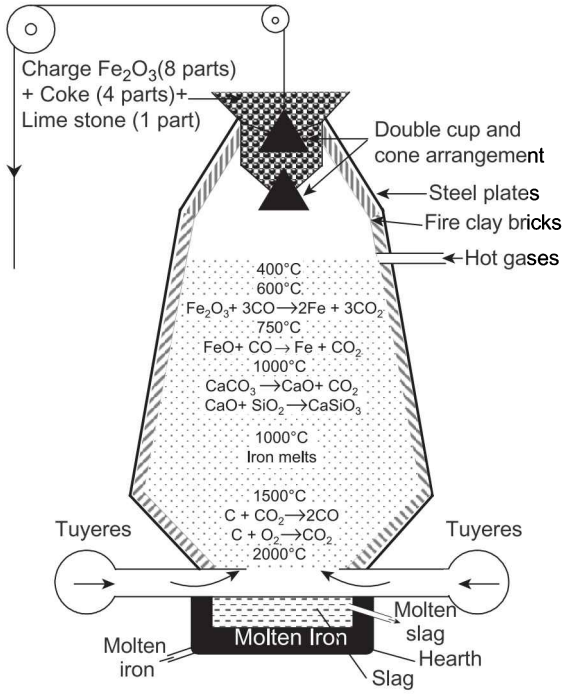


Figure 8.11 Smelting of Iron ore in blast furnace

Products of blast furnace			
	Major products		By-products
Composition	Pig iron Cast iron	Slag	Blast furnace gases
Composition	Iron (85% to 95%) Carbon (2.5% to 5%) Silicon (0.5% to 5%) Phosphorus (0.02% to 2%)	$CaSiO_3$	Carbon monoxide (30%) Carbon dioxide (10%) Nitrogen (60%)
Uses	(i) Manufacture of steel (ii) Making drain pipes, manhole cover, gates, machinery, etc.	In the manufacture of cement, slag wool, roadbeds	(i) Preheating the tuyeres. (ii) In coke ovens for making coke.

Conversion of Cast Iron to Wrought Iron

Wrought iron is the purest form of iron. Apart from iron, it has very small quantities of carbon (0.2%), silicon (0.15%), phosphorous (0.02%), sulphur (0.04%) and manganese (0.05%). It is the refined form of cast iron.

It is prepared by heating cast iron in a reverberatory furnace. The furnace is lined internally with iron oxide. This oxidizes the carbon in the cast iron to gaseous oxides of carbon. The other impurities are slagged off using lime as flux. Heavy rollers are made to roll over the metal obtained, where the slag is squeezed out.

Conversion of Cast Iron to Steel

Cast iron, the impure form of iron, is converted to steel by Bessemer process. Steel is an alloy of iron. Small amounts of carbon and other metals like chromium, manganese, vanadium and nickel are added to iron to impart special properties required for a variety of uses. The carbon content of steel varies from 0.1% to 1.5% depending on its use. Cast iron is converted to steel by Bessemer process. This process is carried out in a Bessemer convertor.

Structure of the Bessemer Converter

Bessemer converter is a pear-shaped furnace. It is made up of a steel plate lined inside with a refractory material. The lining is made up of silica in case of acidic process and with lime in basic process. Basic process is adopted if the cast iron contains phosphorous as an impurity.

Process of Bessemerization

At first, the converter is tilted to a horizontal position and the charge of molten cast iron is introduced into it. Then it is brought back to the upright position and a blast of air is passed through the tuyeres present at the bottom of the furnace. Carbon and other impurities present in cast iron combine with oxygen to form their respective oxides:

$$C + O_2 \longrightarrow CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

$$S + O_2 \longrightarrow SO_2$$

$$P_4 + 5O_2 \longrightarrow 2P_2O_5 \text{ (in basic process)}$$

$$2Mn + O_2 \longrightarrow 2MnO$$

$$Si + O_2 \longrightarrow SiO_2$$

$$MnO + SiO_2 \longrightarrow MnSiO_3$$

(Slag)

$$6CaO + P_4O_{10} \longrightarrow 2Ca_3(PO_4)_2 \text{ (in basic process)}$$

Oxides of manganese and silicon are removed in the form of slag ($MnSiO_3$). In the basic Bessemer process, phosphorus is removed as $Ca_3(PO_4)_2$ in the form of slag.

After the removal of slag and gaseous oxides, CO burns with a bright flame at the mouth of the converter. The disappearance of flame indicates that iron is free from impurities. At this stage, the required amount of spiegel (an alloy of carbon and manganese) is added to the molten iron and the blast of air continues till the alloy (spiegel) melts and mixes with molten iron.

Finally, the molten steel with desired carbon content is formed which is poured out in moulds and is then cooled.

Open Hearth Process for Making Special Type of Steel

As the name suggests, the shape of the furnace is like a hearth, the top of which is open. The charge is pig iron and steel scrap. The process can be carried out in two ways as listed hereunder:

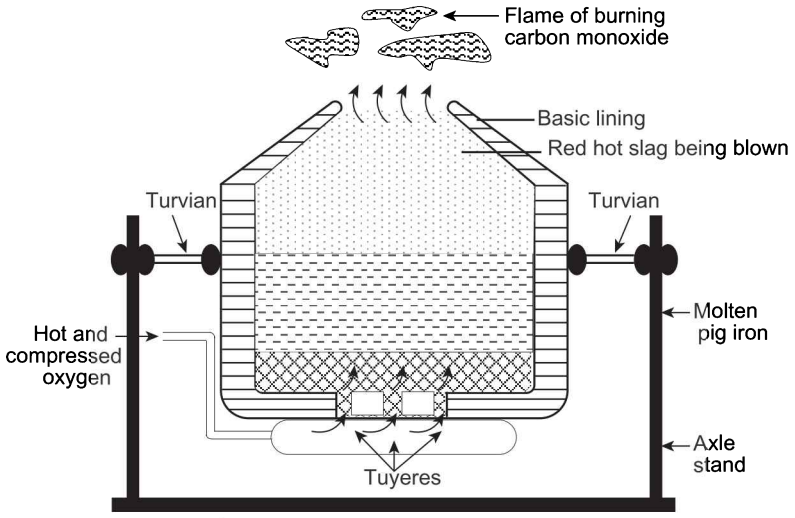


Figure 8.12 Bessemer converter

(i) Acid process: In this process, the furnace is lined with acidic refractories, i.e., silica brick.

(ii) Basic process: In this process, the furnace is lined with magnesite or dolomite.

The temperature on the top of the hearth is generated by a hot fuel gas which burns on the hearth and produces a temperature of 1600°C to 1650°C. The final composition of the steel is adjusted by adding ferrosilicon or ferromanganese alloy.

It is a very lengthy process and takes about 5 to 15 h.

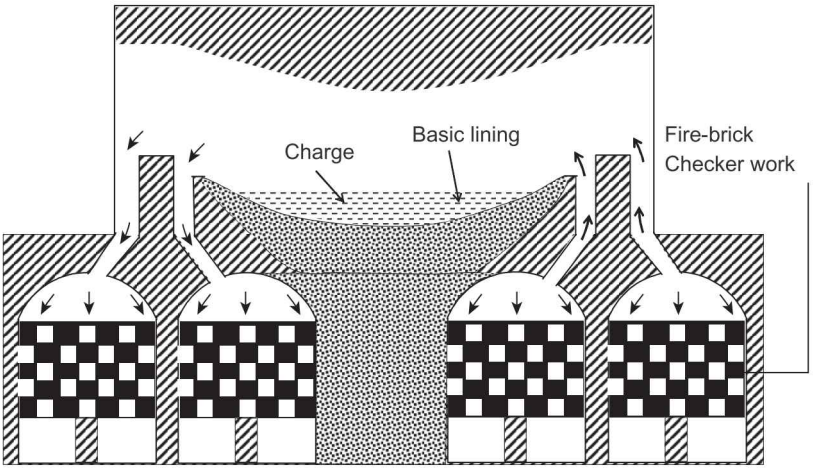


Figure 8.13 An open hearth furnace

Raw materials used in open hearth process have low content of phosphorous and sulphur in them; hence, the steel made by this process is of a better quality.

L–D Process for Making Steel

The latest development in steel making process is the L–D process. The name of this process is taken from two separate plants situated in Austria, at Linz and Donawitz. It is a very fast process and takes about 20 min to produce steel.

Pure oxygen (99.5%) is lanced from the top of the converter at supersonic speed. This oxygen produces temperature of about 2500°C to 3000°C and oxidizes the impurities present in it and finally steel is produced. The L–D converter is lined with basic refractory.

Varieties of steel: Many varieties of steel are available. These can be categorized based on the following:

(i) the percentage of carbon in steel and

(ii) the metals (small amounts) present in the alloy.

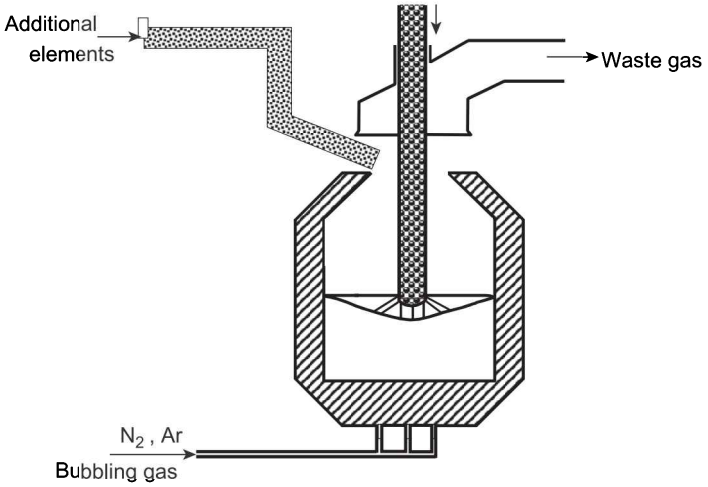


Figure 8.14 Schematic diagram of L–D converter

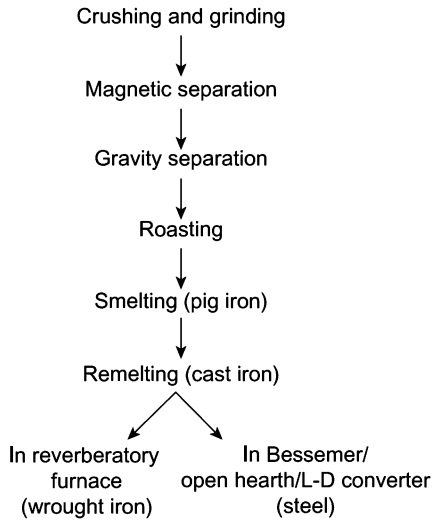


Figure 8.15 Process flow sheet for metallurgy if iron

Mild Steel	Hard Steel
Carbon content in mild steel is less and ranges from 0·15 to 0·5%.	The carbon content here is slightly more ranging from 0.5 to 1.7%.
It is a highly elastic form of steel with greater malleability and ductility.	It is a less elastic form of steel which is tough and has high tensile strength. It is less malleable and ductile.
It is used in making powerful magnets.	It is used in making tools which are used for cutting.

There are five different types of steel based on the other metals present in steel along with iron.

	Stainless Steel	Manganese Steel	Tungsten Steel	Chrome Steel	Vanadium Steel
Composition	Iron (82% to 84%) Chromium (12% to 14%), Nickel (1% to 2%)	Iron (83% to 84%), Mn (15%), C (0.9% to 1·5%)	Wolfram (1% to 20%)	Chromium (1% to 4%)	Vanadium (0.2% to 1%)
Property	Resistant to corrosion, mild organic acids, alkalis	Extremely hard	Very hard, tough	Very hard, tough	Very hard, not very brittle
Uses	Utensils, surgical instruments	Safes, army helmets, hammering machines	Swords, armour, ball bearings	Swords, armour, ball bearings	Springs, crank shaft, axles of automobiles

Altering the Properties of Steel by Controlling Temperature

Steel when heated to high temperature and subsequently cooled in different ways shows different properties.

(i) Hardening of steel

The process of heating steel to a temperature of 1000 K to 1250 K and cooling suddenly by plunging it into cold water or oil is called hardening of steel. It is also called quenching of steel. Due to hardening, the steel becomes much harder but brittle.

(ii) Annealing or tampering of steel

The process of heating hardened steel to 500 K to 610 K followed by slow cooling is called annealing or tempering of steel.

The annealed steel is hard and very tough. It has high tensile strength and can withstand a lot of load.

Extraction of Copper

Copper is a transition metal which belongs to the IB group. It shows variable valencies of +1 and +2. It is highly reactive and found in combined state.

Ores of Copper

Cuprite, Cu_2O

Copper pyrites, $CuFeS_2$

Extraction of Copper from Sulphide Ore

Dressing of ore: The ore is crushed in big jaw crushers and then finely powdered in ball mills.

Concentration of ore: The ore is concentrated by the froth floatation process.

Roasting

The process of roasting is carried out in a reverberatory furnace. The finely powdered ore is heated strongly on the hearth of the furnace in the presence of excess of air. The impurities of sulphur, arsenic, antimony and phosphorous are expelled as volatile impurities. Moisture is also expelled out.

During this process, copper pyrites ore is converted to ferrous sulphide and copper sulphide. During heating, the temperature is maintained below the melting point of the ore:

$$S + O_2 \rightarrow SO_2$$

$$4As + 3O_2 \rightarrow 2As_2O_3$$

$$4Sb + 3O_2 \rightarrow 2Sb_2O_3$$

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$$

The sulphides partially get oxidized to their corresponding oxides:

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

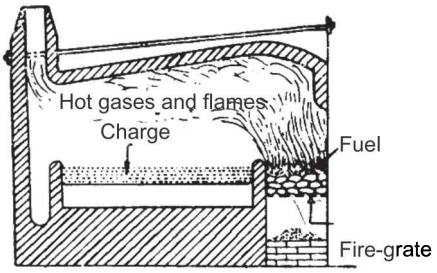


Figure 8.16 Reverberatory furnace

Smelting

The process of smelting is carried out in a blast furnace. The roasted ore is mixed with sand and coke. A blast of air is sent through the tuyeres at the bottom. In this process of smelting, the sulphides are converted to oxides. The oxides combine with sand to form a fusible slag. Apart from the removal of impurities in the form of slag, in smelting process conversion of cuprous oxide (formed by partial oxidation in roasting process) to cuprous sulphide also takes place:

$$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \rightarrow FeSiO_3$$

Impurity Flux Slag

$$Cu_2O + FeS \rightarrow Cu_2S + FeO$$

Slag is removed and the resultant molten ore containing a little of ferrous sulphide is called matte. This is taken out from the exit at the bottom.

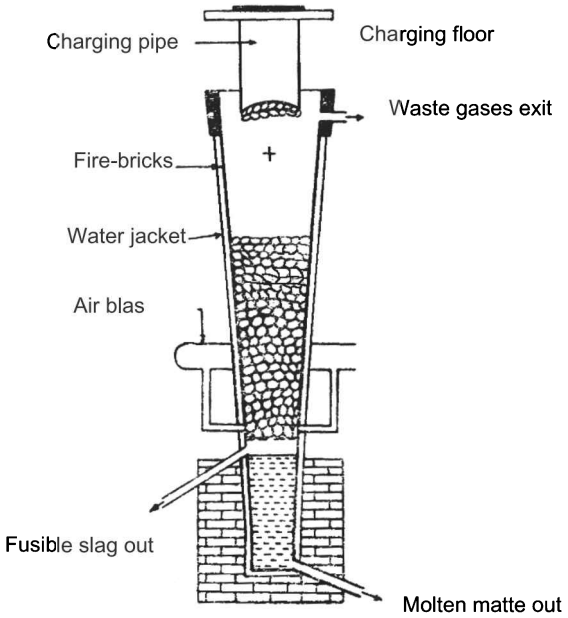


Figure 8.17 Blast furnace for copper

Bessemerization

Bessemer converter is a pear-shaped furnace. It is made up of steel plates and lined by MgO or CaO. It is mounted on trunions in such a way that it can be tilted in either direction. The matte from the process of smelting is transferred into the Bessemer converter. A blast of sand and air is blown inside. The molten metal drops below the level of tuyeres which escapes from oxidation.

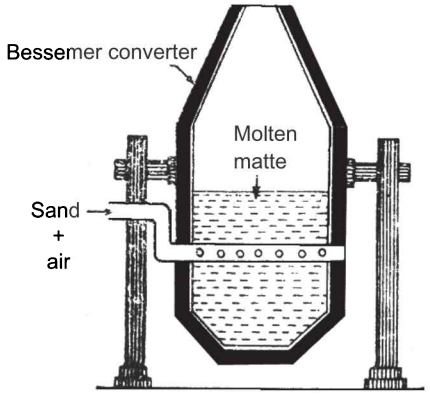


Figure 8.18 Bessemer converter for copper

The reaction of roasting and smelting get completed. Entire iron is removed in the form of slag. Cu_2O and Cu_2S react to give copper and SO_2 escapes out:

$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2$$

After the completion of the above reactions the molten copper obtained is poured off. When the molten mass is subjected to solidification, SO_2 gas escapes out. The copper so obtained gets a blister-type appearance and hence is called blister copper. Blister copper is purified through electrolytic process.

Electrolytic Purification

The crude copper is subjected to electrolysis by taking the impure copper as anode and a strip of pure copper as cathode. Acidified copper sulphate solution is taken as an electrolyte. Pure copper from anode dissolves and gets deposited at the cathode. The cathode becomes thicker due to the deposition of copper. The impurities are collected in the form of anode mud:

Anode reaction: $Cu \rightarrow Cu^{+2} + 2e^-$

Cathode reaction: $Cu^{+2} + 2e^{+2} \rightarrow Cu$

Process Flow Sheet for Metallurgy of Copper

Crushing → Grinding → Froth floatation → Roasting → Smelting → Bessemerization → Electrolytic refining

Figure 8.19 Metallurgy of Copper

Important Alloys and Their Uses

Major component: Copper (Cu)					
Alloy	Brass	Bronze	Gun metal	German silver	Bell metal
Composition	Cu (60% to 80%), Zn (20% to 40%)	Cu (80%), Zn (10%), Sn (10%)	Cu (88%), Sn (10%), Zn (1%), Pb (1%)	Cu (30% to 60%), Zn (20% to 30%), Ni (15% to 20%)	Cu (80%), Sn (20%)
Properties	Lustrous, more malleable and ductile than copper	Hard but brittle, resistant to corrosion, takes very high polish	Very hard, gives a very good cast	White like silver, malleable and ductile	Hard and brittle, produces sonorous sound
Uses	For making shells of ammunition utensils, electrical switches, statues	For making shells, statues, coins and utensils	For making barrels of guns, gears and bearings	For making imitation silver jewellery, utensils, etc.	For making bells

Major component: Iron (Fe)				
Alloys	Stainless steel	Manganese steel	Tungsten steel	Alnico
Composition	Fe (83%), C (1%), Cr (15%) and Ni (1%)	Fe (84%), Mn (15%) and C (1%)	Fe (79% to 84%), W (20% to 15%) and C (1%)	Fe (50%), Al (20%), Ni (20%) and Co (10%)
Properties	Resists corrosion	Very tough and hard	Very very hard	Highly malleable
Uses	For making utensils and surgical instruments	For making safes, armour and rock cutter	For making high speed tools	For making powerful magnets

Major component: Aluminium (Al)		
Alloy	Duralumin	Magnalium
Composition	Al (95%), Cu (4%) Mn (0.5%) and Mg (0.5%)	Al (95%) and Mg (5%)
Properties	Light in weight and as strong as steel	Light in weight, strong and resistant to corrosion
Uses	For making aircraft frames, rockets, speed boats, automobiles	For making aeroplane parts, house appliances, mirrors and scientific instruments

Major component: Nickel (Ni)	
Alloy	Monel metal
Composition	Cu (28%), Ni (67%) and Fe (5%)
Properties	Resistant to corrosion, malleable and ductile
Uses	Used for making sinks, doors and window screws

Major component: Tin	
Alloy	Solder
Composition	Sn (50%–60%) Pb (50%–40%)
Properties	Low melting point and resistant to corrosion
Use	Soldering purposes

Major component: Lead	
Alloy	Type metal
Composition	Pb (75%) Sn (5%) Sb (20%)
Properties	Hard and expands on cooling
Use	For making printing type

Comparative Study of Properties of Iron, Zinc and Aluminium

Physical Properties

Property	Copper	Aluminium	Zinc	Iron
Colour	Reddish orange	Bluish white solid	Bluish white when freshly cut	Light grey
Malleability ductility	High malleability and ductility	High malleability and ductility	Malleable and ductile between 150°C and 200°C. Brittle above and below these temperatures.	Tough, malleable and ductile
Conductivity	Very good conductor of heat and electricity	Very good conductor of heat and electricity	Good conductor of heat and electricity	Good conductor of heat and electricity
Melting point	1085°C	720°C	419°C	1535°C
Boiling point	2562°C	2467°C	907°C	2750°C
Density	8.96 g/cm^3	2.7 g/cm^3	7.1 g/cm^3	7.8 g/cm^3
Magnetic property	Does not show magnetic property	Does not show magnetic property	Does not show magnetic property	Highly magnetic. Loses its magnetic property above 770°C.

Chemical Properties

Properties	Copper	Aluminium	Zinc	Iron
Action of air				
(i) Dry air	No reaction with dry air or moist air	No reaction with dry air	No reaction with dry air	No reaction with dry air
(ii) Moist air	Formation of superficial coating of green basic carbonate $CuCO_3.Cu(OH)_2$	A thin layer of oxide is formed on the surface: $4A1 + 3O_2 \rightarrow 2Al_2O_3$	A layer of oxide is formed which is then converted to carbonate with atmospheric carbon dioxide: $2Zn + O_2 \rightarrow 2ZnO$ $ZnO + CO_2 \rightarrow ZnCO_3$	Formation of a brown powder of hydrated ferric oxide (rust): $4Fe + 3O_2 + xH_2O \rightarrow 2Fe_2O_3\ xH_2O$ (rust)
(iii) Strong heating	Forms copper oxide. $Cu + O_2$ CuO $Cu + O_2$ Cu_2O	Burns with bright white light giving a lot of heat	Burns with a bluish white flame	Burns with brilliant white flames: $3Fe + 2O_2 \rightarrow Fe_3O_4$ (triferric tetraoxide)
Action with water				
(i) Pure Water	Passive to pure water	No reaction due to the formation of protective oxide layer	Passive to pure water	No reaction
(ii) With steam	No reaction with steam	Red hot aluminium reacts with steam. The reaction is rapid in the beginning and becomes slow later: $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$ (steam)	Hot zinc reacts with steam to form zinc oxide liberating hydrogen gas $Zn + H_2O \rightarrow ZnO + H_2\uparrow$ (heated) (steam):	Steam with red hot iron form triferric tetraoxide and hydrogen gas. The reaction is reversible: $3Fe + 4H_2O$ (steam) $\therefore Fe_3O_4 + 4H_2$

Properties	Copper	Aluminium	Zinc	Iron
With Non-metals				
(i) Chlorine	Forms chloride on heating with chlorine: $Cu + Cl_2 \rightarrow CuCl_2$	Forms chloride on heating: $2Al + 3Cl_2 \xrightarrow{heat} 2AlCl_3$	Forms chloride on heating: $Zn + Cl_2 \xrightarrow{heat} ZnCl_2$	Forms chlorides when chlorine is passed over red hot iron: $2Fe + 3Cl_2 \rightarrow 2FeCl_3$
(ii) Sulphur	Forms sulphide on heating: $Cu + S \rightarrow CuS$	Forms sulphide on heating: $2Al + 3S \xrightarrow{heat} Al_2S_3$	Forms sulphide on heating: $Zn + S \xrightarrow{\Delta} ZnS$	On strong heating with sulphur, it forms sulphide: $Fe + S \xrightarrow{\Delta} FeS$
(iii) Carbon	No reaction with carbon	Aluminium carbide is formed: $4Al + 3C \rightarrow Al_4C_3$	–	–
With Acids				
(i) Dilute and concentrated hydrochloric acid and dilute sulphuric acid	No reaction with the liberation of hydrogen gas	Forms respective salts liberating hydrogen gas: $2Al + 6HCl \downarrow 2AlCl_3 + 3H_2$ $(2Al + 3H_2SO_4 \downarrow Al_2(SO_4)_3 + 3H_2)$	Liberates hydrogen gas forming respective salts: $Zn + 2HCl \downarrow ZnCl_2 + H_2$ $Zn + H_2SO_4 \downarrow ZnSO_4 + H_2$	Forms chloride and sulphate salts, liberating hydrogen gas: $Fe + 2HCl \downarrow FeCl_2 + H_2$ $Fe + H_2SO_4 \downarrow FeSO_4 + H_2$
(ii) Concentrated sulphuric acid	Copper dissolves with the evolution of SO_2 gas: $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$	Forms aluminium sulphate, water and sulphur dioxide gas: $2Al + 6H_2SO_4 \downarrow Al_2(SO_4)_3 + 6H_2O + 3SO_2$	Liberates sulphur dioxide on boiling: $An + 2H_2SO_4 \rightarrow \downarrow ZnSO_4 + 2H_2O + SO_2$	Forms ferrous sulphate with the liberation of sulphur dioxide gas: $Fe + 2H_2SO_4 \downarrow FeSO_4 + SO_2 + 2H_2O$
(iii) Dilute nitric and concent rated nitric acid.	$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$ $Cu + 4HNO_3 \therefore \Theta \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2$	Oxidizes the outer layer to aluminium and renders it passive for further corrosion.	Zinc nitrate and nitric oxide gas with dilute acid $3Zn + 8HNO_3(dil) \downarrow 3Zn(NO_3)_2 + 4H_2O + 2N_2O(g)$ Liberates nitrogen dioxide gas with conc. acid: $Zn + 4HNO_3 \downarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$	Dilute acid liberates nitric oxide gas: $3Fe + 8HNO_3$ (dil) $\downarrow 3Fe(NO_3)_2 + 4H_2O + 2NO$ Concentrated acid oxidizes the outer layer which makes the metal passive.

Properties	Copper	Aluminium	Zinc	Iron
Action with caustic alkalis	No reaction with alkalies	Dissolves in concentrated caustic alkalis forming aluminates: $2Al + 2NaOH + 2H_2O \xrightarrow[(powder)]{(conc)} 2NaAlO_2 + 2H_2$	Forms zincates and hydrogen with concentrated aqueous alkalis: $Zn + 2NaOH \xrightarrow{(conc)} Na_2ZnO_2 + H_2$	No reaction with alkalis
Displacement reactions	Displaces less active metals from their aqueous solutions: $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$	Displaces less active metals from their aqueous salt solutions $3AgNO_3 + Al \rightarrow Al(NO_3)_3 + 3Ag$	Displaces the lesser active metals from their aqueous salt $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$	Displaces the less active metal from its aqueous salt solution: $CuSO_4 + Fe \rightarrow FeSO_4 + Cu$
Reducing property	Oxidizes metals: $2CuO + C \rightarrow 2Cu + CO_2$	Good reducing agent, reduces metal oxides to metal by the liberation of huge amount of heat: $Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe + heat$	It reduces the metals which are less reactive than it: $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$	It reduces the metals which are below it in the reactivity series: $Fe + CuSO_4 \rightarrow FeSO_4 + Cu$

EXAMPLE

In L-D converter pure oxygen is used for oxidation while in Bessemer process air is used for the same purpose. Which of these is better and why?

SOLUTION

Usage of oxygen is better because of the following reasons.

(i) Nitrogen in air makes the steel brittle.

(ii) Nitrogen carries away a lot of heat and hence attaining the required temperature is tedious.

EXAMPLE

Wrought iron is more malleable than cast iron. Give reason.

SOLUTION

Wrought iron is the purest form of iron. Its carbon content is the least. Hence it is highly malleable.

EXAMPLE

What is meant by blister copper? What is the reason for the formation of blister copper?

SOLUTION

Copper obtained from Bessemer converter by the process of Bessemerisation gets blister type appearance. This is called blister copper. During the process of Bessemerisation, Cu_2O and Cu_2S react to produce copper and SO_2 gas. In this process, copper is obtained in the molten form and then it is solidified. During solidifaction, SO_2 gas escapes and hence blister copper is obtained.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. What is metallurgy?
2. Which metals are mostly found in free state and why?
3. The mineral from which a metal can be extracted profitably is called _____.
4. What are the different steps of metallurgical processes?
5. The process of the removal of gangue from the ore is called _____.
6. What is pulverization?
7. Which metal has its ore concentrated chemically?
8. Distinguish between calcination and roasting.
9. What type of ore is concentrated using froth floatation process?
10. What is zinc spelter? How is it purified?
11. How is alumina melted in the electrolytic extraction process of molten alumina?
12. What is the process called when ZnS is converted to ZnO during the extraction of zinc?
13. In thermite welding, crucible is lined with _____.
14. How can aluminium be used in the extraction processes of metals?
15. How are slag and molten metal separated from blast furnace?
16. The region in the blast furnace where the temperature range is 1500°C to 2000°C is called _____ zone.
17. Which is the purest form of iron? How is it useful?
18. What are the major products and by-products of blast furnace in the extraction of iron?
19. What is the slag formed in the basic process of the above conversion?
20. The charge in the manufacture of special type of steel in open hearth process _____ and _____.
21. What is the basic process adopted for the conversion of cast iron to steel? What is the difference between acidic and basic process of conversion of cast iron to steel?
22. What type of changes take place in the property of steel if the carbon content is more?
23. Zinc on reaction with steam liberates _____ gas.
24. Polling method is generally employed to _____ with _____ as impurity.
25. What are the products formed when chlorine reacts with
    (i) aluminium
    (ii) zinc
    (iii) iron
26. Copper on reaction with moist air gives _____.
27. Alnico is an alloy of Al, Ni, Co and _____.
28. Which method is employed for the concentration of copper pyrites?
29. Magnalium is an alloy of _____ and _____.
30. Refining of zinc and mercury is carried out by using _____ process.

Short Answer Type Questions

31. What is the basic purpose of roasting and calcination? Compare these two processes.
32. How does bauxite get concentrated in the extraction of aluminium? Explain.
33. Compare cast iron, steel and wrought iron.
34. Compare the composition, properties and uses of different types of steel based on the different metals present in it.
35. State the reactions that take place at the cathode and anode during the process of electrolytic reduction of alumina.
36. Compare the different physical properties of aluminium, iron and zinc.
37. What are the different processes involved in the dressing of ore? Explain.
38. Describe the conversion of cast iron to steel through Bessemerization in brief.

39. Explain froth floatation process for concentrating sulphide ores.
40. How is aluminium refined in Hoope's electrolytic process?
41. What is meant by blister copper? Why is it called so?
42. Describe the reduction of zinc oxide to zinc in brief.
43. Write the reactions of aluminium, iron and zinc with both dilute and concentrated nitric acids.
44. Classify the different types of ores depending on the negative radical present in them. Mention the name of each ore.
45. Describe the processes of conversion of cast iron to wrought iron in brief.

Essay Type Questions

46. Describe smelting of iron in blast furnace. Write all the reactions which take place in different zones of blast furnace.
47. What are the different reducing agents which are used to reduce the metal oxides? Describe how they work with different oxides of metal.
48. Explain the process of roasting and smelting in the extraction of copper from copper pyrites
49. Describe the different purification processes applied for different metals.
50. Compare the composition, properties and uses of different alloys of
    (i) copper and
    (ii) aluminium

CONCEPT APPLICATION

Level 1

Direction for questions from 1 to 7: **State whether the following statements are true or false.**

1. In metallurgy, the concentration of ore is followed by the dressing of ore.
2. In calcination and roasting, volatile impurities are removed.
3. Metals which have low melting point are refined by liquation.
4. In froth flotation process, pine oil is usually added to wet the gangue particles in the ore.
5. Mercuric oxide is reduced by thermal decomposition.
6. Monel metal is an alloy of Cu, Ni and Fe.
7. In purification of metals, during distillation, metal is strongly heated above its boiling point in the presence of air.

Direction for questions from 8 to 14: **Fill in the blanks.**

8. In the upper region of blast furnace _____ helps in the reduction of iron oxide to iron.
9. In Bessemer converter _____ is removed as phosphate slag.
10. _____ and _____ are partially oxidized during roasting in the extraction of copper.
11. Iron pyrites are converted to iron oxide by the process of _____.
12. The reaction which is not associated with the middle region of blast furnace during smelting is _____.
13. Chromium and manganese oxides are reduced to metals by using _____.
14. The components in solder are _____.

PRACTICE QUESTIONS

Direction for question 15: **Match the entries given in column A with the appropriate ones in column B.**

15.

Column A		Column B
A. Pulverization	( )	a. Used for reduction
B. Roasting	( )	b. Concentration of aluminium
C. Coke	( )	c. Reduction of iron
D. Bayer's process	( )	d. Heating in absence of oxygen
E. Vacuum distillation	( )	e. Dressing of ore
F. Smelting	( )	f. Refining of zinc
G. Calcination	( )	g. Heating in presence of oxygen

Direction for questions from 16 to 45: **For each of the questions, four choices have been provided. Select the correct alternative.**

16. Electromagnetic separation is employed for the concentration of those ores in which
(a) the ore is magnetic
(b) the gangue is magnetic
(c) both the ore and the gangue are magnetic
(d) either the ore or the gangue is magnetic

17. The following flow chart represents the extraction of _____.

Froth flotation
↓
Roasting
↓
Smelting
↓
Bessemerization
↓
Electrolytic refining

(a) copper (b) zinc
(c) iron (d) aluminium

18. In the extraction of iron, the most preferred ores are
(a) hematite and limonite
(b) copper pyrites and siderite
(c) magnetite and iron pyrites
(d) limonite and copper pyrites

19. An ore contains arsenic and antimony as impurities. How are they removed during the process of roasting?
(a) by conversion into As_2O_3 and Sb_2O_3
(b) by conversion into As_2O_5 and Sb_2O_5
(c) by conversion into both trioxides and pentoxides
(d) by conversion into sulphides

20. Aluminium is added in Bessemer process to remove certain impurities, but not in L–D process. This is because
(a) pure oxygen is passed in Bessemer process
(b) pure oxygen is passed in L–D process
(c) air is passed in L–D process
(d) of addition of spiegel in Bessemer process

21. Which among the following is an oxide ore of lead?
(a) led ochre (b) galena
(c) anglesite (d) dolomite

22. Zinc is refined by
(a) liquation (or) distillation under reduced pressure
(b) electrolytic method or polling
(c) liquation or electrolytic method
(d) distillation under reduced pressure or electrolytic method

23. Lustre of metal is attributed to
(a) loosely bound electrons present in the valence shell of the metal atoms
(b) strong electrostatic force of attraction between electrons and metal kernels
(c) omnidirectional nature of metallic bond
(d) none of the above

24. The volatile impurities associated with zinc spelter are _____.
(a) Cd and Fe (b) Fe and As
(c) Cd and C (d) Cd and As

25. Match the entries in column-A with appropriate ones in column-B.

Column A		Column B
(1) German silver	( )	(a) for making printing type
(2) Tungsten steel	( )	(b) soldering
(3) Alloy of Sn and Pb	( )	(c) for making high speed tolls
(4) Alloy of Pb, Sn and Sb	( )	(d) for making jewellery

(a) 1 → b 2 → c 3 → d 4 → a
(b) 1 → c 2 → d 3 → a 4 → b
(c) 1 → d 2 → c 3 → b 4 → a
(d) 1 → d 2 → a 3 → b 4 → c

26. The process employed for the purification of copper with cuprous oxide as the impurity is
(a) polling (b) liquation
(c) electrolytic process (d) oxidation

27. "Alclad" is perfectly resistant to corrosion by sea water. The alloy is
(a) magnalium coated with aluminium
(b) duralumin coated with aluminium
(c) r-alloy duralumin
(d) a mixture of magnalium and duralumin

28. Hardened steel on heating in the range of 220°C to 330°C and on slow cooling gives
(a) hard steel (b) brittle steel
(c) hard and brittle steel (d) hard and tough steel

29. If an ore contains impurity of SiO_2, identify the appropriate flux for the removal of it
(a) MnO (b) P_4O_{10}
(c) O_2 (d) SO_2

30. In the electrolytic reduction of alumina, the electrolyte is covered with coke powder because it
(a) prevents oxidation of aluminium formed
(b) reacts with aluminium forming aluminium carbide
(c) prevents heat loss from the electrolyte
(d) none of the above

31. Sequence the following steps involved generally in the extraction of a metal in pure form from its ore.
(1) The metal obtained from its oxide requires further purification for end use.
(2) The ore should be converted to its oxide form.
(3) The ore is beneficial to us if it is hand-picked then metal crushed and ground, and later subjected to pulverization as per the requirement.
(4) The ore in the form of oxide is required to be reduced.
(5) Dressed ore is required for it to be concentrated.
(a) 5 3 2 4 1 (b) 3 5 2 4 1
(c) 3 5 2 1 4 (d) 3 5 4 2 1

32. Select the steps required for the extraction of aluminium and sequence them.
(1) froth flotation
(2) chemical separation
(3) electrolytic reduction
(4) smelting
(5) distillation under low pressure
(6) electrolytic refining
(7) pulverization
(8) conversion of concentrated ore into oxide
(9) crushing and grinding
(a) 9 5 7 2 3 8 6 1 (b) 3 2 1 4 5 6 7 8
(c) 9 7 2 8 3 6 (d) 9 7 2 3 8 6

33. The reactions given below represent the processes of reduction to obtain metals from their respective ores. Arrange them in the following order.
Sodium, aluminium, zinc, chromium, iron, copper and mercury
(1) Metal oxide + metal sulphide → Metal + SO_2
(2) Metal oxide + CO → Metal + CO_2
(3) Metal oxide + C → Metal + CO
(4) Metal oxide → Metal + O_2
(5) Metal oxide $\xrightarrow{\Delta}$ Metal + O_2
(6) Metal oxide + Aluminium → Aluminium oxide + Metal
(7) Metal chloride → Metal + Chlorine
(a) 7 4 3 6 2 1 5 (b) 7 4 3 6 2 5 1
(c) 1 3 2 4 6 7 5 (d) 7 4 5 2 6 1 5

34. $X + CuSO_4 \rightarrow XSO_4 + Cu$,
$Y + CuSO_4 \rightarrow YSO_4 + Cu$, in these reactions X and Y may be _____.
(a) Zn, Ag (b) Zn, Fe
(c) Fe, Ag (d) Ag, Al

35. The composition of thermite mixture is
(a) iron (III) oxide and aluminium powder in the ratio 1 : 3
(b) aluminium powder and iron (III) oxide in the ratio 1 : 3
(c) aluminium powder and barium peroxide in the ratio 1 : 3
(d) barium peroxide and aluminium in the ratio 1 : 3

PRACTICE QUESTIONS

36. The order of processes involved in the dressing of an ore is
(i) grinding and crushing (ii) hand-picking
(iii) pulverization
(a) (i), (ii), (iii) (b) (i), (iii), (ii)
(c) (ii), (iii), (i) (d) (ii), (i), (iii)

37. Chemical separation is one of the methods employed in
(a) dressing of ore
(b) concentration of ore
(c) extraction of metal from its oxide
(d) conversion of ore to oxide

38. Aluminium liberates hydrogen gas on reaction with
(a) concentrated sulphuric acid
(b) nitric acid
(c) hydrochloric acid
(d) none of these

39. The reaction which is not associated with the middle region of blast furnace during smelting is ____.
(a) $CO_2 + C \rightarrow 2CO$
(b) $CaCO_3 \rightarrow CaO + CO_2$
(c) $CaO + SiO_2 \rightarrow CaSiO_3$
(d) $C + O_2 \rightarrow CO_2$

40. Gas liberated when zinc is treated with concentrated nitric acid is ———.
(a) nitrous oxide (b) nitric oxide
(c) nitrogen dioxide (d) nitrogen

41. Bell metal is an alloy of _____.
(a) Cu, Zn (b) Cu, Pb
(c) Cu, Sn (d) Cu, Ni

42. Identify the metal which reacts with concentrated H_2SO_4 or HNO_3, but not with concentrated HCl.
(a) Fe (b) Zn
(c) Cu (d) Al

43. Which of the following metals is soft in nature?
(a) platinum (b) iron
(c) aluminium (d) sodium

44. Which of the following metals forms amphoteric oxide when it reacts with oxygen?
(a) sodium (b) magnesium
(c) aluminium (d) potassium

45. Which among the following metals is not present in german silver?
(a) Cu (b) Ag
(c) Zn (d) Ni

Level 2

1. Why is it necessary to replace carbon anode from time to time in the electrolytic extraction of aluminium?

2. Why are more electropositive elements extracted only by electrolytic reduction?

3. What is the role of cryolite and fluorspar during the extraction of aluminium? However, addition of these produces a harmful gas. Explain.

4. "In the process of reduction of concentrated ore to zinc spelter, ZnO is made into briquettes." Give reasons.

5. Why are most of the metals hard and have high melting and boiling points?

6. Explain the principle involved in the purification of red bauxite by Bayer's process.

7. Green wooden poles are used during the process of refining of copper. What purpose do they serve?

8. Zinc, aluminium and iron give different products when reacted with sulphuric acid of different strengths (dilute and concentrated), whereas copper reacts only with concentrated sulphuric acid. Justify.

9. Why are aluminium alloys widely used in aircrafts and ships?

10. Why is the iron obtained from the blast furnace not used for making any articles?

11. Metal articles to be electroplated are treated with HCl or H_2SO_4 before electrolysis. Give reasons.

12. Explain the role of aluminium in the extraction of chromium or manganese.

13. Which property of Mn of the alloy spiegel is exploited in the manufacture of steel?
14. What is the effect of Cu on the ZnAl alloys?
15. How are the noble metals containing other metals as impurities purified?

Directions for questions from 16 to 25: **Application-Based Questions**

16. One day Dimpy visited an aluminium industry with her father. She found that molten alumina was taken in the fused state for electrolytic reduction process. She asked her father the reason for using fused alumina as an electrolyte instead of the solution of aluminium salt, although the latter can save ample amount of energy. Dimpy's father was pleased with her concern for saving energy, hence he explained to her why nothing could be done about that wastage of energy in that particular instance. What could be his explanation?
17. In L–D converter pure oxygen is used for oxidation while in Bessemer process, air is used for the same purpose. Which of these is better and why?
18. What is meant by blister copper? What is the reason for the formation of blister copper?
19. A, B, C and D are four metals. Both A and B react with concentrated alkali and also with steam. Reaction of A with steam is rapid in the beginning and becomes slow later. Oxide of C on treatment with A liberates huge amount of heat and C produces brown-coloured flakes on exposure to humid atmosphere. D forms two types of oxides below 1370 K and above 1370 K. Identify A, B, C and D and write all the balanced chemical equations.
20. Explain the role of coke and sand added during smelting process in the extraction of copper.
21. Auro, a 10th standard student was asked to identify iron, copper, zinc and aluminium only by observing the effect of action of concentrated nitric acid and caustic soda on each metal. How did he put the reactions of these metals with each of the reagents?
22. Two samples of iron, A and B were given to two students, Rini and Riki, respectively. One of the samples is wrought iron and the other is pig iron. They were asked to observe and study their properties. Rini found that the sample given to her broke easily, whereas Riki's sample was more malleable. Apart from this, it was observed that Rini's sample could be welded at a relatively lower temperature than Riki's sample. Based on the above observations, identify A and B and justify your answer.
23. Extraction of metals always involves reduction processes. Explain.
24. During metallurgy of iron, its ore, coke and limestone are added to the blast furnace.
    (a) What is the role of limestone?
    (b) Identify the reducing agent in the extraction of iron during the above process.
    (c) Identify slag formed during the above process.
    (d) What are the different gases liberated in this process?
25. Wrought iron is more malleable than cast iron. Give a reason.

Level 3

1. "Addition of cryolite and fluorspar to alumina produces a dangerous by-product." Comment.
2. Why L–D process is preferred to Bessemer process?
3. The alloy alnico finds application in the instruments which requires a very stable temperature. Explain.
4. During the quenching of steel, it is plunged either into a water bath or in an oil bath. Explain why different baths are used.
5. Why is brass preferred to stainless steel for door settings?

Directions for questions from 6 to 10: **Application-Based Questions.**

6. In spite of the addition of cryolite and fluorspar to alumina only Al^{+3} and O^{-2} ions are discharged at their respective electrodes. Justify.
7. Explain what happens if bauxite containing iron oxide and silica as impurities is directly subjected to

the process of electrolytic reduction without prior purification.

8. The presence of phosphorus is harmful during the manufacture of steel. Give reasons.

9. Steel manufactured using the open hearth process is of better quality compared to steel manufactured by Bessemer process and L–D converter. Give reasons.

10. Ms Joan was teaching metallurgy in a class. She taught her students how an intensely heated steel ingot when plunged into a water bath or an oil bath can acquire different properties. Then she asked the students the reason for using different cooling agents. What would be your answer for making use of different cooling agents?

CONCEPT APPLICATION

Level 1

True or false

1. False
2. True
3. True
4. False
5. True
6. True
7. False

Fill in the blanks

1. carbon monoxide
2. phosphorus
3. Cu_2S, FeS
4. Roasting
5. $C + O_2 \rightarrow CO_2$
6. Aluminium
7. Sn, Pb

Match the following

15. A : e B : g C : a D : b
    E : f F : c G : d

Multiple choice questions

16. d 17. a 18. a 19. a 20. b
21. a 22. d 23. a 24. d 25. c
26. a 27. b 28. d 29. a 30. c

31. (i) The ore is beneficial to us if it is hand-picked and then ore is crushed and grounded, and later subjected to pulverization as per the requirement.
    (ii) Dressed ore is required to be concentrated.
    (iii) Ore is required to be converted to its oxide form.
    (iv) Ore in the form of oxide is required to be reduced.
    (v) The metal obtained from its oxide requires further purification for end use.

32. (i) Crushing and grinding
    (ii) Pulverization
    (iii) Chemical separation
    (iv) Conversion of concentrated ore into oxide
    (v) Electrolytic reduction
    (vi) Electrolytic refining

33. (i) Metal chloride → Metal + chlorine
    (ii) Metal oxide → Metal + O_2
    (iii) Metal oxide + C → Metal + CO
    (iv) Metal oxide + aluminium → aluminium oxide + metal
    (v) Metal oxide + CO → Metal + CO_2
    (vi) Metal oxide + metal sulphide → Metal + SO_2
    (vii) Metal oxide $\xrightarrow{\Delta}$ Metal + O_2

34. Zn and Fe are more reactive than copper.

35. Thermite mixture is 1 : 3 ratio of Al powder and ferric oxide.

36. Dressing of ore can be carried out by hand-picking, crushing and grinding, pulverization.

37. Chemical separation is one of the methods employed in concentration of ore.

38. $2Al + 6HCl_{(idl)} \rightarrow 2AlCl_3 + 3H_2 \uparrow$

39. $C + O_2 \rightarrow CO_2$. This reaction takes place in the lower region of blast furnace.

40. $Zn + 4HNO_3$ (Conc.) $\rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

41. Bell metal is an alloy of copper and tin.

42. Copper being less active metal, does not react with HCl. But H_2SO_4 and HNO_3 being strong oxidizing agents oxidize copper, releasing SO_2 gas or NO_2 gas.

HINTS AND EXPLANATION

43. Sodium is a soft metal.

44. Al_2O_3 is an amphoteric oxide which reacts with both acids and bases.

45. Ag is not present in german silver.

25. A drop of water contains.
Millions of molecules of water

26. Germanium has the properties of metals as well as nonmetals; hence, it is a metalloid

27. The process is decantation as mud being heavier than water settles down at the bottom due to gravity and separates from water

28. Lime water is a saturated solution of calcium hydroxide; hence, it is a mixture

Level 2

1. (i) Reactions taking place at anode
(ii) Electrolyte used in the extraction of aluminium
(iii) Ions obtained
(iv) Products obtained at the anode
(v) Reaction between the product obtained and the anode

2. (i) Electrode potentials of highly electropositive elements
(ii) The form (ore) in which the metals are available in nature
(iii) Relation between electropositivity of the metal and the chemical stability of the respective ore
(iv) Relation between the electropositivity of the metal and the tendency of it to get reduced
(v) Mechanism of electrolytic reduction

3. (i) Nature and property of an electrolyte
(ii) Electrolyte used for the extraction of aluminium
(iii) Thermal stability of the electrolyte
(iv) Relation between the presence of impurity and melting point of solid
(v) Effect of addition of cryolite and fluorspar on the melting point of the electrolyte
(vi) Mechanism of conduction of electricity
(vii) Effect of addition of cryolite and fluorspar on the conduction of electrolyte
(viii) Product obtained at the anode during electrolysis
(ix) Anodic product obtained at the end of the electrolysis

4. (i) Comparison between briquette and powder form
(ii) Furnace in which the reduction of concentrated ore takes place
(iii) Process of reduction
(iv) Physical state of the raw material in which they react
(v) Physical state of the product

5. (i) Nature of metal atoms
(ii) Type of bond present in metals
(iii) Relation between the strength of the bond and the properties of metal (melting point, boiling point).

6. (i) Nature of impurity present in red bauxite
(ii) Chemical composition of the red bauxite and the impurity present in it
(iii) Comparison of chemical behaviour of red bauxite and the impurity with acids and bases
(iv) Separation technique that can be adopted for removing the impurity based on the above chemical behaviour

7. (i) Composition of wood
(ii) Impurities present in copper
(iii) Constituents of green wooden poles
(iv) Gases produced from green poles
(v) Role of these gases for converting the impure form of metal to pure metal

8. (i) Comparison of reactivity of Zn, Al, Fe and Cu
(ii) Comparison of oxidation potentials of zinc, iron, aluminium with hydrogen
(iii) Type of reaction that takes place when the above metals react with dilute H_2SO_4
(iv) Change in the property of H_2SO_4 with the increase in concentration
(v) Change in the product due to the change in the concentration
(vi) Comparison of oxidation potential of copper with hydrogen
(vii) Type of reaction that can takes place between copper and concentrated H_2SO_4

9. (i) Property of aluminium
(ii) Comparison of properties of metal and its alloy

10. (i) Gases in the blast furnace
(ii) Reactions that take place in blast furnace
(iii) Products obtained and their physical state
(iv) Effect of the physical state of the product on the iron obtained
(v) Effect of the impurities on the property of iron

11. (i) Reactivity of HCl, H_2SO_4 with the impurities present
(ii) Reactivity of metals
(iii) Effect of reactivity of metal on its surface
(iv) Change in composition of the surface of metal
(v) Reactivity of the substances which are formed on the surface of the metal
(vi) Reaction between the above substances with HCl or H_2SO_4

12. (i) Reactivity of aluminium
(ii) The reaction that the ore should undergo in the extraction of the metal
(iii) Chemical property of aluminium that is exploited to extract the metal from its ore

13. (i) Reactivity of Mn with the impurities
(ii) Kinds of impurities present in iron obtained from the blast furnace
(iii) Chemical behaviour of manganese
(iv) Affinity of manganese towards certain impurities
(v) Formation of slag
(vi) Type of bond that can be formed between iron and manganese
(vii) Effect of the formation of the above bonds on the property of steel

14. (i) Mechanical properties of substance
(ii) Type of bond present in metal
(iii) Change in the type of bond during the formation of alloy
(iv) Effect of change in the type of bond on the physical property of the metal

15. (i) Reactivity of noble metals
(ii) Comparison of reactivity of noble metals with other metals
(iii) Separation technique adopted for the removal of impurities from the noble metal based on the difference in reactivity

16. Aluminium cannot be prepared from its salt solution because of its highly electropositive nature. It does not get discharged at the cathode. H_2 gas is liberated at the cathode when a solution of a salt of aluminium is electrolysed.

17. Usage of oxygen is better because of the following reasons:
(i) Nitrogen in air makes the steel brittle.
(ii) Nitrogen carries away a lot of heat and hence attaining the required temperature is tedious.

18. Copper obtained from the Bessemer converter by the process of Bessemerization gets a blister type of appearance. This is called blister copper. During the process of Bessemerization, Cu_2O and Cu_2S react to produce copper and SO_2 gas. In this process, copper is obtained in the molten form and then it is solidified. During solidification, SO_2 gas escapes and hence blister copper is obtained.

19. Since A and B reacts with concentrated alkali, they are Al and Zn. Reaction of A with steam is rapid in the beginning and becomes slow later and hence A is Al.

$$2H_2O + 2Al + 2NaOH \longrightarrow 2NaAlO_2 + 2H_2 \uparrow$$

(A)

$$Zn + NaOH \longrightarrow Na_2ZnO_2 + H_2 \uparrow$$

(B)

$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$

$$Zn + H_2O \longrightarrow ZnO + H_2$$

Since oxide of C produces huge amount of heat with A and flakes with humid atmosphere, it is iron.

$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3 + \text{Heat.}$$

(C)

As D forms two types of oxides above and below 1370 K, it is Cu.

$$Cu + O_2 \xrightarrow{<1370\,K} Cu_2O$$

(D)

$$Cu + O_2 \xrightarrow{>1370\,K} Cu_2O$$

20. Coke is the source of heat in smelting and also it acts as reducing agent, which reduces Cu_2O to Cu:

$Cu_2O + C \rightarrow 2Cu + CO$

SiO_2 combines with the impurities like FeO and is removed as slag:

$FeO + SiO_2 \rightarrow FeSiO_3$

21.

Action concentrated nitric acid	Action of caustic alkali	Inference
No characteristic change	No characteristic change	Iron
Liberates brown coloured NO_2 gas	No characteristic change	Copper
Liberates brown coloured NO_2 gas	Liberates hydrogen gas	Zinc
No characteristic change	Liberates hydrogen gas	Aluminium

22. In wrought iron, carbon content is much lesser than that in pig iron. Presence of carbon that is a nonmetal reduces the malleability of a metal and the metal becomes hard and brittle. Moreover, presence of impurity reduces the melting point of a solid. Hence pig iron, in which carbon content is more, can be welded at a lower temperature. From these two observations, it can be concluded that Rini's sample is pig iron and Riki's sample is wrought iron.

23. Metals are always available in nature in the form of ores, in which the metal remains as cation. Extraction of the metal from the ore is to get the metal in its elemental state. For this purpose any metal compound always requires to be reduced.

24. (a) Limestone ($CaCO_3$) undergoes thermal decomposition and gives CaO and CO_2. CaO acts as a flux.

(b) Carbon monoxide acts as a reducing agent:

$FeO + CO \rightarrow Fe + CO_2$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(c) CaO reacts with the impurity SiO_2 and forms the slag $CaSiO_3$:

$CaO + SiO_2 \rightarrow CaSiO_3$

(d) $C + O_2 \rightarrow CO_2(g)$

$CO_2 + C \rightarrow 2CO(g)$

$CaCO_3 \rightarrow CaO + CO_2(g)$

$FeO + CO \rightarrow Fe + CO_2(g)$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2(g)$

CO_2 gas is liberated. CO gas is formed, but takes part in the process of reduction of Fe_2O_3 and forms CO_2.

25. Wrought iron is the purest form of iron. Its carbon content is the least. Hence, it is highly malleable.

Level 3

1. (i) Common element present in cryolite and fluorspar.

(ii) Ions present in cryolite and fluorspar.

(iii) Products obtained at the electrodes on complete electrolysis.

(iv) Nature of the products.

2. (i) Comparison of the type of fuel used.

(ii) Comparison of the composition of gases passed through the charge in L–D and Bessemer process.

(iii) Comparison of the process of passing the gases in L–D and Bessemer converter.

(iv) Reactions that takes place in L–D and Bessemer converter.

(v) Change in the rates of reactions due to difference in the above two processes.

(vi) Effect of the presence of the non-reactive component of the gas blasted in Bessemer process on the property of steel.

3. (i) Comparing properties of constituent metals and alloy.

(ii) Composition of alnico

(iii) Property of alnico

(iv) Effect of composition on retention of this at higher temperatures

4. (i) Comparing cooling properties of oil and water

(ii) Comparison of the property related to rise in temperature of oil and water

(iii) Effect of property on the rate of cooling of steel

(iv) Relation between the rate of cooling and the change in the properties of steel

5. (i) Composition of brass and stainless steel

(ii) Relation between the composition and the property of the alloy

(iii) Comparison among the given properties of alloys

(iv) Requisite for door settings

6. Cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added to alumina to reduce its melting point. Al^{+3} discharges preferentially over Na^+ and Ca^{+2} at cathode, because of lower discharge potential of Al^{+3} than Na^+ and Ca^+ and at anode, O^{-2} gets discharged due to its lower discharge potential than F^- and is evolved as O_2, which reacts with carbon anode forming CO_2 gas.

7. Crude bauxite contains iron oxide and silica as impurities. If any iron is present in the bauxite, it will get deposited at the cathode in preference to aluminium because iron is less electropositive than aluminium.

8. Phosphorus imparts cold-shortness, i.e., high brittleness at normal and especially at room temperature. It increases the tensile strength but at the same time reduces the impact strength due to the formation of iron phosphide.

9. Open hearth process produces better quality steel because

(i) Open hearth process is a lengthy process due to which the composition of the product can be controlled by checking from time to time.

(ii) As blast of air is not passed in the open hearth process, blow holes are not formed which could make the steel brittle and loss of iron in the form of slag is multified.

(iii) Pure oxygen makes the process of removal of impurities faster and more effective.

10. Different baths are used for quenching steel for different use. Water and oil have different specific heat. Due to the difference in specific heat, dissipation of heat through the bath becomes different. Water has high specific heat. For this reason, dissipation of heat through water is more than that through oil. For decreasing the dissipation of heat through water, hot or boiled water is also used. Sudden cooling makes steel harder, and more brittle. Hence different baths provide different hardness to the steel and make it useful for different end uses.

Chapter

9

Industrial Chemistry

Remember

Before beginning this chapter, you should be able to:

- know the classification of matter and concept related to elements
- describe the industrial applications of derivatives of some elements.

Key Ideas

After completing this chapter, you should be able to:

- Understand the preparation, properties and uses of elements and their compounds
- study their manufacturing processes and applications
- do a comparative study of allotropes of elements such as sulphur.
- know methods of preparation, properties and uses of some industrially useful compounds.

INTRODUCTION

Nature is endowed with a variety of metals and nonmetals existing in their native state as well as in combined state. These elements like carbon, sulphur, nitrogen, etc., are extracted from the natural resources through different processes. After purification, these elements are either used directly in the elemental state or used as raw materials for the manufacture of a variety of compounds. These compounds have a wide range of applications in various fields. Industrial chemistry deals with the manufacture of these compounds like different acids, ammonia, quick lime, slaked lime, washing soda, etc. Some of the compounds are further used for the manufacture of cement, glass, ceramics, fertilizers, etc., which find applications in the construction of buildings, decorative items, sanitary ware, interiors, telecommunication, spacecraft and various other fields and the study of the manufacture, properties and uses of these materials also come under the scope of industrial chemistry.

SOME IMPORTANT NONMETALS

Carbon

Carbon belongs to IV A group of the periodic table. Carbon is one of the most important non-metallic elements since it is invariably present in all animals and plants in the form of various compounds. In addition to this, carbon exists in combined form in the form of many minerals and also in the form of carbon dioxide in the atmospheric air. However, in elemental form carbon is available in the form of diamond, graphite, etc.

Allotropy

The existence of the same element in different physical forms with similar chemical properties is known as allotropy.

Carbon exhibits allotropy and the allotropes of carbon are broadly classified into two main categories, viz., crystalline and amorphous allotropes. Crystalline allotropes are diamond, graphite and fullerene while coke, charcoal, lamp black, gas carbon are amorphous allotropic forms.

Diamond

In diamond, each carbon atom is bonded covalently by single bonds, to four other carbon atoms resulting in a single tetrahedral unit of crystal. These tetrahedral crystal units lie in different planes accounting for a rigid three-dimensional structure. The C-C bond length is 1.54 A and bond angle is 109°28′.

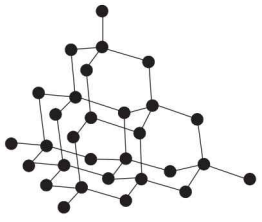


Figure 9.1 Structure of Diamond

Diamond can be prepared by heating carbon in the form of sugar charcoal in molten iron up to 3800°C−4000°C which, on subsequent and sudden cooling, crystallizes to diamond.

Physical Properties: Diamond is a hard crystalline substance with a high density (3.5g/cc) and melting point of 3700°C. It also has a very high refractive index of 2.5.

Chemical Properties: Diamond, on heating in the presence of air, catches fire around 800°C to form CO_2:

$$C + O_2 \xrightarrow{800°C} CO_2$$

Uses: Diamond due to its brilliance is used as a precious gem and, due to its sharpness, is used in performing delicate operations.

Graphite

Graphite is another crystalline allotropic form of carbon. Artificially, graphite can be prepared by taking a mixture of sand, coke and ferric oxide in an electric arc furnace. The temperature increases to 3500°C due to the resistance applied by the sand and at this high temperature coke orients itself to form graphite.

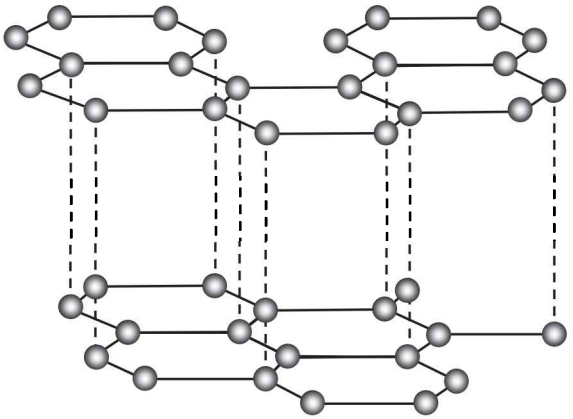


Figure 9.2 Structure of graphite
1. Covalent bonds 2. Van der Waals forces

In graphite, each carbon atom is bonded to three other atoms resulting in the formation of a layer of hexagonal rings. The remaining unpaired electron in each carbon atom helps to develop weak forces of attraction between different layers. These layers in turn arrange parallel one over the other and are held together by weak forces.

Physical Properties: Graphite a dark greyish soft lustrous solid has a density of 2.25g/cc and melting point around 3600°C.

Chemical Properties: Graphite, on heating in an atmosphere of pure oxygen, catches fire at 700°C forming a mixture of CO_2 and CO:

$$3C + 2O_2 \xrightarrow{700°C} CO_2 + 2CO + \Delta Q$$

Uses: Graphite is mainly used in making leads of pencil, electrodes, refractory crucibles and as a solid lubricant.

Buckminster Fullerene

Buckminsterfullerene is another crystalline allotropic form of carbon discovered recently. These fullerene molecules are synthesized by subjecting graphite to sublimation using laser radiation. The

vapour formed is subsequently cooled in the atmosphere of noble gases. The fullerene molecules mainly consist of C_{60} with smaller amounts of C_{70} and traces of other fullerenes consisting of even number of carbon atoms up to 350.

C_{60} molecule consists of 12 pentagons and 20 hexagons of carbon arranged in 32 rings as a whole. This allotrope of carbon acts as a superconductor on forming compounds with noble gases.

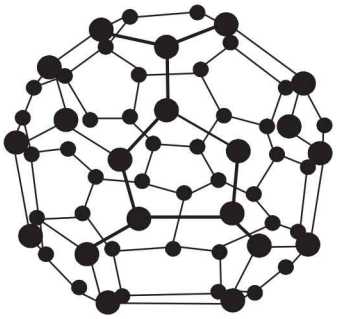


Figure 9.3 Structure of Fullerene

Physical Properties: Buckminsterfullerene is a brown-powdered substance with a density of 1.65 g/cc that sublimes at 527°C. It has a refractive index of 2.2.

Compounds of Carbon

Apart from the various organic compounds, carbon occurs in the form of compounds such as oxides, carbides, carbonates, bicarbonates, etc. Carbon can form two oxides, namely, carbon monoxide and carbon dioxide.

Carbon Monoxide

Carbon monoxide is not a natural component of atmospheric air. Carbon monoxide is produced by incomplete combustion of automobile fuels or biomass. This is a harmful gas due to its high solubility in the blood. It bonds with haemoglobin forming carboxy haemoglobin which decreases the supply of oxygen to the tissues.

Carbon Dioxide

It is one of the minor components of atmospheric air. Carbon dioxide is added to the atmosphere by means of natural phenomena such as degradation of organic matter, respiration, fermentation and chemical weathering of rocks. Carbon dioxide is a colourless gas which is soluble in water and is heavier than air. It is consumed by plants during the process of photosynthesis. Carbon dioxide present in the atmosphere should be balanced because excess amount of CO_2 in the atmosphere leads to increase in temperature of the earth which causes global warming.

Silicon

Silicon is the second most abundant element in earth's crust. Just like carbon, silicon is also a nonmetal belonging to the IVA group of the periodic table and is present below carbon.

Occurrence: Silicon occurs mostly in the combined state in nature. It exits in the form of oxides, silicates in sand and clay. Aluminium silicate is the most widely distributed silicate in the form of

clay. Like carbon, silicon also exhibits allotropy existing in both amorphous and crystalline forms. It is present as a constituent of semi-precious stones like garnet, zircon, opal, etc.

Extraction

Silicon can be extracted from quartz. A mixture of finely powdered quartz with magnesium powder is heated in a fire clay crucible. On heating, magnesium undergoes oxidation while silicon dioxide undergoes reduction leading to the formation of silicon. The product is washed with HCl to dissolve MgO. Unreacted silica is washed away using hydrofluoric acid.

$$SiO_2 + 2Mg \rightarrow 2MgO + Si$$

Silicon can also be prepared by reducing silica with coke, but the silicon obtained in this method has lesser purity:

$$SiO_2 + 2C \rightarrow Si + 2CO$$

Physical Properties: Silicon is a dark brown powder, and insoluble in water. Its melting point is 1683 K and boiling point is 2628 K.

Chemical Properties

Properties	Reaction
With oxygen	$Si + O_2 \rightarrow SiO_2$
With steam	$Si + 2H_2O \underset{\text{(red hot)}}{\rightarrow} SiO_2 + 2H_2$
With carbon	$Si + Coke \xrightarrow{\text{(at high temperature)}} SiC$

Uses of Silicon

Silicon is widely used in the field of electronics for the manufacture of semiconductor devices. It is also used for the preparation of some alloys like ferrosilicon and silicon bronze. The compounds of silicon have wide range of applications in industry.

Applications of Compounds of Silicon

Silica is used for the manufacture of glass, porcelain, building materials and threads of high elasticity.

Silicon carbide is used as an abrasive for cutting and grinding glass.

Sodium aluminium silicate is used for softening of hard water.

NITROGEN

Nitrogen is the most abundant element in the atmosphere. It is placed in the VA group of the periodic table.

Occurrence

Nitrogen exists in the atmosphere in elemental state. In combined state, nitrogen is present in the form of nucleic acids and amino acids in living systems and ammonium or nitrate salts in soils.

Laboratory Preparation

In the laboratory, nitrogen can be prepared from air.

Procedure

Soda lime is taken in a U-tube and air is slowly pumped through it. The sodium hydroxide present in soda lime reacts with CO_2 present in air forming sodium bicarbonate and the water vapour present in the air reacts with calcium oxide to form calcium hydroxide. Thus, both CO_2 and H_2O are removed.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$NaOH + CO_2 \rightarrow NaHCO_3$$

The leftover air is passed over red hot copper where the O_2 present in air turns copper to copper oxide. The nitrogen gas present in air, thus, does not undergo chemical reaction and can be collected by the downward displacement of water.

$$2Cu + O_2 \rightarrow 2CuO$$

Compounds of Nitrogen

Ammonia and nitric acid constitute the most important compounds of nitrogen since they are used as raw materials in various industries.

Ammonia

Occurrence: In free state, ammonia is found in traces in air as well as in water.

In combined state, ammonical liquor is obtained by destructive distillation of coal and small deposits of ammonium salts in craters.

Laboratory Preparation

(i) Ammonia gas can be prepared by heating ammonium salts with alkalis:

$$2NH_4Cl + Ca(OH)_2 \xrightarrow{\Delta} CaCl_2 + 2H_2O + 2NH_3$$

(ii) Ammonia gas can be prepared by treating metal nitrides with warm water:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

Industrial method of preparation: Ammonia can be synthesized in large scale by Haber's process.

Manufacture of Ammonia by Haber's Process

Principle

Ammonia can be synthesized by the reaction of nitrogen and hydrogen in 1 : 3 ratio under high pressure at a moderately high temperature. It is an exothermic reaction.

$$N_2 + 3H_2 \therefore 2NH_3 + \text{heat}$$

Conditions Required for the Process

Pressure	–	200–900 atm
Temperature	–	450°C–500°C
Catalyst	–	Iron
Promoter	–	Molybdenum

Presence of traces of impurities such as carbon dioxide, carbon monoxide and hydrogen sulphide act as catalytic poisons and reduce the yield of ammonia. Hence, the removal of these impurities from the raw materials is an essential step in this process.

Impurities	Method of removal
CO_2	Dissolution in water under pressure
CO	By passing through cuprous formate or cuprous acetate
H_2S	Absorption in KOH solution under pressure

Procedure

Pure and dry H_2 and N_2 are mixed in the ratio of 3 : 1 and the mixture is compressed under high pressure of about 200–900 atm. The compressed gases are led into catalytic chamber containing finely divided iron with molybdenum at 450°C. The product ammonia, unreacted nitrogen and hydrogen exchange their heat with incoming nitrogen and hydrogen. The outgoing hot mixture contains only 10% NH_3 and condenses at –33°C and 8 atm pressure. The cold mixture is allowed to expand suddenly so that ammonia gets liquefied and when it is passed through water, it dissolves and forms liquid ammonia. The unreacted N_2 and H_2 are recirculated through the plant.

Physical Properties

Ammonia is a colourless, pungent smelling gas. It has a boiling point of 33°C and a freezing point of −78°C.

Chemical Properties

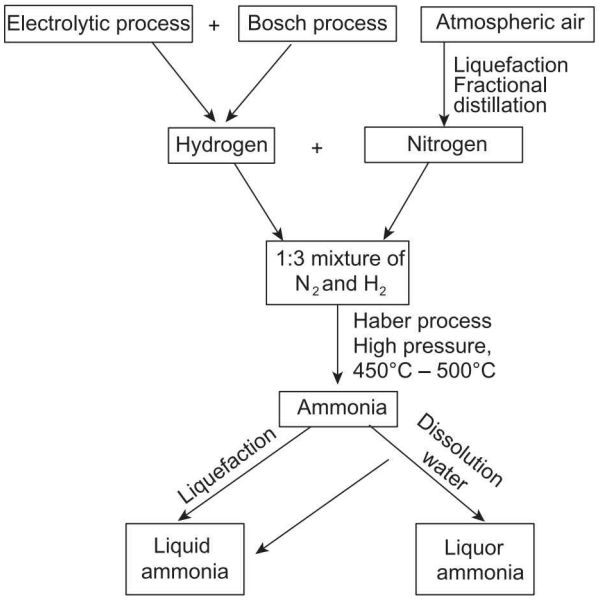


Figure 9.4 Flow chart for the manufacture of ammonia by Haber's process

Properties	Reactions
Combustion	NH_3 is a non-combustible gas and also does not support combustion.
Oxidation	$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$ $4NH_3 + 5O_2 \xrightarrow{Pt/900°C} 4NO + 6H_2O$
Reducing agent	$3CuO + 2NH_3 \xrightarrow{\Delta} 3Cu + 3H_2O + N_2$ (reducing agent)
Complex formation	$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$ $(NH_4)_2SO_4 + Cu(OH)_2 + 2NH_4OH \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$

Uses

Ammonia is used in the manufacture of fertilizers, plastics, industrially useful compounds like HNO_3, baking soda and washing soda.

Nitric Acid

Nitric acid is a very strong acid which has strong oxidizing properties. Nitric acid is one of the constituents of aquaregia which can dissolve even noble metals.

Occurrence

Nitric acid occurs in traces in the atmosphere in free state.

In combined state, nitric acid occurs in the form of its mineral nitrates like sodium nitrate, potassium nitrate and calcium nitrate.

Laboratory Preparation

A mixture of sodium nitrate or potassium nitrate with concentrated sulphuric acid on distillation produces nitric acid.

$$KNO_3 + H_2SO_4 \xrightarrow{<200°C} KHSO_4 + HNO_3$$

Industrial Preparation of Nitric Acid by Oswald's Process

Principle

Preparation of nitric acid in industry involves the catalytic oxidation of ammonia and subsequent dissolution in water. The entire process takes place in three different stages as listed hereunder:

(i) Oxidation of ammonia into nitric oxide in a catalytic chamber: A mixture of ammonia and dry oxygen in the ratio of 1 : 2 when passed over platinum gauze, maintained electrically at 800°C produces nitric oxide and steam:

$$4NH_3 + 5O_2 \xrightarrow{Pt-800°C} 4NO + 6H_2O(steam)$$

(ii) Oxidation chamber: Nitric oxide gets oxidized to nitrogen dioxide when the mixture of NO, O_2 and steam is allowed to cool to 50°C in the oxidation chamber:

$$2NO + O_2 \xrightarrow{H_2O} 2NO_2$$

(iii) Absorption tower: Dilute nitric acid is formed when a mixture of nitrogen dioxide and oxygen along with water vapour is passed through water.

Removal of Colour

(i) By passing dry CO_2 or dry air through coloured nitric acid, which drives out nitrogen dioxide gas.

(ii) By the addition of water drop by drop to nitric acid, the nitrogen dioxide present in it is oxidized to nitric acid:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

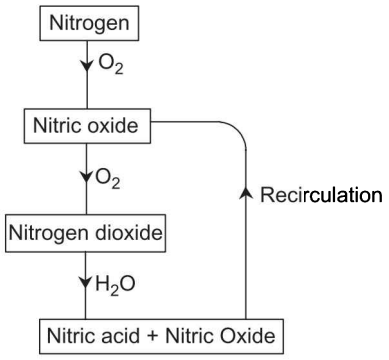


Figure 9.5 Flow chart for the manufacture of nitric acid by Oswald's process

Precautions

(i) Impurities should not be present in the gases entering the catalytic chamber to avoid poisoning of the catalyst.

(ii) Electric heating of the catalyst should be stopped when the reaction speeds up since the reaction is exothermic in nature.

(iii) The excess oxygen helps to move the reaction forward.

(iv) Gases must be cooled to 50°C before they are sent into the oxidation chamber.

(v) The acid in the absorption tower can be concentrated by evaporation under reduced pressure.

Physical Properties

Nitric acid is colourless acid with suffocating smell and taste. It is highly soluble in water.

Chemical Properties

Properties	Reactions
With metal oxide	$K_2O + 2HNO_3(dil) \rightarrow 2KNO_3 + H_2O$
Decomposition	$C + 4HNO_{3(conc)} \xrightarrow{\text{boiling}} CO_2 + 2H_2O + 4NO_2$ $3Cu + 8HNO_3(dil) \rightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$
With metallic carbonates and bicarbonates	$K_2CO_3 + 2HNO_3(dil) \rightarrow 2KNO_3 + H_2O + CO_2$ $KHCO_3 + HNO_3(dil) \rightarrow KNO_3 + H_2O + CO_2$

Uses

Nitric acid is mainly used in the manufacture of explosives and fertilizers. Due to its oxidizing properties, it is used in purification of gold and as an oxidant in rocket fuel.

Phosphorus

Phosphorus is a nonmetal belonging to the VA group in the periodic table, and it is known as phosphorus, as it glows in the dark.

Occurrence

Phosphorus cannot exist in the free state, but in the combined state it occurs in the form of phosphates like phosphorite ($Ca_3(PO_4)_2$), chloropatite ($3Ca_3(PO_4)_2 \cdot CaCl_2$) and fluorapatite ($3Ca_3(PO_4)_2 \cdot CaCF_2$).

Extraction

Phosphorus is mainly extracted from phosphorite ore by heating the mixture of powdered ore along with sand and coke in an electric furnace. The temperature maintained in the furnace is 1400°C to 1500°C. At this temperature calcium phosphate on reaction with sand converts into phosphorus pentoxide. Phosphorus pentoxide so formed reacts with coke to form phosphorus:

$$Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5$$

$$2P_2O_5 + 10C \rightarrow 10CO + P_4$$

The by-product calcium silicate formed is removed as a slag. The vapours of carbon monoxide and phosphorus are collected from the outlet at the top. These vapours are passed through water, where phosphorus solidifies while CO escapes out. The crude yellow phosphorus is then purified by melting under water, followed by treatment with dilute sulphuric acid and potassium dichromate to remove the impurities by oxidation and redistillation.

Allotropes

Phosphorus exists in two allotropic forms, namely, white phosphorus and red phosphorus. We now provide a comparative study of white and red phosphorus.

White phosphorus	Red phosphorus
A molecule of white phosphorus consists of four atoms which are arranged at four corners of a regular tetrahedron. There exist weak forces between P_4 molecules.	Red phosphorus consists of infinite chains of phosphorus atoms which results in a covalent crystal lattice.
It is a whitish yellow soft solid with density of 1.8 g/cc.	It is a reddish brown solid with density of 2.1 g/cc.
It melts at 317 K and has a very low ignition temperature.	It sublimes at about 565 K when heated in the absence of air and its ignition temperature is 533 K.
It is insoluble in water but readily soluble in non-polar solvents like chloroform, benzene, etc.	It is insoluble in water as well as carbon disulphide.
It is poisonous in nature.	It is non-poisonous in nature.

Chemical Properties

Properties	Phosphorus
Reaction with air	$P_4 + 5O_2 \rightarrow 2P_2O_5$
Reaction with chlorine	$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 10Cl_2 \rightarrow 4PCl_5$

Properties	Phosphorus
With acids	$P + 5HNO_3 \rightarrow H_3PO_4 + 5NO_2 + H_2O$ $2P + 5H_2SO_4 \rightarrow 2H_3PO_4 + 5SO_2 + 2H_2O$

Red phosphorus does not react with any alkali.

Uses

Phosphorus is widely used in the match industry due to its low ignition temperature. It is also used in making rat poison, smoke bombs, fireworks, fertilizers, etc.

Sulphur

Sulphur is a non-metallic element belonging to the VIA group in the periodic table. The word "sulphur" has been derived from the Sanskrit word "sulvari" meaning enemy of copper, as it destroys the properties of metals due to its reactivity.

Occurrence of Sulphur: In nature, sulphur occurs both in the free and in the combined states.

Free State

Sulphur, in the free state, is found in the earth's crust (0.03% of the earth's crust is elemental sulphur). In the volcanic regions like Sicily and Japan, it is present near the earth's crust and in the non-volcanic regions of the United States like Texas and Louisiana it is found much below the earth's crust (300 to 400 m below the earth's crust).

Combined State

Sulphur in the combined state is found in the form of sulphides (in ores), sulphates (in salts) and in organic matter.

Sulphates		Sulphides		Organic matter
Salt	Formula	Ores	Formula	In insulin, glucosinolates of plants and animals, natural gas, petroleum, crude oil, coal gas, water springs
Gypsum	$CaSO_4 \cdot 2H_2O$	Cinnabar	HgS	
Epsom salt	$MgSO_4 \cdot 7H_2O$	Galena	PbS	
Glauber's salt	$Na_2SO_4 \cdot 10H_2O$	Iron Pyrites	FeS	
		Copper pyrites	CuS	
		Zinc Blend	ZnS	

Sulphur has a wide variety of uses in industries. It is extracted from the earth's crust by the following processes:

(i) the Sicilian process and
(ii) the Frasch process.

(i) Sicilian process

This process is used to extract sulphur which is near the earth's crust (deposits in Sicily). This process is carried out in brick kilns built on sloping hill sides.

(ii) Frasch process

This process is used to extract sulphur which lie 150–400 m below the earth's crust. This process is also called Louisiana process as large deposits of this are found in Louisiana. A direct mining is not possible as sulphur is present in layers of quick sand and gravel.

Process

In this process, three concentric pipes of diameters 25 mm, 76 mm and 152 mm are drilled through the ground to the sulphur deposits. Superheated steam (170°C) under pressure is sent through the outermost pipe. This melts the sulphur below (m.p. of sulphur = 112°C). Hot compressed air (up to 35 atm) is sent through the innermost pipe, which froths up the molten sulphur below. The sulphur foam formed rises up the middle pipe and is collected.

Advantages

The sulphur extracted in this process is 99.5% pure and doesn't need further purification.

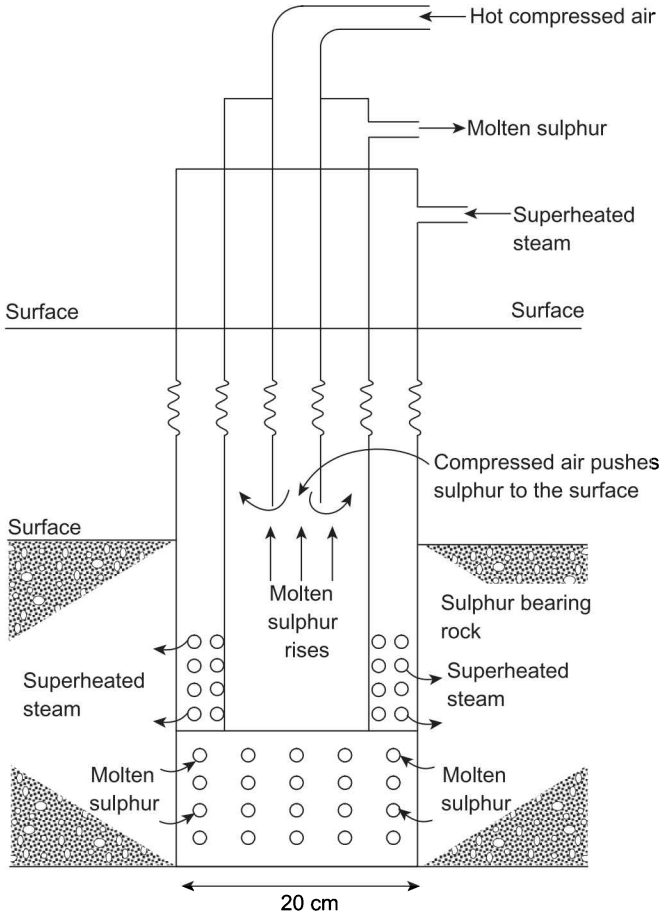


Figure 9.6 The Frasch process for extracting sulphur

Allotropes of Sulphur

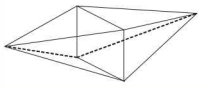
The phenomenon of existence of an element in more than one physical form is called allotropy, and the various forms of the element are called allotropes. Sulphur exists in different allotropic forms. Allotropes have same chemical properties but different physical properties.

The three main allotropic forms of sulphur are the following:

(i) rhombic sulphur,
(ii) monoclinic sulphur and
(iii) plastic sulphur.

Rhombic sulphur and monoclinic sulphur are crystalline, whereas plastic sulphur is amorphous.

Comparative Study of the Allotropic Forms of Sulphur

	Rhombic sulphur	Monoclinic sulphur	Plastic sulphur
Other names	Octahedral sulphur, alpha-sulphur	Prismatic sulphur, beta-sulphur	Gamma-sulphur
Preparation	Roll sulphur is dissolved in carbon disulphide. This is allowed to evaporate slowly by slight heating. Rhombic sulphur crystals are left behind.	Roll sulphur is heated in an evaporating dish till it melts to pale yellow liquid. This on cooling forms a crust on the surface. Holes are pierced on the crust and the molten sulphur is drained out. Needle-shaped sulphur (monoclinic sulphur) crystals are left behind.	Roll sulphur is heated to above 300°C till it turns to dark brown, and this is poured into cold water and the sulphur formed is plastic sulphur.
Colour	Pale yellow	Amber	Dark brown
Shape/structure	Octahedral 	Needle shaped	Amorphous
Density	2.08 g/cm^3	1.98 g/m^3	1.92 g/cm^3
Solubility	Soluble in carbon disulphide	Soluble in carbon disulphide	Insoluble in carbon disulphide
Melting point	112.8°C	119°C	No sharp melting point

Rhombic sulphur is the most stable form at normal temperature. Monoclinic sulphur and plastic sulphur change to rhombic form on long standing.

Transition Between Rhombic Sulphur and Monoclinic Sulphur

Rhombic sulphur is stable below 95.6°C and above this temperature it changes to monoclinic sulphur. Conversely, monoclinic sulphur is stable above 95.6°C, but changes to the rhombic variety below this temperature. Hence 95.6°C is called the transition temperature of these two allotropes of sulphur.

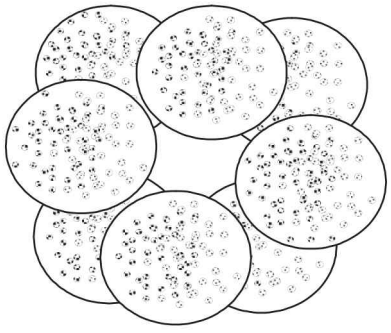


Figure 9.7 Puckered ring structure

Puckered Ring Structure of Sulphur

Both rhombic and monoclinic sulphur exists in the form of S_8 molecules. These S_8 molecules are in the form of a ring. It forms a crown-shaped molecule with four atoms on the top and four atoms at the bottom.

The rhombic and the monoclinic forms differ in the arrangement of these S_8-puckered rings. In rhombic sulphur, these rings fit snugly into each other while in monoclinic sulphur the rings are stacked one on top of the other.

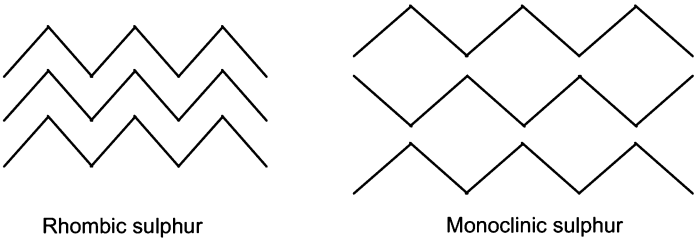


Figure 9.8

Action of Heat on Sulphur

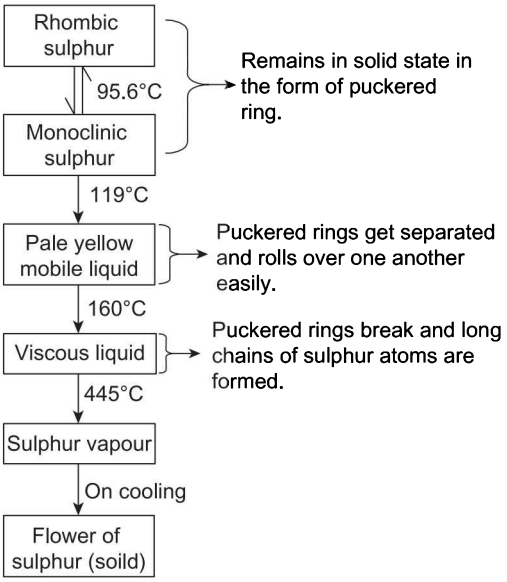


Figure 9.9 Process flow chart for heating of sulphur

Chemical Properties

Properties	Reactions
	1. With nonmetals
(i) Oxygen	$S + O_2 \xrightarrow{300°C} SO_2$
	$2S + 3O_2 \rightarrow 2SO_3$ (trace amounts)
(ii) Hydrogen	$S + H_2 \rightarrow H_2S$ (boiling)
(iii) Carbon	$C + S \rightarrow CS_2$ (coke)
(iv) Chlorine	$2S + Cl_2 \rightarrow S_2Cl_2$
	2. With metals
(i) Mercury	$Hg + S \rightarrow HgS$
(ii) Copper	$2Cu + S \rightarrow CuS$
(iii) Iron	$Fe + S \rightarrow FeS$
	3. With acids
(i) Sulphuric acid	$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
(ii) Nitric acid	$S + 6HNO_3 \rightarrow H_2SO_4 + 6NO_2 + 2H_2O$

Uses

Sulphur is used in the manufacture of insecticides, gunpowder and crackers. The most important use of sulphur is in the vulcanization of rubber.

Compounds of Sulphur

Sulphur due to its high reactivity forms a wide variety of compounds. The industrially useful compounds are sulphuric acid, hydrogen sulphide and sulphur dioxide.

Hydrogen Sulphide (H_2S)

Hydrogen sulphide is prepared by the action of dilute hydrochloric acid or dilute sulphuric acid on iron sulphide:

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

Physical Properties

It is heavier than air and dissolves moderately in water due to partial ionization. It is acidic in nature. It is also known for its characteristic rotten egg smell.

Chemical Properties

Properties	Reactions
Reducing nature	$2H_2S + O_2 \rightarrow 2S + 2H_2O + CuS$
1. with oxygen	
2. with metals	$CuSO_4 + H_2S \rightarrow H_2SO_4 + CuS$ (acidified solution of Cu)
3. with potassium permanganate	$2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$
4. with nonmetals	$H_2S + Cl_2 \rightarrow 2HCl + S$

Uses

It is used as a laboratory reagent as it gives coloured precipitates with metal salts. It is also used as a reducing agent.

Sulphur dioxide (SO_2)

Occurrence

Sulphur dioxide exists in trace amounts in the atmosphere in the industrial areas. It is mainly present in atmosphere due to burning of coal and petroleum products.

Preparation

Copper on treating with concentrated sulphuric acid evolves SO_2 gas:

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

Physical Properties

It is a colourless, pungent smelling gas which is fairly soluble in water. It is heavier than air and boils at −10°C.

Chemical Properties

Chemical Properties	Reaction involved
Acidic nature	Sulphur dioxide changes blue litmus to red.
(i) With litmus	Sulphur dioxide with water forms an unstable sulphurous acid.
(ii) Reaction with water	$H_2O + SO_2 \rightarrow H_2SO_3$
Reducing properties Bleaching action	Sulphur dioxide on reaction with moisture or water, produces nascent hydrogen which helps in the reducing action.
	$SO_2\uparrow + H_2O \rightarrow H_2SO_4 + 2[H]$ (reducing agent). The nascent hydrogen produced on being exposed to moisture acts as a bleach.
Addition reactions	$SO_2 + Cl_2 \rightarrow SO_2Cl_2$
Oxidizing property	$2Mg + SO_2 \rightarrow 2MgO + MgS$

Uses

It is used for the preparation of sulphuric acid and different germicides, insecticides, etc. It is used as a bleaching agent, and antichlor in textile industry.

Sulphuric acid

Sulphuric acid is the most widely used chemical in the industry. The role of sulphuric acid in chemical industry is so significant that it is generally termed as the king of chemicals. It is also known as oil of vitriol as it is being prepared by the distillation of green vitriol ($FeSO_4.7H_2O$).

Occurrence

Sulphuric acid mainly occurs in free state in the hot water of sulphur springs. In combined state, it occurs in mineral sulphates, such as Epsom salt ($MgSO_4.7H_2O$). Glauber's salt ($Na_2SO_4.10H_2O$) and green vitriol ($FeSO_4.7H_2O$).

Manufacture of Sulphuric Acid

The large-scale manufacture of sulphuric acid is carried out by the contact process.

Contact Process

In this process, the basic raw material required is SO_2, which is produced by burning sulphur:

$$S + O_2 \rightarrow SO_2$$

Manufacture of sulphuric acid from SO_2 takes place in two steps.

Step I

Sulphur dioxide and oxygen in the ratio of 2 : 1 by volume is passed over vanadium pentoxide, maintained at 450°C under high pressure conditions. Under these conditions, the sulphur dioxide and oxygen react with each other to form sulphur trioxide. Platinized asbestos can also be used in the place of V_2O_5.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Step II

Sulphur trioxide thus obtained is dissolved in sulphuric acid to form pyrosulphuric acid or oleum:

$$\underset{\text{(Oleum)}}{SO_3} + H_2SO_4 \rightarrow H_2S_2O_7$$

The pyrosulphuric acid on treatment with water gives out sulphuric acid:

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

The sulphuric acid prepared by this method is pure and highly concentrated.

Physical Properties

It is a colourless, odourless liquid with density of 1.85 g/cc. It has a boiling point of 338°C.

Chemical Properties

Properties	Reactions
1. As an oxidizing agent	$2H_2SO_4 \xrightarrow[\text{retort}]{\text{red hot}} 2H_2O2SO_2 + O_2$
2. With metals	$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$
3. With bases	$KOH + H_2SO_4 \rightarrow KHSO_4 + H_2O$ $2KOH + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O$
4. With non-metals	$C + H_2SO_4 \rightarrow CO_2 + 2H_2O + 2SO_2$
5. As a dehydrating agent	$C_6H_{12}O_6 \xrightarrow{H_2SO_4} 6C + 6H_2O$

Uses

It is used as a raw material in the manufacture of fertilizers, batteries, rubber, detergents, etc. It is also used as a dehydrating agent.

Sulphuric acid forms some salts like blue vitriol ($CuSO_4 \cdot 5H_2O$), green vitriol ($FeSO_4 \cdot 7H_2O$), alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$) and ammonium sulphate $(NH_4)_2SO_4$, which play a significant role in the industries.

Copper Sulphate ($CuSO_4 \cdot 5H_2O$)

Copper sulphate is a blue coloured crystalline substance. It loses its crystalline property when heated at 250°C where it loses its 5 molecules of water and becomes a white amorphous powder.

In the aqueous state, it can conduct electricity and thus be helpful in electroplating, electrotyping, etc. It is also used as a germicide due to its poisonous nature.

Green Vitriol ($FeSO_4 \cdot 7H_2O$)

Green vitriol is a light green crystalline solid. It turns to reddish brown colour on exposure to air due to aerial oxidation to ferric sulphate. It is used in dyeing and tanning industries.

Alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)

Alum is a double salt. It is a white crystalline solid soluble in water. On heating, it loses its water of crystallization above 92°C and forms a swollen mass called burnt alum which is used in medicines. It is mainly used to purify drinking water, as a mordant in dyeing and also in paper and tanning industries.

Ammonium Sulphate $(NH_4)_2SO_4$

Ammonium sulphate is the most common nitrogenous fertilizer in agriculture. This is prepared by passing ammonia gas and carbon dioxide through a suspension of powdered gypsum in water.

It is a white crystalline solid which is used for the preparation of alum, ammonium chloride and is also used as a laboratory reagent.

Chlorine

Chlorine is a nonmetal belonging to the VIIA group of the periodic table and is called a typical halogen. It is a highly reactive element and generally exists in combined state. The most widely used compound of chlorine is hydrogen chloride. On dissolution in water, it gives out hydrochloric acid.

Hydrogen Chloride and Hydrochloric Acid

Hydrogen chloride was first synthesized by Glauber by heating common salt with concentrated sulphuric acid.

Occurrence

In free state, hydrogen chloride gas is found in trace amounts in volcanic regions. Hydrochloric acid is secreted as gastric juices in the stomach during digestion.

Laboratory Preparation

Metallic chloride on treatment with conc. H_2SO_4 liberates HCl. This when passed through water gives out hydrochloric acid:

$$NaCl + H_2SO_4 \xrightarrow{<200°C} NaHSO_4 + HCl$$

Physical Properties

It is a colourless gas with pungent odour and has sour taste. It is extremely soluble in water. Its melting point is −115°C and boiling point is −85°C.

Chemical properties

Properties	Reactions
With water	$HCl + H_2O \therefore H_3O^+ + Cl^-$
With ammonia	$NH_3 + HCl \rightarrow NH_4Cl$

Physical Properties

It is a colourless gas with pungent odour and has sour taste. It has a boiling point of 109.8°C and is a corrosive acid.

Chemical Properties

Properties	Reactions
1. With water	$HCl_{(g)} + H_2O \therefore H_3O^+ + Cl^-$ (dil)
2. With metals	$Mg + 2H\underset{(dil)}{Cl} \rightarrow MgCl_2 + H_2$ $Ca + 2HCl_{(g)} \rightarrow CaCl_2 + H_2$

Properties	Reactions
3. With base	$K_2O + \underset{(dil)}{2HCl} \rightarrow 2KCl + H_2O$
4. With metal carbonates	$NH_3 + HCl \rightarrow NH_4Cl$ $K_2CO_3 + \underset{(dil)}{2HCl} \rightarrow 2KCl + H_2O + CO_2$
5. With metal sulphides	$Na_2S + \underset{(dil)}{2HCl} \rightarrow 2NaCl + H_2S$
6. Reducing properties	$MnO_2 + \underset{(Conc)}{4HCl} \rightarrow MnCl_2 + 2H_2O + Cl_2$
7. With metal sulphites	$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2$

Uses

Hydrochloric acid is mainly used in the manufacture of silver chlorides, dyes, drugs and paints. It is used in the extraction of glue, soldering metals, leather industry and pickling of metals.

EXAMPLE

In the preparation of ammonia gas from ammonium chloride and calcium hydroxide, the reactants are ground thoroughly. Why?

SOLUTION

It increases the surface area of the reactants which helps in speeding up the reaction.

EXAMPLE

The yellowish tinge of nitric acid can be removed by the dropwise addition of water to it. Give reasons.

SOLUTION

By the addition of water drop by drop to nitric acid, nitrogen dioxide present in it gets converted to nitric acid. Since the yellow tinge is due to NO_2, HNO_3 becomes almost colourless by this process.

EXAMPLE

Gold and platinum do not dissolve either in concHCl or concHNO$_3$, but dissolves in the mixture of 3 parts of conc HCl and 1 part of conc HNO_3. Give reason and write the necessary chemical equations.

SOLUTION

The dissolution of noble metals in aquaregia can be justified as follows.

(i) The concentrated nitric acid oxidises concentrated hydrochloric acid to liberate nascent chlorine.

$HNO_{3(conc)} + 3HCl_{(conc)} \rightarrow NOCl + 2H_2O + 2[Cl]$

Nitrosyl chloride Nascent chlorine

(ii) Nascent chlorine reacts with noble metals to form their soluble chlorides which pass into the solution.

$Au + 3[Cl] \rightarrow AuCl_3$

Gold Gold[III]chloride

$Pt + 4[Cl] \rightarrow PtCl_4$

Platinum Platinum(IV)chloride

EXAMPLE

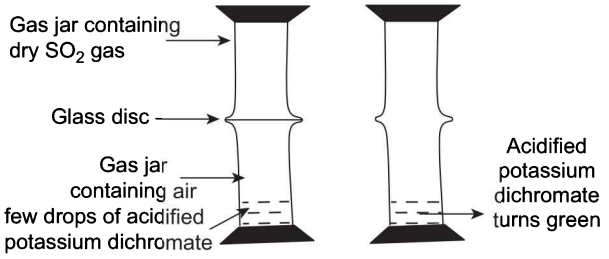
(a) Explain an activity to prove that sulphur dioxide is heavier than air.

(b) Experimentally prove that sulphur dioxide is fairly soluble in water.

SOLUTION

(a) Experiment to prove that sulphur dioxide is heavier than air.

A clean gas jar containing air is taken. Few drops of acidified potassium dichromate is taken in it. A dry glass disc is placed over it. Over this, another gas jar containing sulphur dioxide gas is inverted and then the glass disc is removed. After few minutes acidified potassium dichromate turns green. This proves that sulphur dioxide is heavier than air.

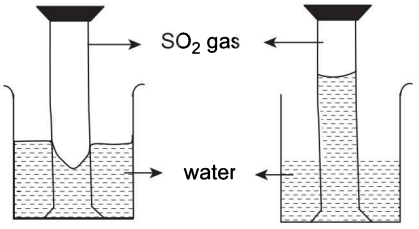


$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(b) Experiment to prove that sulphur dioxide is fairly soluble in water:

A gas jar containing sulphur dioxide gas is inverted in a trough of water and the initial level of water in the jar is noted.

After sometime it is found that the level of water rises up in the jar. It is because, sulphur dioxide gas dissolves in water and the water rises up.



$SO_2 + H_2O \rightarrow H_2SO_3$

EXAMPLE

Three jars labelled as A, B and C filled with SO_2 gas are taken. A burning wooden splinter, burning sodium and burning potassium are introduced into the jars, A, B and C respectively. What are the observations? Explain with reason and give the corresponding reactions.

SOLUTION

The burning splinter is put off while burning sodium and potassium, continue burning.

Reason: The heat produced due to burning of metals dissociates the molecule of sulphur dioxide to sulphur and oxygen. The oxygen so liberated sustains combustion of the metals.

$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$

Potassium sulphite — Potassium thiosulphate

$4Na + 3SO_2 \rightarrow Na_2SO_3 + Na_2S_2O_3$

Some Industrially Useful Compounds

Lime

It is also called quick lime, the chemical name of which is calcium oxide.

Manufacture

Principle

Heating of limestone at 1073 K–1273 K in lime kiln gives out lime. In this the decomposition of calcium carbonate takes place. The process is called calcination.

$CaCO_3 \rightarrow CaO + CO_2$

Process

The manufacturing process is carried out in a furnace called lime kiln. Limestone is introduced into the kiln from the top. It is heated to a temperature of about 1500 K. The complete decomposition of limestone takes place at around 1273 K. Since the reaction is reversible in nature, an outlet is arranged at the top of the furnace through which CO_2 is expelled during the process. Lime formed at the bottom is collected at regular intervals.

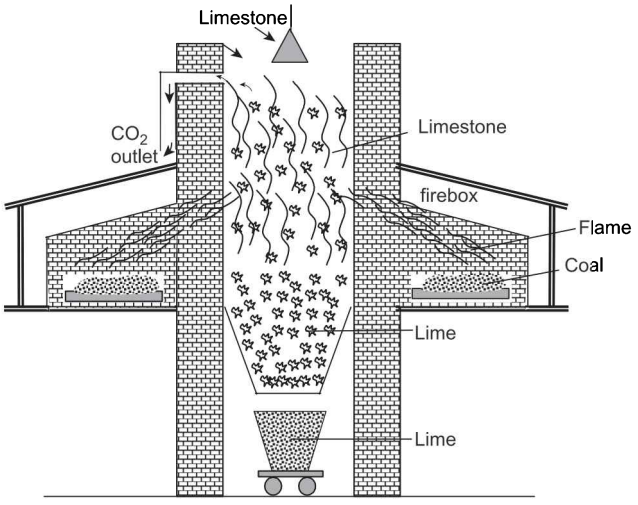


Figure 9.10 A vertical lime kiln

Properties of Lime

(i) Calcium oxide is an amorphous white solid.

(ii) It has a high melting point of 2273 K.

(iii) Heating it at a very high temperature produces white light.

(iv) Reaction with water: Calcium oxide reacts with water to give out calcium hydroxide or slaked lime. This reaction is highly exothermic. A hissing sound is observed during this reaction.

This reaction is called slaking of lime:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat}$$

(v) Reaction with acid: It is a basic oxide and reacts with an acid forming salt and water:

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$

Uses of Lime

(i) Used as a drying agent.

(ii) Used in the manufacture of cement, glass and calcium chloride.

(iii) Used in the manufacture of washing soda and bleaching powder.

(iv) Used as a lining for furnaces.

(v) Extensively used for white washing.

One of the important reactions of CaO is slaking of lime. During slaking of lime, slaked lime is prepared by the reaction of CaO with water.

Slaked Lime ($Ca(OH)_2$)

Slaked lime is an amorphous white substance. It is sparingly soluble in water and its solubility decreases with temperature. It is used in agriculture, in the manufacture of bleaching powder, caustic soda, glass, etc. and also used for removing temporary hardness of water.

Washing Soda

Washing soda is an important constituent of many detergents. The chemical name of washing soda is sodium carbonate decahydrate with the formula $Na_2CO_3.10H_2O$. The anhydrous form of it is known as soda ash.

Manufacture

The process employed for the large-scale preparation of washing soda is ammonia–soda process or Solvay process.

Principle

The basic reaction involved in the process is double decomposition reaction between NaCl and $CaCO_3$:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

But the reaction between NaCl and $CaCO_3$,being reversible, cannot be directly used for the process. Therefore, a process involving other chemical compounds is employed for the manufacture of washing soda.

Raw Materials Used

The raw materials used are sodium chloride, ammonia and limestone.

The entire process takes place in various stages.

Stage 1: *Saturation of brine solution with ammonia*

Brine solution is taken in a saturation tower of the plant. Ammonia gas containing little amount of CO_2 is passed into it. Ammonia reacts with CO_2 to form ammonium carbonate. This ammonium carbonate renders precipitation of impurities of magnesium, calcium and iron as carbonates:

$$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + MgCl_2 \rightarrow MgCO_3\downarrow + 2NH_4Cl$$

The precipitates are removed by filtration. The filtrate is cooled and sent to the next stage.

Stage 2: *Carbonation*

This process takes place in the carbonation tower. The tower consists of perforated plates arranged one above the other. The ammonical brine from saturation tower is dropped into the carbonation tower and CO_2 gas is forced to bubble up under pressure at the base. The perforated plates help in the mixing up of CO_2 thoroughly with the solution. The pure brine solution in the presence of ammonium hydroxide reacts with CO_2 to form sodium bicarbonate and ammonium chloride:

$$NaCl + NH_4OH + CO_2 \rightarrow NaHCO_3 + NH_4Cl$$

Stage 3: *Filtration*

The reaction mixture from carbonation tower is subjected to filtration in a rotary vacuum filter. The sodium bicarbonate precipitate is separated. The filtrate contains ammonium salts and is sent into ammonia regeneration tower, where ammonia is regenerated and can be reused.

Stage 4: *Calcination*

The precipitate of sodium bicarbonate obtained in the third stage is subjected to heating and gives out sodium carbonate. This on recrystallization from water produces hydrated sodium carbonate, i.e., washing soda:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

$$Na_2CO_3 + 10H_2O \rightarrow Na_2CO_3{\cdot}10H_2O$$

Stage 5: *Regeneration of raw materials*

The filtrate from the third stage is sent into a regeneration tower. The calcium oxide from lime kiln dissolves in water to give $Ca(OH)_2$.This, on reaction with ammonium salts present in the filtrate, gives out ammonia again. Carbon dioxide gas produced in stage 4 can be recirculated in the 1st stage.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + 2H_2O$$

Advantages of Solvay Process

(i) Cheap and abundant raw materials.

(ii) CO_2 formed in the process is recycled in the process. So it is not required to take fresh $CaCO_3$ each time.

(iii) $CaCl_2$ is obtained as a by-product.

(iv) The raw materials are regenerated.

Properties of Washing Soda

(i) It is a white crystalline substance which loses water of crystallization on exposure to air and forms a monohydrate. Hence, it is called an efflorescent salt. The loss of water takes place in stages.

$$Na_2CO_3 \cdot 10H_2O \rightarrow Na_2CO_3 \cdot 9H_2O \rightarrow Na_2CO_3 \cdot H_2O$$

(ii) Action of heat: The hydrated salt loses water of crystallization completely to form an anhydrous salt.

$$Na_2CO_3 \cdot 10H_2O \rightarrow Na_2CO_3 + 10H_2O$$

Uses of Washing Soda

(i) Used in glass industry

(ii) Used in soap industry

(iii) Used in softening of hard water

(iv) Paper and textile industry

(v) Metal refining

(vi) Used in paints and dyes

(vii) Used in laundry

(viii) Used in the manufacture of other compounds of sodium

Baking Soda

It is an important constituent of baking powder and is used for cooking purposes. The chemical name of baking soda is sodium hydrogen carbonate or sodium bicarbonate.

Manufacture

Solvay process is employed for the preparation of sodium bicarbonate on a large scale. The precipitate obtained in stage 3 of Solvay process being sodium bicarbonate can be dried and used as a commercial sample:

$$NaCl + NH_4OH + CO_2 \rightarrow NaHCO_3 + NH_4Cl$$

Properties of the Baking Soda

(i) Baking soda is a white crystalline solid.

(ii) It is sparingly soluble in water and gives out an alkaline solution.

(iii) A solution of sodium bicarbonate on heating evolves CO_2 gas forming sodium carbonate:

$$2NaHCO_3 \xrightarrow{\text{Heat}} Na_2CO_3 + H_2O + CO_2$$

Due to this property, it is added to food stuffs to aerate the dough and gives puffy nature to the food material made from the dough.

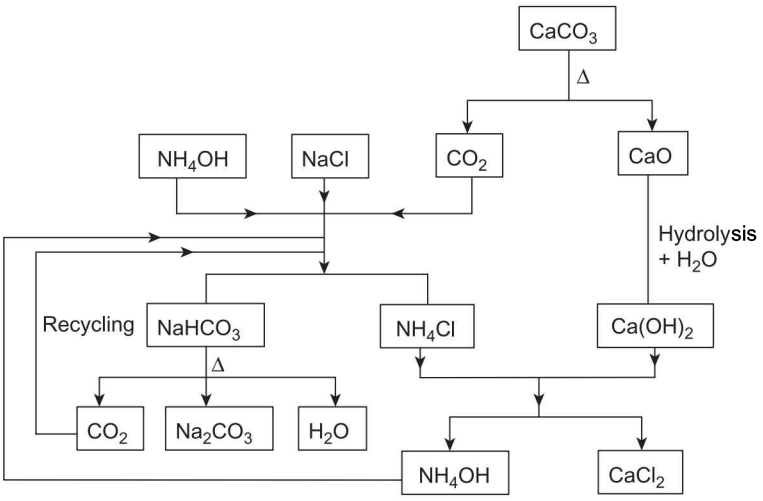


Figure 9.11 Flow Chart representing Solvay process for the preparation of washing soda and baking soda

Uses of Baking Soda

(i) It is used as an antacid.

(ii) A mixture of sodium bicarbonate and tartaric acid is called baking powder. It is an important additive for food and drinks. Sodium bicarbonate, on decomposition, gives out CO_2, which causes bread and cakes to rise. Sodium carbonate produced in the process gets neutralized by tartaric acid present in baking powder.

(iii) Sodium bicarbonate is taken as one of the constituents in fire extinguishers. A solution of sodium bicarbonate and sulphuric acid is taken in an extinguisher. These are kept separately and they come in contact with each other when the knob is pressed or the extinguisher is inverted. When these two solutions react, CO_2 gas is liberated and it puts out the fire. These are called soda acid fire extinguishers.

Bleaching Powder

It is the major constituent of domestic cleaning agents and is also called the chloride of lime. The chemical name of bleaching powder is calcium oxychloride and formula is $CaOCl_2$.

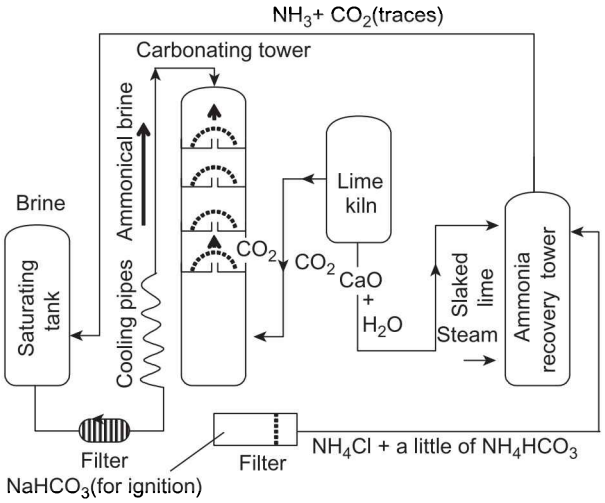


Figure 9.12 Flow diagram of Solvay process

Manufacture

Bleaching powder can be prepared on large scale in Hasenclever plant or in Bachmann plant. In both the cases, the principle and process are the same.

Principle

Chlorine reacts with dry slaked lime to form calcium oxychloride:

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$

Manufacturing Process in Hasenclever Plant

The plant consists of a number of horizontal cylinders provided with rotating shafts with blades. Slaked lime is dropped into the topmost cylinder. The revolving blades allow the downward movement of slaked lime into the other cylinders. Chlorine gas is introduced into the bottommost cylinder. The counter currents allow a thorough mixing of the raw materials and complete conversion into bleaching powder.

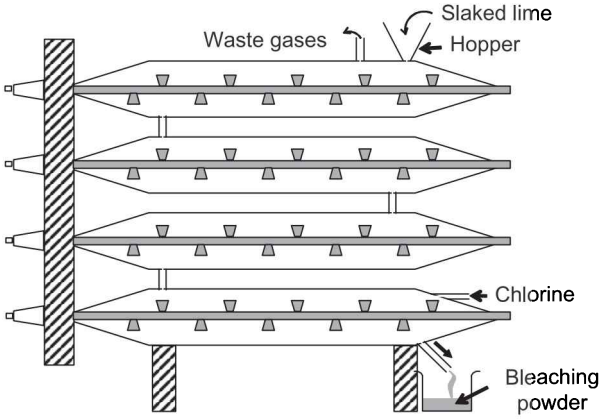


Figure 9.13 Hasenclever plant for the manufacture of bleaching powder

Properties of Bleaching Powder

(i) Bleaching powder is a white amorphous powder with a pungent smell of chlorine. It is considered a mixed salt of calcium chloride and calcium hypochlorite [$CaCl_2 + Ca(OCl)_2$].

(ii) **Reaction with moist air**: On long standing, bleaching powder undergoes auto-oxidation and loses chlorine:

$$6CaOCl_2 \xrightarrow[\text{air}]{\text{Moist}} 5CaCl_2 + Ca(ClO_3)_2$$

(iii) **Reaction with cold water**: On dissolution in water, bleaching powder dissociates to give chloride and hypochlorite ions:

$$CaOCl_2 + 2H_2O \rightarrow Ca(OH)_2 + HCl + HOCl$$

$$HOCl \rightarrow HCl + [O]$$

hypochlorous acid

$$HCl \rightarrow H^+ + Cl^-$$

chloride

(iv) **Reaction with hot water**: In hot water, the hypochlorite ion undergoes autooxidation to give chlorate ions and chloride ions:

$$3ClO^- \rightarrow ClO_3^- + 2Cl^-$$

(v) Reaction with dilute acids: On reacting with a small amount of dilute acid, bleaching powder dissociates to give hypochlorous acid which can furnish nascent oxygen. This is the reaction used for determining the quality of bleaching powder.

$$2CaOCl_2 + H_2SO_4 \rightarrow CaCl_2 + CaSO_4 + 2HOCl$$

$$HOCl \rightarrow HCl + [O]$$

(vi) Reaction with excess dilute acid: On reacting with an excess amount of dilute acid, bleaching powder liberates chlorine gas:

$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2\uparrow$$

(vii) Reaction with CO_2: On passing CO_2 gas along with water through a paste of bleaching powder, chlorine gas is evolved:

$$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2\uparrow$$

Uses of Bleaching Powder

(i) Used for the sterilization of drinking water

(ii) Used as a bleaching agent for cotton and paper pulp

(iii) Used in the preparation of chloroform

(iv) Used as an oxidizing agent and chlorinating agent

Plaster of Paris

Plaster of Paris is an important compound used in the construction work and in orthopaedics for joining fractured bones. The chemical name of Plaster of Paris is calcium sulphate hemihydrate with the formula $CaSO_4.½H_2O$.

Manufacture

Principle

Plaster of Paris is manufactured from naturally occurring calcium sulphate dehydrate, which is commonly called gypsum. Gypsum is sparingly soluble in water. On heating it carefully at 120°C to 130°C, it loses water of crystallization and becomes $CaSO_4 \cdot ½H_2O$:

$$CaSO_4 \cdot 2H_2O \xrightarrow{100°C-130°C} CaSO_4\,\tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O$$

Properties of Plaster of Pairs

It is a white amorphous powder. Setting is the most important property of plaster of Paris. On mixing with water, plaster of Paris becomes a paste. On standing, this paste sets to a hard mass of gypsum. This process is called setting.

$$CaSO_4 \cdot ½H_2O + 1½H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

Uses of Plaster of Pairs

(i) Manufacture of crucibles

(ii) Making of casts and moulds

(iii) Dental fillings

(iv) Surgery for setting fractured bones

(v) Preparation of chalks

(vi) Making false ceilings and giving designs on the walls

(vii) For sealing the air gaps in laboratory apparatus for making them air tight

Cement

Cement, more popularly known as Portland cement, is the most important building material. The name "Portland cement" originated on the basis of the fact that it resembled a type of natural limestone available in an island named Portland.

Manufacture

Limestone and clay are the major raw materials used for the manufacture of cement.

Principle

Limestone dissociates at high temperature and provides calcium oxide required for the process. Clay provides SiO_2 and Al_2O_3, which take part in a series of chemical reactions with calcium oxide to produce cement.

Process

The manufacture of cement can be done in two stages. The first stage involves the formation of a homogeneous mixture of the raw materials. This stage can be carried out in two processes, namely, wet process and dry process.

First Stage

(i) *Wet process*

Limestone is crushed to a fine powder. Clay is purified and mixed with fine powder of lime stone in the required proportion. A homogeneous slurry is formed by grinding the above mixture with the required quantity of water.

(ii) *Dry process*

Powdered limestone and clay are mixed in proper proportions. The mixture is then subjected to drying and pulverization. The uniform, finely powdered mixture obtained is called raw meal.

Second Stage

The 2nd stage of the process is carried out in a rotary kiln. The rotary kiln is made up of steel and consists of a long cylinder 6 to 10 ft in diameter and 100 to 250 feet in length. It is lined inside with fire bricks. This cylinder can rotate with a speed of 30 to 60 turns per hour.

The slurry or raw meal formed in the first stage is called charge. The charge is introduced into the rotary kiln through a conveyer arranged at one end. A burner is arranged at the other end of the kiln, and it supplies heat to the kiln. The charge introduced at one end slowly moves towards the hot end of the kiln. As it gets heated up, it loses water and CO_2. Limestone provides calcium oxide. SiO_2 and Al_2O_3 form aluminium silicates. A series of chemical reactions takes place between calcium oxide and aluminium silicates.

A mixture of calcium silicate, aluminium silicate and calcium aluminium silicate is formed. The resultant product formed is in the form of hard agglomerate known as clinker. After cooling, the clinker is ground to a fine powder. Further, 2–3% gypsum is added to this and again made into a fine powder. This fine grey powder is called cement. It is stored in air-tight bags.

Applications of Cement

Cement is a homogeneous fine grey powder, which sets after a few hours when mixed with water and then hardens over a period of time into a hard solid. The addition of gypsum to cement decreases the setting time of cement. This property of setting to a hard mass makes cement useful in construction work in various forms such as mortar, concrete, etc.

Mortar

A mixture of slaked lime, sand and water is known as mortar or lime mortar. This also has the property of setting to a hard mass due to the evaporation of water coupled with the slow conversion of calcium hydroxide into calcium carbonate by atmospheric carbon dioxide. If cement is added to mortar, it is called cement mortar. It is harder than the ordinary mortar and is water proof.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

$$Ca(OH)_2 + SiO_2 \rightarrow CaSiO_3 + H_2O$$

Concrete

For construction purposes, cement is mixed with sand and small pieces of crushed stones. This mixture is known as cement concrete. This sets to a hard mass. If steel rods or bars or any other hard material is embedded in the wet concrete, during setting process, the hard mass holds the steel rod or bar thus increasing the strength and the hardness of the resulting structure. Because of reinforcement by steel structure in the concrete, the total system is called "reinforced concrete cement" (RCC).

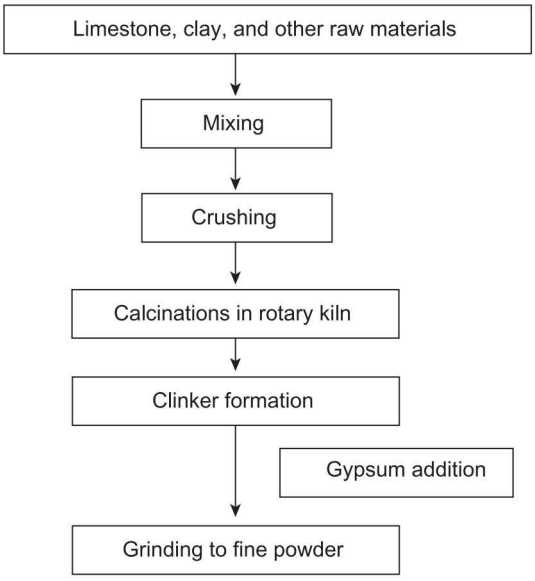


Figure 9.14 Process Flow Chart for the Manufacture of Cement

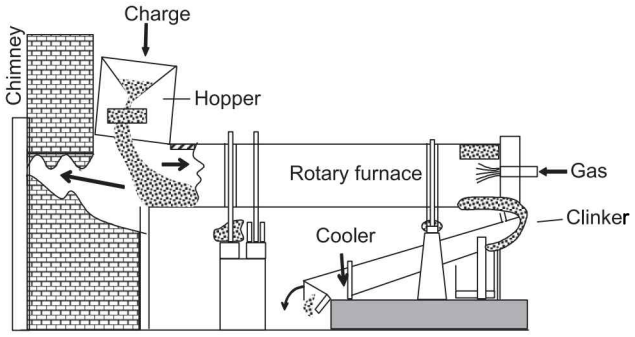


Figure 9.15 Rotary kiln

Glass

Glass is a transparent or translucent material which finds applications in domestic and industrial purposes. Chemically, glass is a homogeneous liquid with very high viscosity made by sodium and calcium silicates with sand. Though these are the major constituents of glass, other compounds are also present in glass depending on the type of glass. Therefore, it has no definite chemical formula.

Manufacture of Glass

The common raw materials used in manufacture of glass are soda ash, limestone and silica sand.

Principle

At high temperature, sodium carbonate and calcium carbonate react with silicon dioxide to give out sodium silicate and calcium silicate with the liberation of CO_2 gas:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2\uparrow$$

Process

A finely powdered mixture of sodium carbonate, calcium carbonate and silicon dioxide is called batch. This batch is mixed with broken glass pieces called cullet. This mixture is subjected to heating at 1600–1700 K. The impurities called glass gall rise to the surface. Due to the high temperature, the mixture is fused. The addition of cullet also increases the fusibility of the mixture. SiO_2 present in the reaction mixture reacts with sodium carbonate and calcium carbonate to form sodium silicate and calcium silicate. Bubbles appear during the process due to the evolution of CO_2 gas. When no more bubbles are observed in the process, the reaction can be considered to have completed. The entire mass is observed as a clear liquid.

Cooling

The process of cooling is a very important step in the manufacture of glass. It should be done very carefully. Rapid cooling results in brittle and fragile glass. Very slow cooling gives opaque glass. Hence, the cooling should neither be too rapid nor too slow. The process of cooling done at a moderate and uniform rate is called annealing. It results in the formation of good quality glass. The process of annealing is carried out by passing the liquid glass through a chamber with varying temperature zones on a conveyer belt.

Process Flow Chart for the Manufacture of Glass

Characteristics of Glass

Glass is a supercooled liquid with very high viscosity. Due to high viscosity, it appears as a solid. Though it is built up of tetrahedral silicate units, the arrangement of these units is not regular in glass. Hence, it has no definite softening point.

Glass Blowing

This is a technique of shaping of glass articles. This is done by melting glass partially and blowing hot air by machine. This can be applied only for heat resistant varieties of glass.

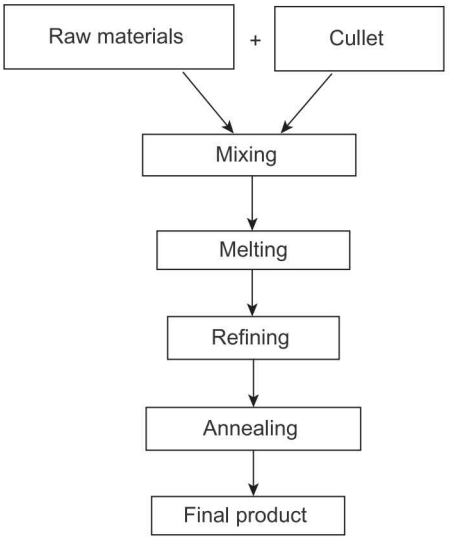


Figure 9.16 Process flow sheet for the manufacture of glass

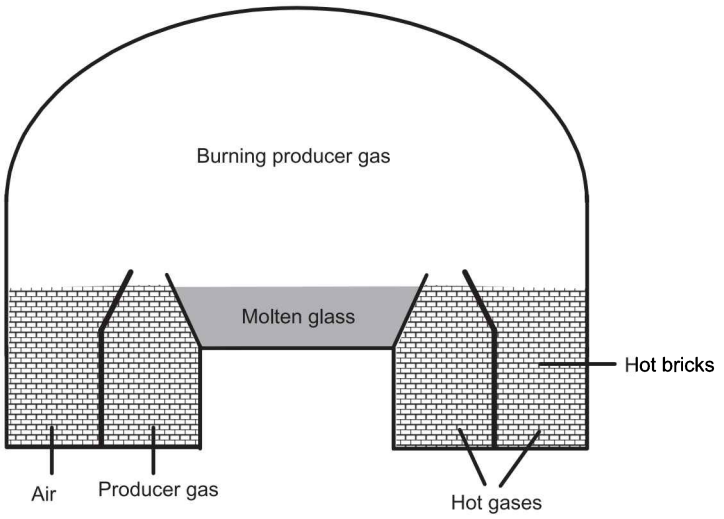


Figure 9.17 Manufacture of glass (tank furnace)

Varieties of Glass

Since glass has a wide range of applications in different fields of industry, it is expected to have the required characteristics suitable for different purposes. Different characteristics can be attributed to glass by varying the composition of glass with doping of suitable compounds.

Types of glass	Composition	Properties	Uses
1. Soda glass or soft glass	Common type Na_2CO_3, $CaCO_3$ and SiO_2	a. Fuses at low temperature b. Brittle c. Cracks easily d. ttacked by chemicals e. Cheap	Window glass, mirrors, common glassware
2. Hard glass	K_2CO_3 and $CaCO_3$ and SiO_2	a. Hard b. Resistant to acids	Hard glass apparatus
3. Lead crystal glass	K_2CO_3, PbO and SiO_2	a. High refractive index b. Sparkling	Expensive glass ware, decorative items
4. Pyrex glass	SiO_2, CaO, borax	a. Resistance to chemicals b. Thermal resistance	Laboratory apparatus, injection ampules, ovenware
5. Optical glass and flint glass	$SiO_2 + Pb_3O_4 + K_2CO_3 + CaCO_3$	a. More lustre b. High refractive index c. Soft d. Scratches easily	Prisms, lenses, optical devices
6. Photochromatic glass	$SiO_2 + Na_2CO_3 + CaCO_3 + AgX$	Darkens on exposure to bright light	Sunshield goggles, photogrey spectacles
7. Safety glass	A layer of transparent plastic between two layers of glass	Not broken easily	Wind screens of aeroplanes, automobiles, bullet proof glasses, etc.
8. Coloured glass	Transition metal oxides (trace amount as dopants are added to impart colour)	Different colours	Decorative articles, window panes, artificial gems
9. Crookes glass	Flint glass + Cerium oxide	Cuts off UV light	Optical lenses

Coloured Glasses

Compounds as dopants	Colours of glass
Cr_2O_3	Green
MnO_2	Purple
$AuCl_3$	Ruby
$CuSO_4$	Blue
Cu_2O	Red

Ceramics

Ceramics are materials containing non-metallic oxides, borides, carbides and nitrides. These are hard and brittle and are resistant to heat and chemicals. They are non-conductors of electricity. Therefore, ceramics are used as good insulators. However, silicon carbide is an excellent conductor of electricity.

Ceramics find applications from very simple pottery to very high technological areas of modern science.

Manufacture of Ceramics

Principle

The way the ceramics is manufactured is called powder metallurgy route. In the process, different raw materials (inorganic oxides like clay, lime stone, feldspar, magnetite, dolomite, synthetic oxides like fused alumina, fused magnesia, etc.) are mixed in a definite proportion depending on the end product. The mixed oxides are calcined and then crushed into different sizes. The different-sized fractions are mixed with binders, pressed into components and sintered at high temperature.

Process flow chart for the manufacture of specific ceramic products like refractory, pottery or porcelain

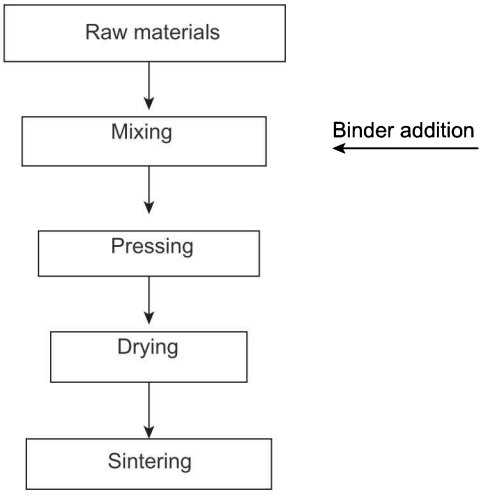


Figure 9.18 Process flow sheet for the manufacture of ceramics

Process of the Manufacture of Specific Ceramic Products

(i) Simple pottery

Crushed and finely powdered clay is taken. Water is added to this powder and kneaded to a hard mass. This mass can be moulded into various shapes on a rotating wheel. Then, these articles are dried in air. The dried articles are arranged in a kiln and subjected to heating up to 1373 K. The heating is done in a careful and controlled way. It loses water at 923 K and CO_2 at 1173 K. At this high temperature, SiO_2 and Al_2O_3 react with each other to form aluminium silicate. On heating further to a slightly higher temperature, these silicate units cling together and form interlocking units. Thus, the articles become hard, brittle and porous on heating.

(ii) Earthenware and Porcelain ware

Raw materials used for this type of ceramics are kaolin, fine sand and feldspar. The pulverized mixture of raw materials is kneaded with water into a thick mass. This paste is moulded into various shapes and then dried in air chambers. These dried articles are subjected to fixing at much higher

temperatures than to what is done in case of simple pottery. The heating of these goes up to 1300 to 1500 K. The articles obtained are porous.

Since feldspar contains some metal oxides in addition to SiO_2 and Al_2O_3, at a high temperature, a mixture of silicates is formed. The earthenware obtained after the process of firing is porous. To make it impervious to liquids, these articles are subjected to a process called glazing. A molten mixture of feldspar, silica, borax and water is made into a paste by heating. The articles obtained after the process of firing are dipped in this paste and then they are subjected to reheating strongly. Thus, the pottery gets glazy appearance and also loses its porosity.

(i) Areas of application of ceramic materials

High temperature applications

(a) in refractories

(b) heat insulation material

(ii) Electrical applications

(a) Electrical insulator used in electric transmission lines

(b) Electrical charge arrestor

(c) Magnetic materials used in power applications, telecommunications, microwave applications, etc.

(iii) Other applications

Abrasive materials, cutting tools, bioceramics like dental implants, artificial bones, etc.

Common Fertilizers

Plants require around 12 elements for their healthy growth. Among these, the elements required in major amounts are called macronutrients. They are nitrogen, phosphorous and potassium. The elements required in lesser amounts are called micronutrients. They are calcium, sodium, sulphur and magnesium. Apart from these, some other elements like copper, molybdenum, manganese, cobalt, zinc, boron and iron are also required in trace amounts.

Most of these nutrients are available in the form of their compounds in the soil. Plants absorb these water soluble minerals from soil through roots. Over a period of time, the minerals in the soil get exhausted and the soils become deficient of these nutrients. Hence, it becomes essential to replenish the soils with the nutrient elements in order to make them useful for further growth of crops. Those materials added to the soil for this purpose are called fertilizers.

Fertilizers are basically of two types as listed hereunder:

(a) natural fertilizers and

(b) synthetic fertilizers.

(i) Natural fertilizers

They include manures like cow dung and compost. Decayed products of animal wastes and plant wastes also can be used as natural fertilizers.

(ii) Synthetic or chemical fertilizers

Depending on the macronutrient available in a particular fertilizer, the fertilizers are classified into three types.

Nitrogen Fertilizers

Any ammonium salt can be used as a nitrogen fertilizer, since all ammonium salts are water soluble. The most commonly used ones are ammonium nitrate, ammonium chloride, urea and ammonium

sulphate. Among these, urea is the most preferred one due to the easy preparation method and also due to the presence of high percentage of nitrogen in it.

Preparation of urea

$$CO_2 + 2NH_3 \xrightarrow{200\ atm} NH_2COONH_4$$

(ammonium carbamate, an intermediate)

$$NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

Urea

Apart from these, calcium cyanamide (CaNCN) and calcium ammonium nitrate (CAN) have wider uses as nitrogenous fertilizers. They have an added advantage of providing calcium to the soil in addition to nitrogen.

Phosphate Fertilizers

Calcium and ammonium phosphates are the most commonly used ones due to their highly water soluble nature. Superphosphate of lime which is a mixture of calcium biphosphate and gypsum in 2 : 3 ratio is used as a phosphate fertilizer. In recent times, triple superphosphates are prepared and used in preference to superphosphate of lime. Ammoniated phosphates are also superior to others as they provide both nitrogen and phosphorous. Nitrophosphates can also be used for the same purpose.

Preparation of superphosphate of lime

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4 \cdot 2H_2O$$

Superphosphate of lime can be prepared by the treatment of powdered phosphate rock with conc. H_2SO_4. The mass obtained is hard due to the presence of gypsum. This is crushed to a fine powder and sold as superphosphate of lime.

Potassium Fertilizers

Most of the potassium salts, being water soluble, can be used as potassium fertilizers. They are KCl, K_2SO_4 and KNO_3. They can also be prepared by easy methods, since they are mostly naturally available in crude form.

Preparation

(i) Potassium chloride can be extracted from a mineral carnallite which is naturally available. Its formula is $KCl \cdot MgCl_2 \cdot 6H_2O$.

(ii) Potassium sulphate is also present in naturally occurring mineral schonite with the formula $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$.

(iii) Potassium nitrate, also known as nitre or Indian saltpetre, can be prepared from naturally occurring Chile salt petre ($NaNO_3$).

Depending on the mode of use, the fertilizers are again classified into three categories.

(i) Single fertilizers

A fertilizer which provides only one macronutrient is called a single fertilizer.

Example: NH_4Cl, NH_4NO_3, KCl, $Ca(NO_3)_2$

(ii) Compound fertilizers

A fertilizer which contains two or more macronutrients in a single compound is called a compound fertilizer.

Example: KNO_3, $(NH_4)_3PO_4$

(iii) Mixed fertilizers

The mixture of two or more fertilizers in the required proportions can be used according to the requirement of the soil. Such fertilizers are called mixed fertilizers.

Example: Commercial ones such as Nitrophoska

In addition to these three types, microfertilizers are a class of fertilizers which provide micronutrients for the soil depending on the requirement.

Talcum Powder

It is the most widely used cosmetic containing a mixture of inorganic and organic substances. Basically the main ingredients are TiO_2, ZnO, MgO, magnesium silicate, salts of stearic acid, calcium or magnesium carbonate, kaolin and colloidal clay. Perfumes are added in minor amounts which impart pleasant aroma to the face powder.

EXAMPLE

What is the composition of baking powder? How does it work?

SOLUTION

A mixture of sodium bicarbonate and tartaric acid is called baking powder. It is an important additive for food and drinks. Sodium bicarbonate on decomposition gives out CO_2 which makes bread and cakes puffy. Sodium carbonate produced in the process gets neutralised by tartaric acid present in baking powder.

EXAMPLE

What is a soda acid fire extinguisher? Explain the working process.

SOLUTION

Sodium bicarbonate is one of the constituents in soda acid fire extinguishers. A solution of sodium bicarbonate and sulphuric acid is taken in an extringuisher. They are kept separately and they come in contact with each other when the knob is pressed. When these two solutions react, CO_2 gas is liberated and it puts off the fire.

EXAMPLE

What is meant by annealing of glass? What is its significance?

SOLUTION

The process of cooling is a very important step in the manufacture of glass. It should be done very carefully. Rapid cooling results in brittle and fragile glass. Very slow cooling gives opaque glass. Hence the cooling should neither be too rapid nor too slow. The process of cooling done at a moderate and uniform rate is called annealing. Annealing results in the formation of good quality glass.

EXAMPLE

How is superphosphate of lime manufactured?

SOLUTION

Superphosphate of lime can be prepared by the treatment of powdered phosphate rock with concH_2SO_4. The mass obtained is hard due to the presence of gypsum. This is crushed to a fine powder and sold as superphosphate of lime.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \rightarrow Ca(H_2PO_4)_2.H_2O + 2CaSO_4.2H_2O$$

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. Give the allotropic forms of
   (i) carbon (ii) phosphorus (iii) sulphur
2. Give the action of metals on HCl, H_2SO_4 and HNO_3.
3. What is the action of heat on washing soda? Give equation.
4. What is lime? What is the principle involved in the preparation of lime?
5. What happens when bleaching powder is stored over a long period of time? Give equation.
6. What is meant by slaking of lime? Give equation.
7. The amorphous form of sulphur which is insoluble in CS_2 is _____.
8. What is clinker? Why is gypsum added to it?
9. What is RCC? How is it made?
10. A mixture of slaked lime, sand and water is known as _____.
11. What is the chemical name of plaster of Paris? How is it prepared? Give equation.
12. What is the difference between glass and ceramic?
13. Why is glass called a supercooled liquid?
14. What happens when dried pots are subjected to firing?
15. What is meant by superphosphate of lime? Give its composition.
16. What is the need of adding fertilizers to soil at regular intervals?
17. The powdered mixture of raw materials taken for the manufacture of glass is called _____.
18. What is the reason for the shiny glaze of some ceramic articles?
19. A type of glass darkens on exposure to sunlight. What is it? Why does it show that characteristic property?
20. Give the composition of pyrex glass. Give its uses.
21. What is the composition of the common type of glass?
22. _____ are doped during the manufacture of glass to impart colour.
23. Why is urea the most commonly used nitrogenous fertilizer?
24. Why are potassium fertilizers easily available?
25. How does glass gets its colour?
26. Give an example of a compound fertilizer and give its advantage over the single fertilizer.
27. Why is the same process of manufacture employed for both washing soda and baking soda?
28. Mixture of calcium dihydrogen phosphate and gypsum is called _____.
29. What is green house effect?
30. Mention one property of each blue vitriol, green vitriol and alum.

Short Answer Type Questions

31. What is the chemical name of bleaching powder? How is it prepared?
32. Explain the structure of diamond.
33. Why does SO_2 act as a bleaching agent?
34. Why is carbon monoxide called a harmful gas?
35. How is ammonia gas prepared in laboratory?
36. What is meant by annealing? What is its significance?
37. How is superphosphate of lime manufactured?
38. What is the composition of baking powder? How does it work?
39. Explain the difference in the manufacturing process of simple pottery and porcelain ware.
40. How is urea manufactured? What are the other nitrogenous fertilizers?
41. What is a soda-acid extinguisher? Explain the working process.
42. What is glass blowing? Which type of glass is suitable for that purpose? Why?

43. Give the occurrence of sulphur and phosphorus.
44. How is hydrochloric acid prepared in laboratory?
45. What is the principle involved in the use of bleaching powder for the sterilization of drinking water? Explain.

Essay Type Questions

46. Explain the extraction of phosphorus.
47. Explain the puckered ring structure of S_8 and the arrangement of these in rhombic and monoclinic sulphur. Also give the flow chart explaining action of heat on sulphur.
48. Explain the industrial preparation of nitrogen by Haber's process.
49. Give a detailed description of the manufacture of cement.
50. Explain the process of the manufacture of glass. What are its characteristics? Discuss the various types of glass along with their uses.

CONCEPT APPLICATION

Level 1

***Direction for questions from 1 to 7*: State whether the following statements are true or false.**

1. Fullerene molecules are synthesized by subliming coal using laser radiation.
2. HCl can be used to remove rust from iron.
3. A fire extinguisher contains sodium bicarbonate and acid.
4. Impervious nature of ceramics is the effect of glazing.
5. On long standing, bleaching powder undergoes autooxidation.
6. Setting of mortar is the result of reaction between slaked lime and CO_2 of air.
7. Phosphorous is widely used in match industry due to its low ignition temperature.

***Direction for questions from 8 to 14*: Fill in the blanks.**

8. In the preparation of diamonds industrially carbon changes its state from _____ to _____form.
9. The reaction of NaCl and $CaCO_3$ gives sodium carbonate. But this reaction cannot be used for the manufacture of washing soda since it is _____.
10. _____ is the main ingredient used in the preparation of superphosphate of lime.
11. Common name of calcium chloro hypochlorite is _____.
12. _____, _____ are produced during the combustion of fossil fuels.
13. The clay used for the manufacture of earthenware is _____.
14. The type of glass which consists of a layer of plastic embedded in between two layers of glass is called _____.

***Direction for question 15*: Match the entries given in column A with the appropriate ones in column B.**

15.

Column A		Column B
A. $Na_2CO_3 + CaCO_3 + SiO_2$	( )	a. Simple pottery
B. $CaOCl_2$	( )	b. Fertilizer
C. $Fe_2O_3 + Al_2O_3 + SiO_2$	( )	c. Glass
D. $Ca_2HPO_4 + CaSO_4$	( )	d. Cement
E. $CaCO_3 + SiO_2 + Al_2O_3$	( )	e. Bleaching agent

***Direction for questions from 16 to 45*: For each of the questions, four choices have been provided.**

Select the correct alternative.

16. Sugar on treating with H_2SO_4 produces a black mass. In this H_2SO_4 acts as a
    (a) decarboxylating agent
    (b) dehydrogenating agent
    (c) dehydrating agent
    (d) reducing agent

PRACTICE QUESTIONS

17. Noble metals get dissolved in aqua regia, the composition of aqua regia is
(a) $3HCl + HNO_3$ (b) $3HNO_3 + H_2SO_4$
(c) $HCl + 3HNO_3$ (d) $HNO_3 + 3H_2SO_4$

18. Which of the following reactions is called slaking of lime?
(a) $CaCO_3 \rightarrow CaO + CO_2$
(b) $CaO + 2HCl \rightarrow CaCl_2 + H_2O$
(c) $CaO + H_2O \rightarrow Ca(OH)_2 + \text{heat}$
(d) $CaCO_3 + NaCl \rightarrow Na_2CO_3 + CaCl_2$

19. Identify which contributes for strengthening of lime mortar structures and contributes for weakening of RCC structures.
(a) usage of water containing dissolved salts
(b) addition of lime
(c) absorption of CO_2 from atmospheric air
(d) both (2) and (3)

20. Bleaching powder is effective with cold water, but ineffective with hot water. This is because of
(a) oxidation of chloride radical
(b) reduction of chloride radical
(c) reduction of hypochlorite radical
(d) hydrolysis of hypochlorite radical

21. Which among the following substances is not a component of the mixture used for glazing pottery?
(a) feldspar (b) silica
(c) borax (d) alumina

22. Which of the following substances is a compound fertilizer?
(a) CAN
(b) urea
(c) Epsom salt
(d) ammonium phosphate

23. The glass containing litharge as an ingredient makes the optical fibres glow because it
(a) increases the refractive index
(b) has low density
(c) is highly thermally resistant
(d) scatters all the radiations incident on it

24. Which property is imparted to glass by the addition of cerium oxide?
(a) colour
(b) resistance to breakage
(c) increase of refractive index
(d) protection from UV light

25. The composition of flint glass is
(a) $SiO_2 + Na_2CO_3 + CaCO_3$
(b) $SiO_2 + CaCO_3 + CuSO_4$
(c) $SiO_2 + K_2CO_3 + CaCO_3$
(d) $SiO_2 + K_2CO_3 + CaCO_3 + Pb_3O_4$

26. Which of the following statements is true about glass?
(a) Arrangement of silicate units is similar to that of liquid state.
(b) Arrangement of silicate units is similar to that of solid state.
(c) It has low viscosity and hence is not a true solid.
(d) It has high viscosity with sharp melting point and hence is a solid.

27. The broken pieces of glass added to the fused raw materials in the manufacture of glass is called
(a) batch (b) glass gall
(c) cullet (d) none of these

28. When rain water percolates into the cracks of RCC, it further gets weakened due to the
(a) formation of H_2CO_3
(b) increase in pH value
(c) increase in the percentage of free lime
(d) exothermic hydration process

29. Which of the following is not an ingredient of clinker cement?
(a) calcium silicate
(b) aluminium silicate
(c) calcium aluminium silicate
(d) gypsum

30. Which of the nitrogenous fertilizers can meet the needs for immediate requirement of crop?
(a) potassium nitrate
(b) superphosphate of lime
(c) calcium cyanamide
(d) CAN

31. The steps for the manufacture of nitric acid by Ostwald process are given. Arrange them in sequence.
(a) recirculation of nitric oxide
(b) addition of H_2O to nitrogen dioxide
(c) oxidation of nitric oxide
(d) catalytic oxidation of ammonia

(a) 4 3 2 1 (b) 4 3 1 2
(c) 3 4 2 1 (d) 3 4 1 2

32. For the manufacture of cement various steps are given below. Arrange the steps in a proper sequence.
(1) clinker formation
(2) crushing
(3) addition of gypsum
(4) mixing of raw materials
(5) grinding to fine powder
(6) calcination in rotary kiln
(a) 4 2 6 1 3 5 (b) 2 4 6 3 5 1
(c) 4 3 1 6 5 2 (d) 1 2 3 4 5 6

33. For the manufacture of glass, various steps are given below. Arrange the steps in a proper sequence.
(a) melting of raw materials
(b) adding cullet to raw materials
(c) conversion of raw material to fine powder
(d) annealing
(5) refining
(a) 1 2 3 4 5 (b) 2 1 3 5 4
(c) 3 2 1 5 4 (f) 3 2 1 5 4

34. Which of the following gases with a smell of rotten egg is evolved when sulphuric acid is treated with copper sulphide?
(a) sulphur vapour (b) sulphur dioxide
(c) hydrogen sulphide (d) sulphur trioxide

35. Which of the following reagents is used to test the presence of SO_2 gas?
(a) acidified potassium manganate
(b) alkaline potassium manganate
(c) alkaline potassium dichromate
(d) acidified potassium dichromate

36. Excess of nitrogenous fertilizers is harmful because they
(a) increase the acidity of the soil
(b) do not get distributed uniformly in the soil
(c) get leached away from the soil easily and pollute the water bodies
(d) produce extra heat which burns plants

37. The ions responsible for the bleaching action of bleaching powder and the ions responsible for loss of bleaching action of bleaching powder due to the storage for long time respectively are
(a) Cl^-, OCl^- (b) OCl^-, Cl^-
(c) OCl^-, ClO_3^- (d) Cl^-, ClO^-

38. In which of the following uses of graphite, is the presence of van der Waal's forces of attraction in graphite not exploited?
(a) pencil lead (b) electrodes
(c) lubricant (d) refractory crucibles

39. Formula of plaster of Paris is
(a) $CaSO_4 \cdot H_2O$ (b) $3CaSO_4 \cdot H_2O$
(c) $CaSO_4 \cdot 2H_2O$ (d) $CaSO_4 \cdot \frac{1}{2}H_2O$

40. Identify the compound which is the final product of Solvay process
(a) ammonium carbonate
(b) ammonium bicarbonate
(c) sodium carbonate
(d) sodium bicarbonate

41. Manufacture of which of the following does not require limestone as a raw material?
(a) quick lime (b) baking soda
(c) glass (d) plaster of Paris

42. Which among the following is a micronutrient?
(a) potassium (b) phosphorus
(c) nitrogen (d) cobalt

43. Which of the following imparts purple colour to glass?
(a) Cr_2O_3 (b) $AuCl_3$
(c) Cu_2O (d) MnO_2

44. Which of the following fertilizers does not replenish nitrogen in the soil?
(a) CAN
(b) urea
(c) superphosphate lime
(d) ammonium phosphate

45. Which of the following acids is produced by treating KNO_3 with H_2SO_4 under suitable experimental conditions?
(a) HNO_2 (b) H_2SO_3
(c) HNO_3 (d) $H_2S_2O_7$

PRACTICE QUESTIONS

Level 2

1. "Diamond is a very good conductor of heat." Justify.
2. Red phosphorous is used instead of white phosphorous in making matches. Give reasons.
3. How do you account for increase in viscosity of sulphur with increase in temperature from 160°C to 195°C and subsequent decrease beyond this range?
4. Sodium and potassium belong to the same group. But potassium carbonate cannot be prepared by Solvay process like sodium carbonate. Explain with appropriate reasons.
5. In many cases, there are cement plants near a steel plant. Explain why.
6. Explain why baking powder containing monocalcium phosphate monohydrate as one of the constituents is preferred to baking soda for baking or as leavening agent.
7. Borosilicate glasses are used as laboratory wares. Give reasons.
8. Explain the effect of process of cooling on the transparency of glass.
9. The wind screen of a car does not shatter to pieces and scatter when broken. Give reasons.
10. All concrete structures require perfect curing. What purpose does this process serve?
11. How can the glossy, impervious nature of ceramics be obtained? Explain.
12. Older concrete buildings are known to be stronger than newly built concrete structures. How do you account for this?
13. The setting and hardening of cement are the two important stages which take place gradually over a long period of time. Explain the physical and chemical changes associated with them. Justify.
14. In which respect is triple phosphate, as a fertilizer, superior to superphosphate of lime?
15. Inorganic nitrogenous fertilizers are basically of two types—nitrate salts and ammonium salts. Which among these is more preferable? Give reasons in support of your answer.
16. (a) White phosphorus catches fire at room temperature, whereas red phosphorus does not. Explain.
    (b) Phosphor bronze is an alloy of copper, tin and phosphorus. Which properties are imparted to the alloy by adding phosphorus?
17. A divalent metal with atomic number 12 reacts with an acid liberating a gas X. X on treatment with a nonmetal Y gives Z, which on dissolution in water produces the same acid.
    (a) Identify X, Y and Z and write a balanced chemical equation for the formation of Z from X and Y.
    (b) Write the corresponding balanced chemical equations.
    (c) The gas Z is collected by upward displacement of air. Justify.
18. Hydrogen is a clean fuel with highest calorific value. However, it cannot be a substitute for petrol or CNG used in automobiles. Explain.
19. "The air we breathe has 78% nitrogen. But nitrogen is not used to dilute the oxygen in the cylinders carried by scuba divers." Justify.
20. Why does a substance which is bleached using sulphur dioxide regain its colour on exposure to air while that bleached using chlorine does not?
21. Decomposition of baking soda is the principal reaction in the usage of dry powder fire extinguishers. What characteristics of the reaction are exploited in this process?
22. The superphosphate of lime is always used in combination with ammonium fertilizer. Justify.
23. Gold and platinum do not dissolve either in conc HCl or conc HNO_3, but dissolves in the mixture of 3 parts of conc HCl and 1 part of conc HNO_3. Give a reason and write the necessary chemical equations.
24. Three jars labelled as A, B and C filled with SO_2 gas are taken. A burning wooden splinter, burning sodium and burning potassium are introduced into the jars, A, B and C, respectively. What are the observations? Explain with a reason and give the corresponding reactions.
25. Pure nitric acid on long standing turns to yellow colour. Give a reason.

Level 2

1. Photoblackening of photochromatic glass doesn't occur when exposed to tube light or any lamp light during night time or in dark. Justify.
2. Urea is not recommended as a fertilizer in very cold places but recommended for highly acidic soils. Explain with appropriate reasons.
3. Usually, salt is sprinkled on pottery at the end of the firing process. Explain the role of salt in this process.
4. How does glass find application in telecommunication industry?
5. Why does glass become opaque on slow cooling?
6. Reinforced concrete cement contains iron in major proportion. However, it does not get rusted and contributes for greater strength and durability of RCC structures. How do you account for this?
7. Phosphorus is chiefly available as phosphate rock. However, it is converted to superphosphate of lime for usage as a fertilizer. Triple phosphate is considered to be superior to superphosphate of lime. Justify with appropriate reasons.
8. Why are fibre optic cables replacing copper cables in telecommunication?
9. Is a good fertilizer expected to be acidic or basic in nature? Justify your answer.
10. Why is ceramic ring (e.g., alumina, silicon nitride, etc.) used as piston ring in internal combustion engines?

Concept Application

Level 1

True or false

1. False
2. True
3. True
4. True
5. True
6. True
7. True

Fill in the blanks

8. amorphous to crystalline
9. reversible reaction
10. phosphate rock ($Ca_3(PO_4)_2$)
11. bleaching powder
12. CO_2, H_2O
13. Kaolin
14. safety glass

Match the following

15. A : c B : e C : a D : b E : d

Multiple choice questions

16. c 18. c 20. c 22. d 24. d 26. a 28. a 30. a
17. a 19. c 21. b 23. a 25. d 27. c 29. d

31. (i) Catalytic oxidation of ammonia
    (ii) Oxidation of nitric oxide
    (iii) Addition of water to nitrogen dioxide
    (iv) Recirculation of nitric oxide
32. (i) Mixing of raw materials
    (ii) Crushing
    (iii) Calcination in rotary kiln
    (iv) Clinker formation
    (v) Addition of gypsum
    (vi) Grinding to fine powder
33. (i) Mixing of raw materials
    (ii) Adding cullet to raw materials
    (iii) Melting of raw materials
    (iv) Refining
    (v) Annealing
34. Hydrogen sulphide with a smell of rotten eggs is evolved when sulphuric acid is treated with copper sulphide.
35. Acidified potassium dichromate is used to test SO_2. SO_2 when passed through acidified $K_2Cr_2O_7$, turns it green.
36. Nitrogenous fertilizers leach away from the soil easily due to their high solubility in water and pollute water bodies.
37. Bleaching powder contains Ca^{+2}, Cl^- and OCl^- ions. Among these OCl^- ions hydrolyse to give nascent oxygen. Hence these are responsible for the bleaching action. On long standing OCl^- ions get oxidized to ClO_3^- ions which result in loss of bleaching action of bleaching powder.
38. Use of graphite as pencil lead, electrodes and lubricant are due to the presence of free electrons in graphite. Usage in refractory crucibles is due to the high melting point of graphite.
39. $CaSO_4 . ½H_2O$ is the formula of plaster of Paris.
40. Sodium carbonate is the final product of Solvay process.
41. Limestone is not required as a raw material for the manufacture of plaster of Paris. Gypsum is taken as a raw material for plaster of Paris.
42. Cobalt is an example of a micronutrient.
43. MnO_2 imparts purple colour to glass.

44. Superphosphate of lime does not replenish nitrogen in the soil.

45. Nitric acid is produced by treating potassium nitrate with sulphuric acid under suitable experimental conditions.

Level 2

1. (i) Process of conduction of heat
   (ii) Type of bond present in diamond
   (iii) Structure of diamond
   (iv) Role of structure of diamond on conduction of heat

2. (i) Comparison of properties of red and white phosphorus
   (ii) Comparison of the structure of red and white phosphorus
   (iii) Relation between the structure and property of red and white phosphorous
   (iv) Purpose of a matchstick
   (v) Property of phosphorous exploited for this purpose
   (vi) Comparison of red and white phosphorus with respect to this property

3. (i) Structure of stable allotrope of sulphur
   (ii) The transformation undergone when solid sulphur in its stable form is heated.
   (iii) Structural change that takes place in sulphur with the change of temperature from 160°C to 195°C.
   (iv) Effect of the above change on its viscosity.
   (v) Structural change which takes place on further increase in temperature.
   (vi) Effect of the above change on viscosity.

4. (i) Properties of the intermediate products formed during Solvay process.
   (ii) Reaction that takes place in ammonical brine solution due to the passage of CO_2 through it.
   (iii) Products obtained
   (iv) Identification of the product from which washing soda is prepared.
   (v) Physical property of the product that is exploited for separating the above product from the other.
   (vi) Comparison of the physical property of the corresponding potassium compound with the above product.

5. (i) Impurities separated during steel manufacturing.
   (ii) Raw material used for the manufacture of cement.
   (iii) Relation between the raw material and the impurities separated during the extraction of iron in steel plant.

6. (i) Identification of reaction involved.
   (ii) Constituent of baking soda.
   (iii) Chemical change that baking soda undergoes during the process of baking.
   (iv) Products obtained
   (v) Role of the gaseous product
   (vi) Nature of the solid product and its effect on the baked product.
   (vii) Reaction between baking soda and monocalcium phosphate.
   (viii) Products obtained
   (ix) Role of the product in nullifying the effect in (v).

7. (i) Properties of borosilicate glass.
   (ii) Difference between the constituents present in ordinary glass and borosilicate glass.
   (iii) Effect of the constituents on the physical properties.
   (iv) Constituent that is responsible for the change in physical properties.
   (v) Role of this constituent to make the glass suitable for laboratory wares.

8. (i) Relation between process of cooling and physical changes that take place in glass.
   (ii) Relation between structure and rate of cooling.
   (iii) Change in arrangement of constituents of glass during cooling.
   (iv) Effect of the change in arrangement of constituents on physical properties of glass.
   (v) Relation between the arrangement of constituents and transparency of glass.

9. (i) Process of manufacture of wind screen of a car.
   (ii) Type of glass used as a wind screen.
   (iii) Reason for scattering of glass when broken.
   (iv) Role of additional material used to prevent the scattering of glass.

10. (i) Changes involved during curing.
    (ii) Constituents of cement.

(iii) Reaction that takes place between constituents of cement and water.

(iv) Products obtained

(v) Change in the crystalline structure of the product after the reaction.

(vi) Role of this particular type of crystalline structure for the setting of cement.

11. (i) Steps involved in the manufacture of ceramics.

(ii) Substance generally used for glazing.

(iii) Change in physical state of the above substance at high temperatures.

(iv) Reaction between the above substance and silica.

(v) Nature and effect of the product formed on nature of ceramics.

12. (i) Process of hardening of concrete.

(ii) Constituents present in cement.

(iii) Changes that the constituent undergo during curing.

(iv) Comparison of time taken by the constituents for the above change.

13. (i) Composition of cement.

(ii) Reaction of water with the major component of cement.

(iii) Phenomenon associated with the above reaction.

(iv) Effect of the above phenomena on the setting of cement.

(v) Type of changes involved in the above phenomena.

(vi) Effect of these changes on the structure of silicates.

14. (i) Properties of the constituents of the given fertilizer.

(ii) Comparison of constituents of triple phosphate and superphosphate of lime.

(iii) Reactions which take place after addition of the respective fertilizer to soil.

(iv) Products obtained

(v) Effect of the product which is not assimilated by the plant on the nature and utility of the soil.

15. (i) The form in which the plant assimilate nitrogen from fertilizer.

(ii) Identification of the salt which cannot be directly assimilated.

(iii) Comparison of time required for the assimilation of the two fertilizers given.

(iv) Relation between usage of fertilizer and requirement of the soil.

16. (a) In white phosphorus the four phosphorus atoms are arranged at the four corners of a regular tetrahedron and exists as isolated P4 units with weak van der Waals forces of attraction between P_4 units. Hence, it is less stable and highly reactive. However, in red phosphorus, all the P_4 units are interlinked with each other to form long chains and hence it is highly stable with lesser reactivity. White phosphorus catches fire immediately on exposure to air since its ignition temperature is low. Red phosphorus does not catch fire at room temperature since it has a higher ignition temperature.

(b) Phosphorus when added to copper forms Cu_3P (copper phosphide) which decreases the malleability and increases hardness of the alloy.

17. (a) $X = H_2$, $Y = Cl_2$, $Z = HCl$

$$H_2 + Cl_2 \rightarrow 2HCl$$

$$X \quad Y \quad (Z)$$

(b) $Mg + 2HCl \rightarrow MgCl_2 + H_2$

Z in the form of acid reacts with metals like Mg to liberate hydrogen gas along with the formation of the corresponding salt.

$HCl + H_2O \rightarrow HCl$ (acid)

(c) As (Z) HCl gas is heavier than air, it is collected by the upward displacement of air. It is not collected by downward displacement of water as it is highly soluble.

18. Among all fuels, hydrogen has the highest calorific value. Moreover, it is a non-polluting fuel. But it cannot be used as a fuel in automobiles because liquefaction of hydrogen is difficult and it is highly inflammable.

19. Solubility of N_2 in water increases with the increase in external pressure. In deep seas the percentage of nitrogen that gets dissolved in blood is more than that in case of normal atmospheric pressure. When the scuba diver comes up, the depth of the water becomes less and consequently the pressure decreases. Hence nitrogen comes out from the blood in the form of bubbles which hinders the flow of blood.

20. SO_2 in the presence of moisture produces nascent hydrogen, which bleaches. Here bleaching takes place due to reduction. On exposure to air, the bleached substance gets oxidized due to atmospheric oxygen and regains its colour. Cl_2, however, bleaches due to oxidation and hence the bleaching is permanent.

21. In dry fire extinguishers, baking soda decomposes and it is an endothermic reaction. The CO_2 evolved is much denser than air and serves as a blanket and more over it is a nonsupporter of combustion and hence it cuts the contact between air and the combustible substance. Since the decomposition of baking soda is an endothermic process, the temperature of the surrounding area decreases which quickens the process of extinguishing fire.

22. Superphosphate of lime is $Ca(H_2PO_4)_2$ + $CaSO_4.2H_2O$, calcium sulphate on hydrolysis produces sulphuric acid which is not suitable for the soil. In order to neutralize sulphuric acid, it is used in combination with ammonium fertilizer. Ammonium ions neutralize the H_2SO_4 formed.

23. The dissolution of noble metals in aquaregia can be justified as follows:

(i) The concentrated nitric acid oxidizes concentrated hydrochloric acid to liberate nascent chlorine:

$$HNO_{3(conc)} + 3HCl_{(conc)} \rightarrow \underset{\text{Nitrosyl chloride}}{NOCl} + 2H_2O + \underset{\text{Nascent chlorine}}{2[Cl]}$$

(ii) Nascent chlorine reacts with noble metals to form their soluble chlorides which pass into the solution:

$Au + 3[Cl] \rightarrow AuCl_3$

Gold — Gold (III) chloride

$Pt + 4[Cl] \rightarrow PtCl_4$

Platinum — Platinum (IV) chloride

24. The burning splinter is put off while burning sodium and potassium continue burning. This is because the heat produced due to burning of metals dissociates the molecule of sulphur dioxide to sulphur and oxygen. The oxygen so liberated sustains combustion of the metals:

$4K + 3SO_2 \rightarrow K_2SO_3 + K_2S_2O_3$; $4Na + 3SO_2 \rightarrow Na_2SO_3 + Na_2S_2O_3$

25. Pure nitric acid, being unstable, undergoes decomposition and liberates the reddish brown gas NO_2, which turns it yellow.

Level 3

1. (i) Composition of photogrey lenses/photochromatic glass.

(ii) Nature (microscopic or macroscopic) of components of photochromatic glass.

(iii) Arrangement of components of photochromatic glass.

(iv) Type of chemical change taking place on exposure to sunlight.

(v) Nature of the particles formed.

(vi) Combination of the particles formed.

(vii) Effect of this combination on colour.

(viii) Comparison of sunlight and other sources of light.

(ix) Relation between the above required chemical change and the source of light used.

2. (i) Structural formula of urea.

(ii) Identification of the characteristic reaction undergone by urea for usage as a fertilizer.

(iii) Conditions required for the above reaction.

(iv) Nature of the products formed in the above reaction.

(v) Bacterial action on one of the products formed.

(vi) Comparison of basic strength of urea with one of the product formed.

(vii) Nature of the acid required to neutralize the basic character.

(viii) Effect of pH on the characteristic reaction of urea.

(ix) Relation between the temperature of surroundings and the extent of characteristic reaction of urea.

3. (i) Change that takes place during firing of pottery is presence of salt.

(ii) Product obtained due to the reaction between NaCl and a constituent of pottery.

(iii) Physical state of the product at high temperature.

(iv) Effect of the physical state on the surface of the pot.

4. (i) Property of glass required for telecommunication industry.

(ii) Requirements of optical fibre materials used in telecommunications.

(iii) Phenomenon taking place during propagation of signals.

(iv) Property of glass exploited for the above phenomena.

5. (i) Changes that takes place during slow cooling.

(ii) Comparison of arrangement of molecules/ions present in glass during the slow and fast cooling.

(iii) Conditions that make an object opaque.

(iv) Effect of arrangement of molecules/ions on the optical property of glass.

6. Iron is used as a major component in reinforced concrete cement. Though it is in constant contact with moisture and air it does not get rusted. This is because cement slurry is highly alkaline with a pH value of around 12.5. Iron becomes corrosion resistant in a pH range above 9. Due to this reason, iron does not corrode and contributes for strength and durability of RCC.

7. Phosphate rock ($Ca_3(PO_4)_2$) is insoluble in water, whereas superphosphate of lime is soluble and hence can be assimilated by plants, i.e., it provides phosphate (macronutrient) in a water soluble form. But the hydrolysis of superphosphate of lime produces H_2SO_4 which is highly acidic and damages or affects the crop. In combination with the above fertilizer, ammonium fertilizers are added so that these ammonium compounds neutralize the acidity and thus it can be used as an effective fertilizer.

8. In telecommunication a signal is sent through copper cable gets attenuated due to the resistance of the metallic cable. But in fibre optic cables the propagation of signal takes place based on the principle of total internal reflection. Hence there is negligible loss of signal which makes it most effective cable system in telecommunication.

9. Basic soils are generally preferred for crops. The soils in general are slightly acidic due to the dissolution of CO_2, NO_2 and SO_2 in rain water. Hence, a basic fertilizer is preferable as it neutralizes the acidity of the soil and makes the soil slightly basic.

10. In an internal combustion engine, the piston has to undergo a lot of friction. The heat generated in the internal combustion engine is required for burning fuel. Hence, heat should not be dissipated. Ceramic seal rings are mostly made up of alumina and nowadays silicon nitride is used. They are very hard and excellent thermal resistants. Their thermal conductivity is low which limits the dissipation of heat.

Chapter

10

Organic Chemistry–I

Remember

Before beginning this chapter, you should be able to:

- understand the basic features of carbon
- state some terms like nomenclature of organic compounds and concept related to it.

Key Ideas

After completing this chapter, you should be able to:

- study the unique features of carbon
- understand the classification of organic compounds based on characteristics
- understand the nomenclature of organic compounds
- study isomerism of organic compounds
- understand the preparation and properties of simple alkanes, alkenes and alkynes

INTRODUCTION

There are 111 elements in the periodic table. Among all these, carbon is an element which acquires special status due to its characteristic properties. The chemistry of carbon compounds is studied as a separate branch called organic chemistry in contrast to the inorganic chemistry of the rest of the elements. However, elemental carbon and a few compounds of the carbon like oxides, carbonates, sulphides and carbides are considered as inorganic substances.

Initially, the basic distinction between inorganic and organic compounds was considered to be the source of origin of these compounds. Inorganic compounds were believed to have mineral origin, whereas organic compounds were believed to have plant and animal origin.

This kind of distinction stemmed from a vital force theory. According to this theory, a vital force is responsible for the synthesis of organic compounds and this is provided by living beings like plants and animals. The name "organic," meaning living system, also originated from the above concept.

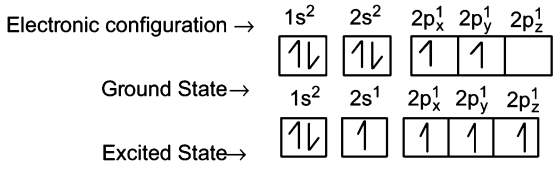
The idea of vital force theory was dispelled when the German scientist, Fredrich Wohler, prepared urea by heating ammonium cyanate. Urea, being a component part of urine, is an organic compound. Synthesis of this compound from an inorganic salt paved the way for further research in this field and organic chemistry received a boost in the later years. The special status given to carbon compounds is now attributed to certain characteristic features of carbon and not to the source of origin of the compounds.

The basic characteristic which distinguishes carbon from other elements is its ability to form millions of compounds. Formation of such innumerable number of compounds by carbon can be further attributed to certain unique features possessed by carbon.

Unique Features of Carbon

(i) Catenation property: The ability of an atom to join with the other atoms of the same element and form long chains is called *catenation*. Carbon is an element which shows maximum catenation.

The ability of catenation can be explained on the basis of the electronic configuration of carbon.



There are four unpaired electrons in the excited state of a carbon atom and this gives tetravalency for carbon. As a result of this, carbon can form strong carbon–carbon covalent bonds. This gives the scope for formation of long chains of carbon.

Carbon atom can form long chains of thousands of atoms or rings of various sizes and chains and rings can have branches and cross-links.

(ii) Multiple bond formation: Due to the presence of four unpaired electrons in the valence shell of a carbon atom in its excited state, there is a possibility of formation of double bonds or triple bonds between carbon atoms. This ability to form multiple bonds also gives rise to various types of carbon chains.

All the organic molecules are generally represented by the "molecular formulae" (which gives the number of atoms of the constituent elements) and the structural arrangement of atoms is represented by "structural formulae" (which gives the exact arrangement of atoms of different elements).

(iii) Isomerism: Isomerism is the phenomenon in which two or more organic molecules have the same molecular formula but differ in the structural arrangement of atoms. Those compounds are called isomers. Due to the difference in structure, the various organic compounds differ in their physical properties and to some extent in their chemical properties. Hence, isomerism is another feature which contributes to the existence of a large number of compounds of carbon.

Classification of Organic Compounds

Though carbon forms millions of compounds, it combines only with a few elements, chiefly with hydrogen. The others are oxygen, nitrogen, halogens, sulphur, magnesium, etc. On this basis, organic compounds which contain only carbon and hydrogen are called hydrocarbons and those which contain other elements in addition to carbon and hydrogen are called organic compounds with heteroatoms.

On the basis of structure, bonding and chemical behaviour, the hydrocarbons are classified into two main categories, namely, aliphatic hydrocarbons and aromatic hydrocarbons.

(i) Aliphatic hydrocarbons: These include open-chain compounds and cyclic compounds based on the skeleton of carbon chain present, aliphatic hydrocarbons are categorised into two classes.

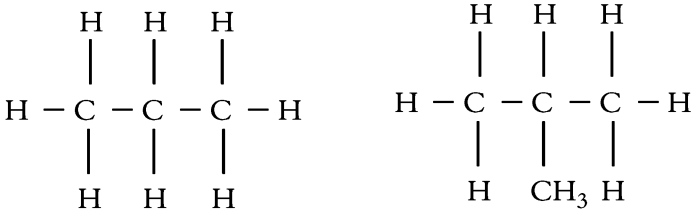
(a) Acyclic hydrocarbons (or) open-chain hydrocarbons

These hydrocarbons contain straight chain or branched chain of carbons with or without multiple bonds. On this basis, they are further classified into saturated and unsaturated hydrocarbons.

(a) Saturated hydrocarbons: In this type of acyclic hydrocarbon molecules, there are no multiple bonds present in the carbon skeleton. Such type of hydrocarbons is referred to as saturated hydrocarbons called alkanes. In saturated hydrocarbons, valencies of all carbon atoms are satisfied by single covalent bonds. General formula of saturated hydrocarbons is C_nH_{2n+2}.

They are commonly called "paraffins."

Example



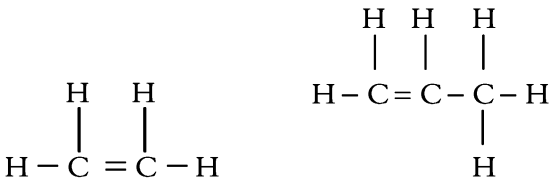
(b) Unsaturated hydrocarbons: If in the carbon skeleton of the acyclic hydrocarbon molecules there are one or more multiple bonds present between carbon atoms, they are called unsaturated hydrocarbons. Based on the type of multiple bond they are further classified as alkenes and alkynes.

Alkenes

Unsaturated hydrocarbons containing at least one carbon–carbon double bond are called *alkenes*. General formula of alkenes is C_nH_{2n} (assuming only one double bond).

They are commonly called "olefins."

Example

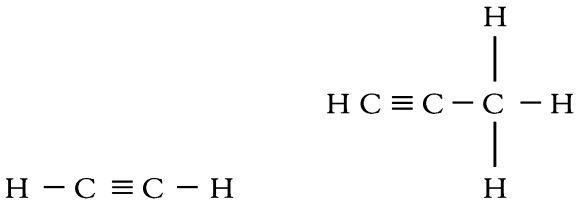


Alkynes

Unsaturated hydrocarbons containing at least one carbon–carbon triple bond are called alkynes. General formula of alkynes is C_nH_{2n-2} (assuming only one triple bond).

They are commonly called "acetylenes."

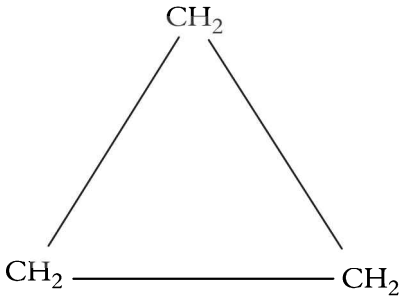
Example



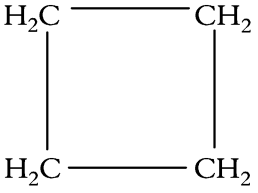
(b) Alicyclic hydrocarbons (or) cycloalkanes: The aliphatic saturated hydrocarbons in which the carbon atoms are joined together to form a cyclic ring are called alicyclic hydrocarbons. They are represented by the general formula C_nH_{2n}.

Examples:

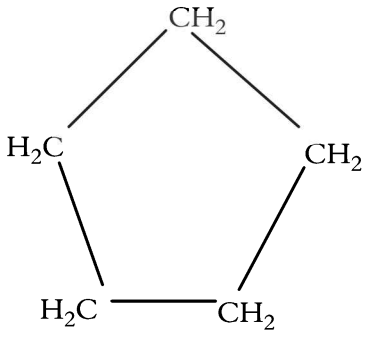
(i) C_3H_6: Cyclopropane



(ii) C_4H_8: Cyclobutane



(iii) C_5H_{10}: Cyclopentane



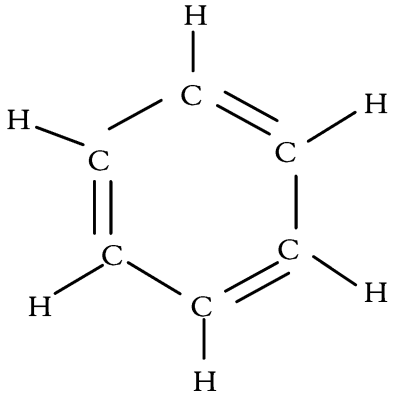
Aromatic compounds

Aromatic compounds are benzene and the compounds that resemble benzene in chemical behaviour.

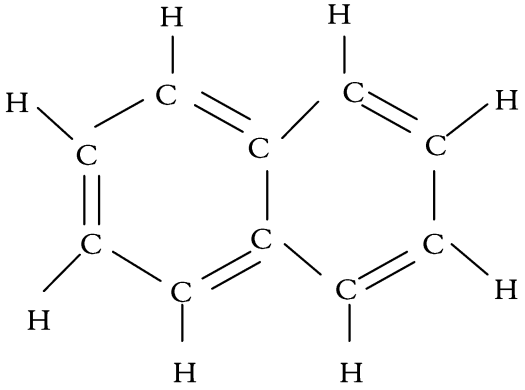
Examples

C_6H_6: Benzene

Structural formulae:



$C_{10}H_8$: Naphthalene



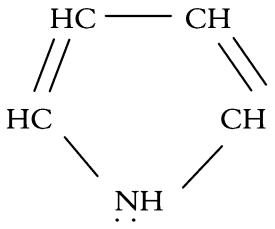
However, there are certain other cyclic compounds in which the ring has atoms other than carbon atoms. Such compounds are called heterocyclic compounds.

Heterocyclic Compounds

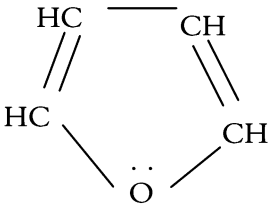
The cyclic compounds in which the ring is made up of carbon atoms chiefly and other heteroatoms like O, N and S (ring made of more than one kind of atoms) are known as heterocyclic compounds.

Examples

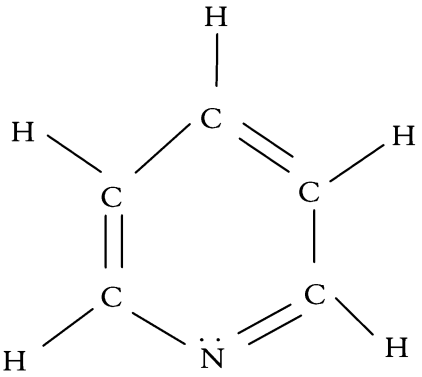
Pyrrole C_4H_5N



Furan: C_4H_4O



Pyridine: C_5H_5N



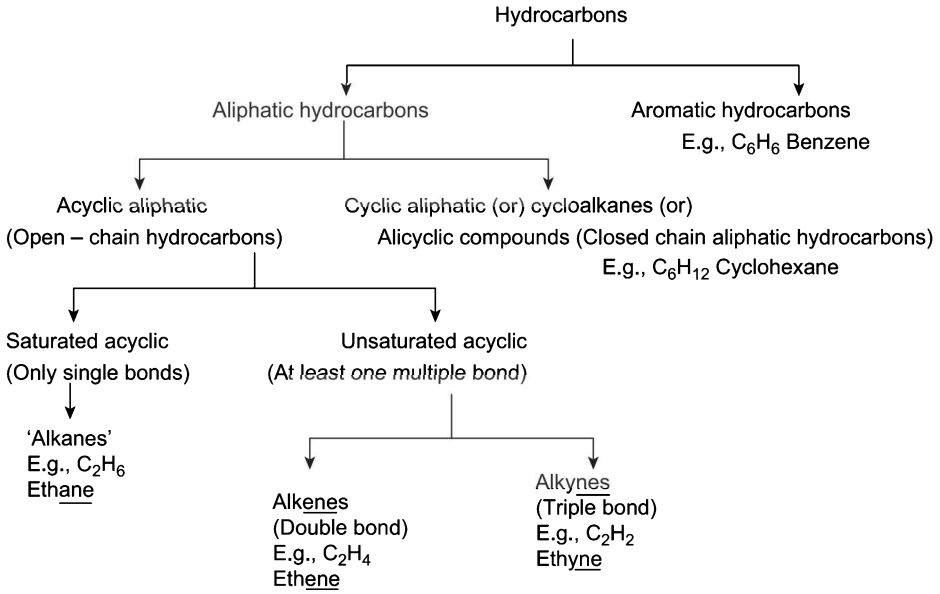
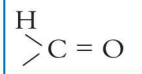
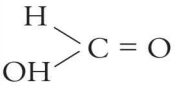


Figure 10.1 Classification of Hydrocarbons

The organic compounds with heteroatoms can be formed by replacing one or more carbon atoms of the corresponding hydrocarbon with another atom or a group of atoms. Hence, these are called derivatives of hydrocarbons. The atom or group attached to the hydrocarbon part is responsible

for the physical and chemical properties of the compound and hence is called a functional group. Therefore, based on the nature of the functional group attached to the carbon skeleton, they are further classified into various classes.

Functional groups	General formulas	Classes of compound	Example Formulas	Common Names
–OH	R – OH	Alcohol	CH_3OH C_2H_5OH	Methyl alcohol Ethyl alcohol
	R – CHO	Aldehyde	HCHO CH_3CHO	Formaldehyde Acetaldehyde
		Ketone		Acetone
		Carboxylic acid		Formic acid
–X	R – X	Alkyl halide	CH_3Cl C_2H_5Cl	Methyl chloride Ethyl chloride

NOMENCLATURE OF ORGANIC COMPOUNDS

Prior to the end of the nineteenth century, the names of the various organic compounds were based on either the source of origin of the compound or on some specific property of the compound. For example, methane gas is found to get released in marshy places. Hence, it is called marsh gas. Since it easily catches fire, it is called fire damp. In fact, the name methane also originated on the basis of the same concept.

Methane is the parent hydrocarbon of methyl alcohol, CH_3OH. Methyl alcohol was originally obtained by the destructive distillation of wood and was named as "wood alcohol." From this arose the word methyl, which is a combination of two Greek words methu (wine) and hule (wood). Another example of this way of naming compounds is acetic acid, which is the chief constituent of vinegar (Latin: acetum, i.e., vinegar).

This method of naming the organic compounds at random could be justified as long as vital force theory could hold good. In the later period, the synthesis of many organic compounds in the laboratory opened new vistas to the branch of organic chemistry. In order to give names for the huge number of organic compounds used all over the world, a more systematic method of nomenclature was required. The names which were in use till then are retained and are now called trivial names or common names.

The International Union of Pure and Applied Chemistry (IUPAC) developed a systematic approach to the nomenclature of organic compounds which is purely based on its structure and reflects the physical and chemical properties.

IUPAC Nomenclature of Hydrocarbons

The IUPAC name of a hydrocarbon basically contains two parts:

(i) root word and
(ii) primary suffix.

(i) **Root word**: It indicates the number of carbon atoms in the chain. For naming the root word, the trivial names of the first four members of alkanes are taken as the basis. Beyond that, Greek numerals are used for indicating the number of carbon atoms.

Number of carbon atoms present in the longest chain	Root words
1	Meth
2	Eth
3	Prop
4	But
5	Pent
6	Hex
7	Hept
8	Oct
9	Non
10	Dec

(ii) Primary suffix: Primary suffix indicates saturation or unsaturation of a hydrocarbon. This is attached to the root word.

Saturated hydrocarbon → ane

Double bonded unsaturated hydrocarbon → ene

Triple bonded unsaturated hydrocarbon → yne

Examples: $H_3C - CH_2 - CH_3 \rightarrow$ propane

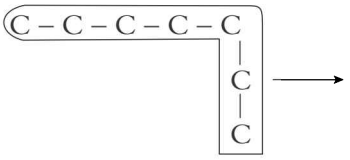
$H_3C - CH_2 = CH_2 \rightarrow$ propene

$H_3C - C \equiv CH \rightarrow$ propyne

Rules for Naming of a Hydrocarbon

(i) The longest possible continuous chain of carbon atoms is selected as the parent hydrocarbon. The root word corresponding to the number of carbon atoms in the longest chain is noted.

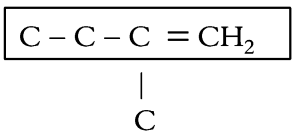
Example



Longest chain with six carbon atoms. The root word corresponding to this is "hex".

(ii) The selected longest chain should possess the double bond or triple bond in case of unsaturation in the chain.

Example



Longest chain with four carbon atoms. The root word corresponding to this is "but".

(iii) The longest carbon chain selected is numbered in such a way that the multiple bonded carbon or the carbon having alkyl substituent gets the least number.

Univalent group formed after the removal of one hydrogen atom from alkane is called *alkyl group*.

Parent hydrocarbons	Alkyl groups (formula)	Alkyl groups (name)
CH_4 (methane)	$-CH_3$	methyl
C_2H_6 (ethane)	$-C_2H_5$	ethyl
C_3H_8 (propane)	$-C_3H_7$	propyl
C_4H_{10} (butane)	$-C_4H_9$	butyl

The position number is added before the root word to indicate the position of multiple bond or substituent (alkyl or functional group).

Examples

$$\overset{5}{CH_3}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_3}$$

2 – Pentene

Double bonded carbon is given 2nd position by numbering the carbon atoms in the chain.

$$\overset{1}{H_3C}-\overset{2}{\underset{\displaystyle CH_3}{\underset{|}{CH}}}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

2 – Methylbutane

→ The carbon chain containing four carbon atoms is numbered in such a way that the carbon having constituent methyl group gets the least position.

Isomerism in Hydrocarbons

The existence of an organic compound with the same molecular formula and different structural formulae is called isomerism.

The isomerism can be of various types depending on the type of variation in the structures of the molecules.

(i) Chain isomerism: The phenomenon in which two or more organic compounds have the same molecular formula but differ in the arrangement of carbon atoms in the longest chain.

All types of hydrocarbons (alkanes, alkenes and alkynes) with more than three carbon atoms exhibit this type of isomerism.

The molecule in which all carbon atoms are arranged in a straight chain is called n-isomer. The molecule in which there is a branched chain arrangement in the molecule a prefix iso or neo is used depending on the type of branching.

Examples

a. Pentane

Chain isomers

$$H_3C-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

Isopentane

$$\begin{array}{c} CH_3 \\ | \\ H_3C-C-CH_3 \\ | \\ CH_3 \end{array}$$

Neopentane

b. Pentene

$$H_2C = CH - CH_2 - CH_2 - CH_3$$

n-Pentene

$$H_2C = CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$$

Isopentene

c. Pentyne

$$HC = C - CH_2 - CH_2 - CH_3$$

n-Pentene

$$HC \equiv C - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_3$$

Isopentyne

(ii) Position isomerism: The phenomenon in which the hydrocarbon has the same chain but differs in the position of multiple bonds or constituents on the parent chain is called position isomerism.

This is exhibited by unsaturated hydrocarbons (alkenes and alkynes) with more than three carbon atoms (or) saturated hydrocarbons with substituents as side chain.

Examples

(a) Butene

Molecular formula – C_4H_8

$H_3C - CH_2 - CH = CH_2$

1-Butene

$H_3C - CH = CH - CH_3$

2-Butene

(b) Pentyen

Molecular formula – C_5H_8

$CH_3 - CH_2 - CH_2 - C \equiv CH$

1-Pentyne

$CH_3 - CH_2 - C \equiv C - CH_3$

2-Pentyne

(c) 5-carbon chain with methyl substituent

$$\overset{1}{H_3C} - \overset{2}{CH_2} - \overset{3}{\underset{\displaystyle CH_3}{\underset{|}{CH}}} - \overset{4}{CH_2} - \overset{5}{CH_3}$$

3 – Methylpentane

$$\overset{1}{H_3C} - \overset{2}{\underset{\displaystyle CH_3}{\underset{|}{CH}}} - \overset{3}{CH_2} - \overset{4}{CH_2} - \overset{5}{CH_3}$$

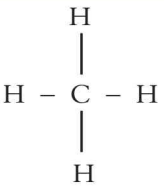
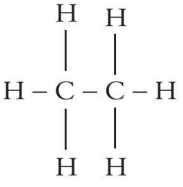
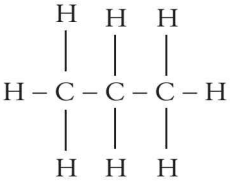
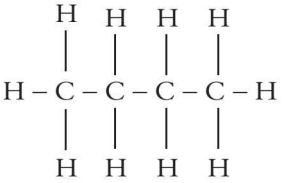
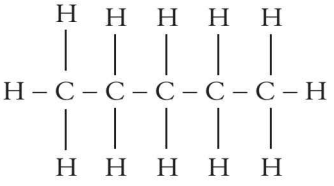
2 –Methylpentane

Homologous Series

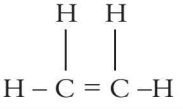
A series of organic compounds in which each member differs from the next member by a constant amount when arranged in an increasing order of their molecular weights is called a homologous series.

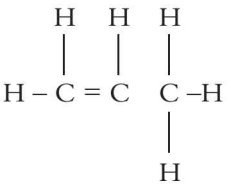
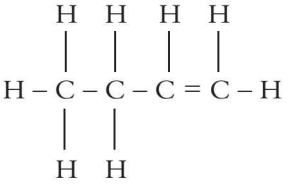
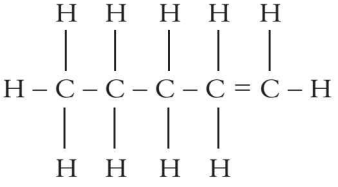
The adjacent members of this series differ by 14 in their molecular weights or $-CH_2$ group and can be represented by the same general formula. The members show a regular gradation in physical properties, similar chemical properties and hence can be prepared by similar methods.

Homologous Series of Alkanes (general formula C_nH_{2n+2})

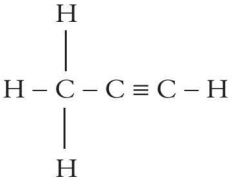
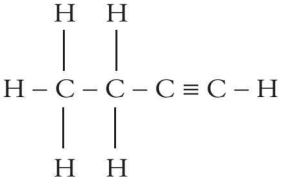
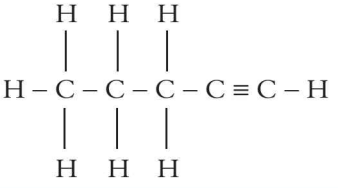
IUPAC name of the alkanes	Molecular formulas	Structural formulas
Methane	CH_4	
Ethane	C_2H_6	
Propane	C_3H_8	
Butane	C_4H_{10}	
Pentane	C_5H_{12}	

Homologous Series of Alkenes (general formula C_nH_{2n})

IUPAC name of the alkenes	Molecular formulas	Structural formulas
Ethene	C_2H_4	

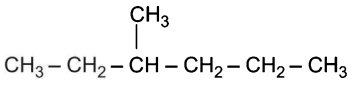
IUPAC name of the alkenes	Molecular formulas	Structural formulas
1-Propene	C_3H_6	
1-Butene	C_4H_8	
1-Pentene	C_5H_{10}	

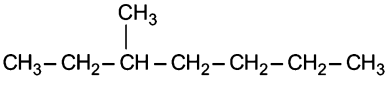
Homologous series of alkynes (general formula C_nH_{2n-2})

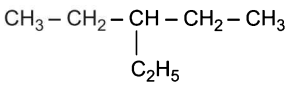
IUPAC name of the alkenes	Molecular formulas	Structural formulas
Ethyne	C_2H_2	
1-Propyne	C_3H_4	
1-Butyne	C_4H_6	
l-Pentyne	C_5H_8	

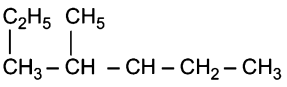
EXAMPLE

Write the IUPAC names of the following compounds.

(a) 

(b) 

(c) 

(d) 

SOLUTION

(a) 3 – Methyl hexane **(b)** 3 – Methyl heptane

(c) 3 – Ethyl pentane **(d)** 3, 4 – Dimethyl hexane

EXAMPLE

(a) Draw the structural formulae of butane and its structural isomers. Mention their IUPAC names.

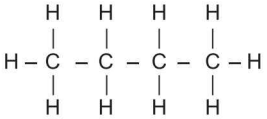
(b) Draw the structural formula of a compound with three carbon atoms in each of the following cases.

(i) An alkane with carbon carbon single bond.

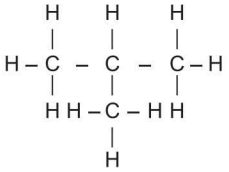
(ii) An unsaturated hydrocarbon with carbon carbon double bond.

SOLUTION

(a) n-butane and 2-Methyl propane are structural isomers.



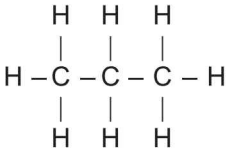
n-butane



2-Methyl propane

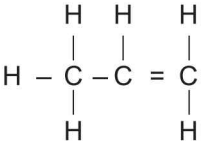
(b) (i)

Propene



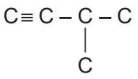
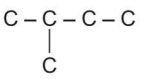
(ii)

Propene



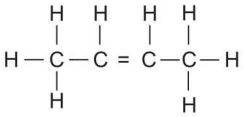
EXAMPLE

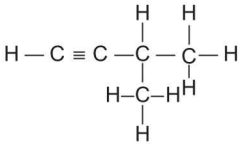
Complete the structures of following hydrocarbons by placing only hydrogens.

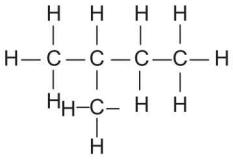
(a) C – C = C – C **(b)**  **(c)** 

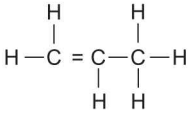
(d) C = C – C **(e)** C – C – C – C – C

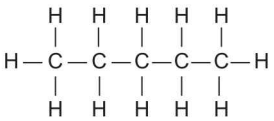
SOLUTION

(a) 

(b) 

(c) 

(d) 

(e) 

Aliphatic Hydrocarbons Alkanes

Comparative Study of Methane and Ethane

Occurrence

Methane gas is found in marsh gas, natural gas, coal gas, gobar gas, sewage gas, bio gas, etc. Ethane is available in a smaller percentage in natural gas.

Preparation of Methane and Ethane

(i) Decarboxylation of sodium salt of carboxylic acids

Methane can be prepared by heating a mixture of sodium acetate and soda lime in a hard glass test tube:

$$CH_3COONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

Ethane can be prepared in the similar fashion by taking sodium propanoate instead of sodium acetate:

$$C_2H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_2H_6 + Na_2CO_3$$

(ii) Preparation by reduction of alkyl halides

Methyl iodide is reduced to methane by nascent hydrogen produced by the action of Zn/Cu couple on ethyl alcohol:

$$CH_3I + 2[H] \rightarrow CH_4 + HI$$

Ethane on the other hand can be prepared by reduction of ethyl iodide by nascent hydrogen:

$$C_2H_5I + 2[H] \rightarrow C_2H_6 + HI$$

(iii) Preparation by hydrolysis of carbides

Pure methane can also be prepared by the action of water on aluminium carbide (Al_4C_3):

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

Physical Properties

These are colourless, odourless, tasteless gases which are insoluble in water, but soluble in non-polar solvents like alcohol, carbon tetrachloride, etc.

Chemical Properties

(i) Substitution reaction: Substitution reaction is a characteristic reaction of alkanes. Here one or more hydrogen atoms of methane or ethane are substituted by some other functional group. If the substitution is carried out by halogen, the reaction is called halogenation. The products depend upon the amount of chlorine.

(a) $CH_4 + Cl_2 \xrightarrow{\text{sunlight}} CH_3Cl + HCl$

(monochloromethane)

In excess chlorine, the reactions are

$CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$

(dichloromethane)

$$CH_4 + 3Cl_2 \rightarrow CHCl_3 + 3HCl$$

(trichloromethane)

$$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$$

(tetrachloromethane)

(b) $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$

(monochloroethane)

$$C_2H_6 + 2Cl_2 \rightarrow C_2H_4Cl_2 + 2HCl$$

(dichloroethane)

$$C_2H_6 + 3Cl_2 \rightarrow C_2H_3Cl_3 + 2HCl$$

(trichloroethane)

$$C_2H_6 + 4Cl_2 \rightarrow C_2H_2Cl_4 + 4HCl$$

(tetrachloroethane)

$$C_2H_6 + 5Cl_2 \rightarrow C_2HCl_5 + 5HCl$$

(pentachloroethane)

$$C_2H_6 + 6Cl_2 \rightarrow C_2Cl_6 + 6HCl$$

(hexachloroethane)

(ii) Combustion

In excess of O_2, these burn with a pale blue flame to form CO_2 and H_2O:

$$CH_4 + 2O_2 \xrightarrow{\text{Excess air}} CO_2 + 2H_2O + \text{heat}$$

$$2C_2H_6 + 7O_2 \xrightarrow{\text{Excess air}} 4CO_2 + 6H_2O + \text{heat}$$

In an inadequate supply of air, CO gas and water vapours are formed:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$

$$2C_2H_6 + 5O_2 \rightarrow 4CO + 6H_2O$$

(iii) Pyrolysis (or) cracking

Heating to a very high temperature in the absence of air is called *cracking* or *pyrolysis*. Methane decomposes to carbon and hydrogen when heated to 1000°C in the absence of air.

$$CH_4 \xrightarrow{1000°C} C + 2H_2$$

Ethane when heated to 450°C in absence of air, decompose to give ethylene, methane and hydrogen:

$$3C_2H_6 \xrightarrow{450°C} 2C_2H_4 + 2CH_4 + H_2$$

Conversions of Methane/Ethane into Useful Organic Compounds

(a) Alkane to alcohol

Formation of ethyl/methly alcohol from their respective alkanes is also a two-step reaction.

1st step

When equal volumes of alkane and chlorine gas are made to react they form their respective alkyl chlorides on exposure to sunlight:

$$CH_4 + Cl_2 \xrightarrow{\text{sunlight}} CH_3Cl + HCl$$

$$C_2H_6 + Cl_2 \xrightarrow{\text{sunlight}} C_2H_5Cl + HCl$$

2nd step

Alkyl chloride so formed when treated with aqueous KOH solution, and gets hydrolysed to the corresponding alcohol:

$$CH_3Cl + (aq.)\ KOH \rightarrow CH_3OH + KCl$$

$$C_2H_5Cl + (aq.)\ KOH \rightarrow C_2H_5OH + KCl$$

(b) Alkane to aldehyde

Formation of formaldehyde from alkane is a 3-step reaction.

1st step

Conversion of alkane to alkyl chloride

2nd step

Conversion of alkyl chloride to alcohol

3rd step

When alcohol vapour is passed over heated cupric oxide, it gets oxidized to aldehyde:

$$CH_3OH + CuO \xrightarrow{300°C} HCHO + Cu + H_2O$$

(formaldehyde)

$$C_2H_5OH + CuO \xrightarrow{300°C} CH_3CHO + Cu + H_2O$$

(acetaldehyde)

(c) Alkane to carboxylic acid

Formation of carboxylic acid from alkane involves a 3-step reaction.

1st step

Conversion of alkane to alkyl chloride

2nd step

Conversion of alkyl chloride to alcohol

3rd step

Alcohol so obtained when treated with acidified $KMnO_4$ gets oxidized to carboxylic acid:

$$CH_3OH + KMnO_4 \xrightarrow{H^+} HCOOH + MnO_2 + KOH$$

$$C_2H_5OH + KMnO_4 \xrightarrow{H^+} CH_3COOH + MnO_2 + KOH$$

Uses

(i) As a fuel

Methane and liquefied ethane are used as non-polluting fuels in automobile industries and other industries also.

(ii) As a source of important organic compounds

These are used for the manufacture of important organic compounds like alcohol, aldehyde and carboxylic acid which are widely used in the paint industry and other different industries for the manufacture of adhesives, plastics, artificial fibre, etc.

(iii) In fertilizer industry

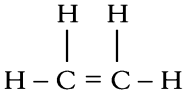
Hydrogen obtained by the pyrolysis of methane is used in the manufacture of ammonia which is further used in the manufacture of nitrogenous fertilizers.

Alkenes

Ethene

The smallest alkene is an ethene. It is an unsaturated hydrocarbon having a carbon–carbon double bond. Out of those, one is a strong sigma bond and another one is a weak pi bond. Its common name is ethylene.

Molecular formula: C_2H_4



Structural formula

Laboratory Preparation of Ethene

(i) Dehydration of ethyl alcohol

Ethyl alcohol on heating with conc. H_2SO_4 at 170°C produces ethene. Aluminium sulphate is added to this mixture to avoid frothing during the heating of the mixture:

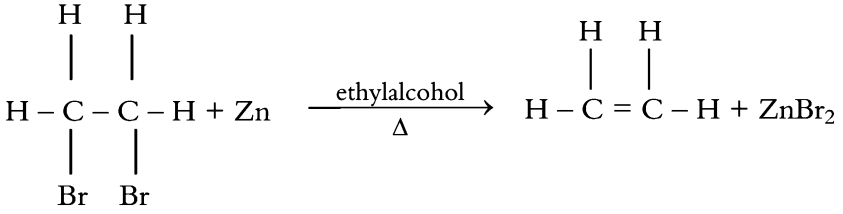
$$C_2H_5OH \xrightarrow[170°C]{95\%\ H_2SO_4} H_2C = CH_2 + H_2O$$

The above reaction can also be carried out by using Al_2O_3 at 350°C:

$$C_2H_5OH \xrightarrow[350°C]{Al_2O_3} H_2C = CH_2 + H_2O$$

(ii) Dehalogenation of 1, 2-Dibromoethane

1, 2-Dibromoethane when heated with Zn dust along with 95% alcohol converts to ethene.



Physical Properties

Ethene is a colourless, tasteless gas with a peculiar odour. It is insoluble in water, but soluble in nonpolar organic compounds like ether, alcohol, benzene, etc.

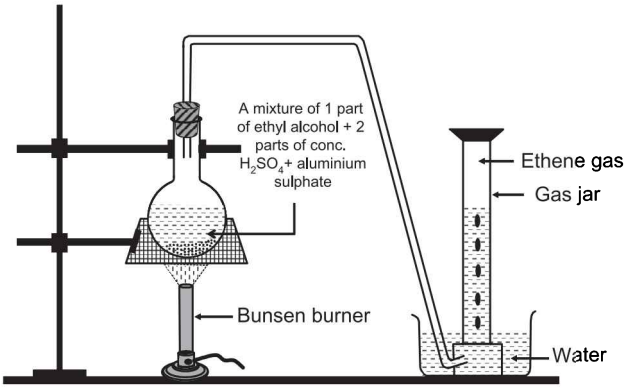


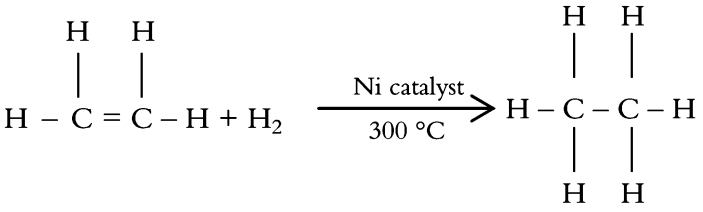
Figure 10.2 Laboratory preparation of Ethene

Chemical Properties

(i) Addition reaction

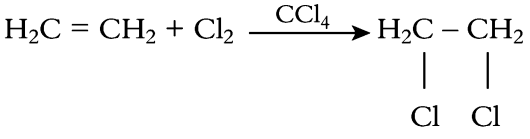
Ethene is an unsaturated hydrocarbon with a single π bond between the carbon atoms. Addition of a molecule of hydrogen, halogen, hydrogen halide or ozone to ethene under specific conditions results in breakage of π bond, forming corresponding addition compounds.

(a) Catalytic hydrogenation: Equal volumes of ethene gas and hydrogen when passed over heated nickel or platinum at 300°C form ethane.

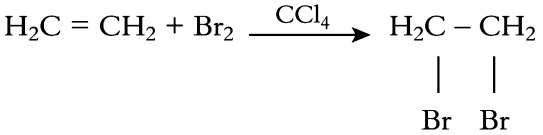


(b) Halogenation (addition of halogen): Alkenes are readily converted to corresponding saturated dihalide upon addition of halogen.

Ethene is readily converted to dichloroethane, (ethylene dichloride) when it is made to react with chlorine, in the presence of inert solvent CCl_4:



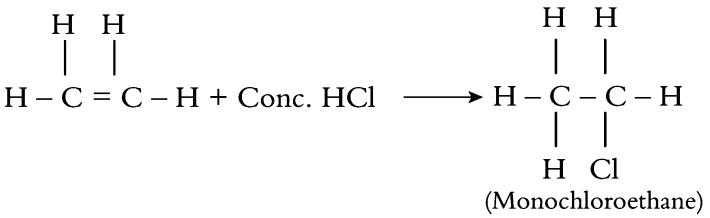
1, 2 – Dichloroethane



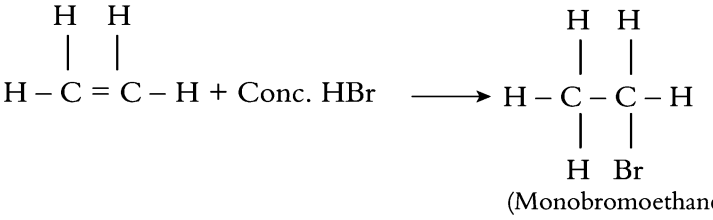
1, 2 – Dibromoethane

Decolourization of bromine is the test for identification of carbon–carbon multiple bond or unsaturation.

(c) Addition of halogen acid: When ethene gas is passed through concentrated halogen acids like HCl, HBr or HI, formation of respective addition compounds takes place.



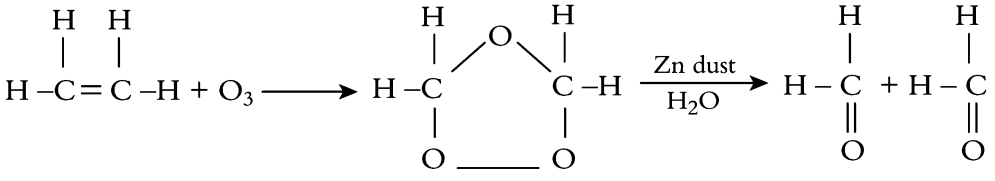
(Monochloroethane)



(Monobromoethane)

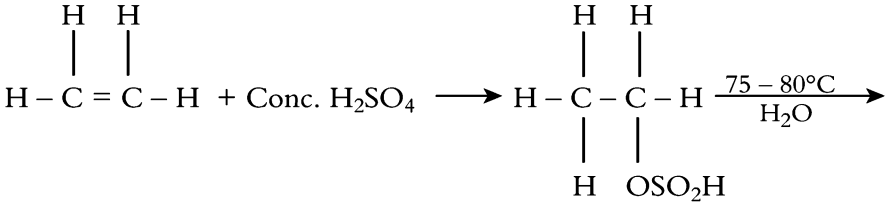
(d) Ozonolysis: On the addition of ozone to an unsaturated hydrocarbon, it forms an intermediate ozonide which on further hydrolysis in the presence of zinc dust gives corresponding carbonyl compound (aldehydes and ketones). This reaction is used to identify and locate the multiple bonds in an unsaturated hydrocarbon.

When a molecule of ozone is added to ethene at room temperature it forms a compound called ethene ozonide which on hydrolysis in the presence of zinc dust gives two molecules of formaldehyde.

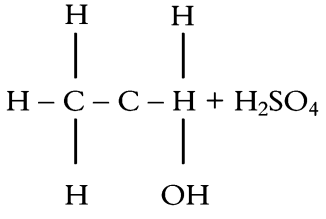


Etheneozonide

(e) Addition of sulphuric acid: An additive compound, ethyl hydrogen sulphate is formed when ethene gas is passed through cold conc. H_2SO_4 at room temperature. This on further hydrolysis with water gives ethyl alcohol.



(ethyl hydrogen sulphate)



(ethylalcohol)

(f) Hydroxylation (introduction of –"OH" groups): Hydroxylation is a reaction which involves oxidation followed by subsequent hydrolysis in the presence of suitable oxidizing agents.

Ethylene when subjected to hydroxylation in the presence of cold, dilute, alkaline potassium permanganate (Baeyer's reagent) gets oxidized to ethylene glycol.(a dihydroxy alcohol containing two –"OH" groups on adjacent carbons).

In this reaction, $KMnO_4$ gets decolourized which is a test for unsaturation.

$$\underset{\text{ethylene}}{3H_2C = CH_2} + 2KMnO_4 + 4H_2O \xrightarrow[\text{alk. } KMnO_4]{\text{Cold.dil}} \underset{\text{ethylene glycol}}{\begin{matrix} 3CH_2 - CH_2 \\ | \quad\quad | \\ OH \quad OH \end{matrix}} + 2MnO_4 + 2KOH$$

(ii) Combustion

Ethene gas completely burns with a pale blue, sooty flame in excess of air forming CO_2 gas and water vapour:

$$C_2H_4 + 3O_2 \xrightarrow[\text{air}]{\text{excess}} 2CO_2 + 2H_2O$$

The reaction is highly exothermic.

(iii) Polymerization

Polymerization is a process in which a large chain like molecule of higher molecular mass is formed due to combination of smaller molecules of similar structure with low molecular mass. The large molecule is called polymer and the constituent smaller molecules are called monomers. Ethene gas when passed through catalysts like HF and H_2SO_4 at a high temperature (2000°C) and under high pressure (1500–2000 atm) polymerizes to form polyethene:

$$\underset{\text{Ethene (or) ethylene}}{nH_2C = CH_2} \xrightarrow[\text{High temp and pressure}]{\text{Catalyst}} \underset{\text{Polyethene (or) polyethylene}}{\{H_2C - CH_2\}_n}$$

Conversion of Ethene into Useful Organic Compounds

Conversion of ethene into ethyl alcohol, acetaldehyde and acetic acid

When ethene is treated with concentrated HCl, monochloroethane or ethyl chloride is produced:

$$C_2H_4 + HCl \rightarrow \underset{\text{ethyl chloride}}{C_2H_5Cl}$$

Ethyl chloride on hydrolysis with aqueous KOH solution forms ethyl alcohol:

$$C_2H_5Cl + KOH\ (aq.) \rightarrow KCl + \underset{\text{(ethyl alcohol)}}{C_2H_5OH}$$

When ethyl alcohol vapours are passed over heated cupric oxide at 300°C, they oxidize to form acetaldehyde, whereas when ethyl alcohol is treated with acidified potassium dichromate, it gets oxidized to acetic acid:

$$C_2H_5OH + CuO \xrightarrow{300°C} \underset{\text{(Acetaldehyde)}}{CH_3CHO} + Cu + H_2O$$

$$C_2H_5OH + 2[O] \xrightarrow[K_2Cr_2O_7]{\text{acidified}} \underset{\text{(Acetic acid)}}{CH_3COOH} + H_2O$$

Uses

(i) Ethylene is used in the manufacture of the above mentioned organic compounds which have a wide application in organic chemical industries.
(ii) It is used in the manufacture of polythene which has an extensive use for different purposes like bags, bucket and various other things.
(iii) Ethylene is used for the manufacture of ethylene glycol which is used as an anti-freeze.
(iv) It is also used for artificial ripening of fruits like bananas and mangoes.

Ethyne

The simplest alkyne possible is ethyne. The trivial or common name of ethyne gas is acetylene. It is an unsaturated hydrocarbon where carbon–carbon triple bond is present. Among these, one is a strong sigma bond and other two are weak pi-bonds.

Molecular formula: C_2H_2

Structural formula: H–C≡C–H

Laboratory Preparation of Ethyne Gas

(i) Hydrolysis of calcium carbide: Calcium carbide on reaction with distilled water evolves acetylene gas:

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

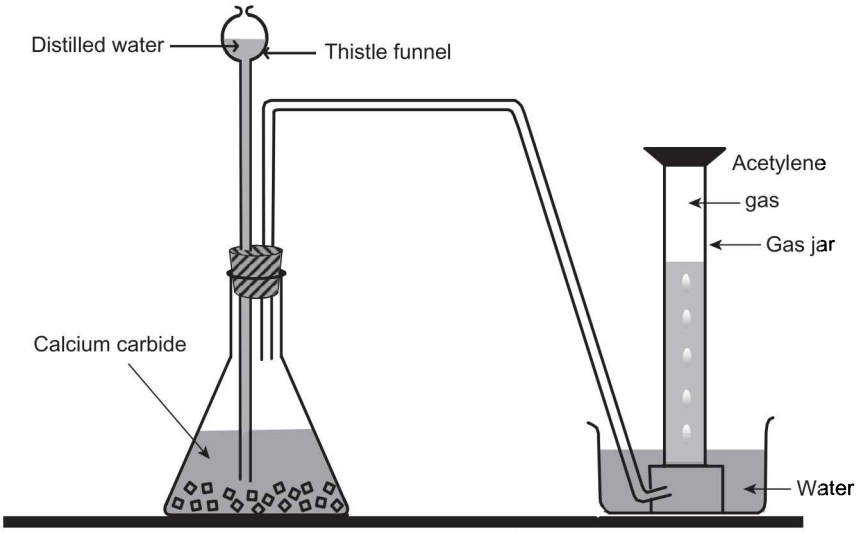
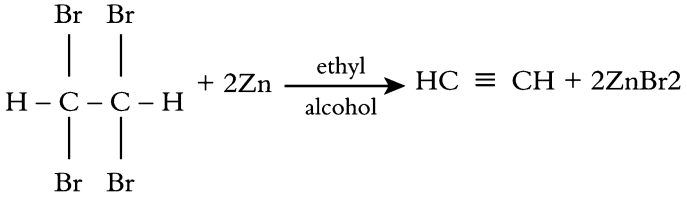


Figure 10.3 Preparation of acetylene gas

(ii) Dehalogenation of tetrahaloethane: A mixture of 95% ethyl alcohol and 1,1,2,2-Tetrabromoethane along with zinc dust when heated gently evolves acetylene gas:



Physical Properties

It is a colourless, tasteless gas with a characteristic garlic odour. It is insoluble in water, but dissolves in organic solvents like CCl_4, benzene, ether, etc. It is slightly lighter than air as its vapour density is 13.

Chemical Properties of Acetylene

(i) Addition reaction: Due to the presence of two weak pi bonds, ethyne molecule is highly reactive. Since two π bonds are present in a molecule of ethyne, addition of two molecules of halogen, hydrogen, hydrogen halide, etc., is possible.

(a) Catalytic hydrogenation: A mixture of one volume of ethyne gas and two volumes of hydrogen gas when passed over heated nickel at 300°C ethane gas is produced.

$$HC \equiv CH + H_2 \xrightarrow[300°C]{Ni} H_2C = CH_2 + H_2 \xrightarrow[300°C]{Ni} \underset{\text{Ethane}}{\overset{CH_3}{\underset{CH_3}{|}}}$$

(b) Halogenation: Addition of a molecule of halogen to ethyne molecule in the presence of CCl_4 gives 1,2-Dihaloethene which undergoes further addition of another halogen molecule to give 1,1, 2, 2-Tetrahaloethane.

When this reaction takes place with bromine, bromine water gets decolourized:

$$\underset{\text{Ethyne}}{HC \equiv CH} + Cl_2 \xrightarrow{CCl_4} \underset{\substack{| \quad | \\ Cl \quad Cl \\ \text{1, 2 – Dichloroethene}}}{HC = CH} + Cl_2 \xrightarrow{CCl_4} \underset{\substack{| \\ CHCl_2 \\ \text{1, 1, 2, 2 – Tetrachloroethane}}}{CHCl_2}$$

(c) Addition of halogen acids: Halogen acids like HCl and HBr form addition compounds with ethyne when the gas is passed through them. This reaction takes place in two stages:

$$HC \equiv CH + H - Br \longrightarrow \underset{\substack{| \\ Br}}{H_2C = CH} + H - Br \longrightarrow \underset{\substack{| \\ CHBr_2 \\ \text{1, 1-Dibromoethane}}}{CH_3}$$

$$HC \equiv CH + H - Cl \longrightarrow H_2C = CHCl + HCl \longrightarrow \underset{\substack{| \\ CHCl_2 \\ \text{1, 1-Dichloroethane.}}}{CH_3}$$

(d) Ozonolysis: Addition of a molecule of ozone to a molecule of ethyne at room temperature gives an addition compound, ethyne ozonide which on further hydrolysis with zinc dust gives glyoxal:

$$\underset{\text{Acetylene}}{HC \equiv CH} + O_3 \longrightarrow \underset{\substack{| \quad | \\ O - O \\ \text{Acetylene ozonide}}}{\overset{O}{\diagup\diagdown}\ HC - CH} + H_2O \xrightarrow[dust]{Zn} \underset{\substack{| \\ CHO \\ \text{glyoxal}}}{CHO + HCOOH}$$

(ii) Combustion: It burns in air with the evolution of a large amount of heat. CO_2 and water vapour are the products if it burns in excess supply of air:

$$2C_2H_2 + 5O_2 \xrightarrow[air]{excess} 4CO_2 2H_2O$$

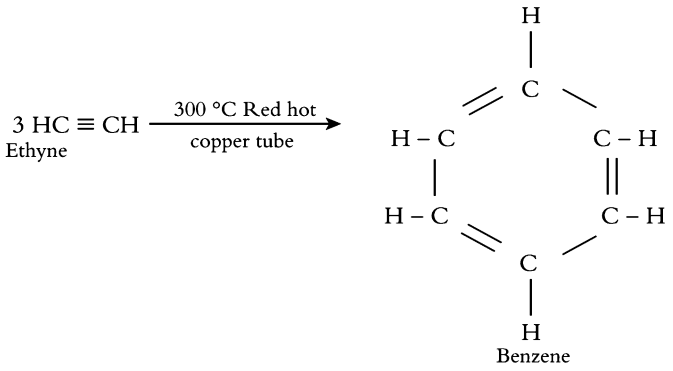
(iii) Action with ammonical cuprous chloride: A reddish brown precipitate of cuprous acetylide is obtained when acetylene gas is passed through ammonical cuprous chloride solution:

$$HC \equiv CH + 2CuCl + 2NH_4OH \rightarrow \underset{\text{(Cuprous acetylide)}}{CuC \equiv CCu} + 2NH_4Cl + 2H_2O$$

(iv) Action with ammonical silver nitrate: White precipitate of silver acetylide is formed when acetylene gas is passed through ammonical silver nitrate solution:

$$HC \equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow \underset{\text{(Silver acetylide)}}{AgC \equiv CAg} + 2NH_4NO_3 + 2H_2O$$

(v) Polymerization: Ethyne gas when passed through red hot Cu tube gives benzene:



Uses

(i) Oxyacetylene flame is used for cutting and welding metals.
(ii) Acetylene lamps are used for illumination purpose.
(iii) Ripening of fruits like apples and mangoes takes place in the atmosphere of acetylene.
(iv) Acetylene gas is hydrogenated to ethene which gets polymerized to form polyethylene which is very useful in packaging industry.

Tests Carried Out for the Distinction of Saturated and Unsaturated Hydrocarbons

(i) Decolourization of bromine water: Reddish brown coloured solution of bromine in CCl_4 disappears when unsaturated hydrocarbons (alkenes or alkynes) are passed through it. Saturated hydrocarbons do not respond to this test.

(ii) Decolourization of alkaline potassium permanganate: Pink colour of potassium permanganate fades away when an unsaturated hydrocarbon (alkene or alkyne) is passed through the alkaline potassium permanganate solution.

Test to Distinguish Alkene and Alkyne: (ethene and ethyne)

Formation of Metal Acetylides

Acetylene can form red precipitate of copper acetylide when it is passed through ammonical cuprous chloride solution. Alkenes do not respond to this test.

EXAMPLE

Straight chain higher alkanes, like hexadecane (an alkane with 16 carbon atoms) are used as lubricant oils. Justify the statement with appropriate reasons.

SOLUTION

Higher alkanes, due to the high molecular mass, remain in the liquid state and hence, they are used as lubricant oils. Hexadecane functions as anti-corrosive agent. Also, as it is hydrophobic in nature, it does not allow water to reach the metal surface.

EXAMPLE

Compared to other hydrocarbons, methane is more effective as a fuel in a gas turbine or steam boiler for electricity generation. Give reasons.

SOLUTION

Compared to other hydrocarbon fuels, burning of methane produces less CO_2 for each unit of heat released. The heat of combustion of methane is lower than that of other hydrocarbons, but if a ratio is made with the atomic weight divided by the heat of combustion, it is found that methane, being the simplest hydrocarbon, actually produces more heat per gram than any other hydrocarbon, that is CH_4 has a high calorific value. Other hydrocarbons may undergo partial combustion thereby adding to pollution, while methane undergoes complete combustion easily.

EXAMPLE

(a) Explain any two methods of preparation of ethene.

(b) Write any two methods of preparation of ethyne.

(c) How does acetylene react with ozone? Write the names of all reactants and products

SOLUTION

(a) Ethene can be prepared by the following processes.

(i) From ethyl alcohol: Dehydration of ethyl alcohol in presence of Conc.sulphuric acid produces ethene.

$$C_2H_5OH \xrightarrow{\overset{CH_3-}{5}\ \overset{CHC_2H_4}{4}} + H_2O$$

(ii) From 1, 2 – Dibromoethane: When 1, 2 – Dibromoethane is warmed with zinc in presence of ethyl alcohol it forms ethene.

$$\begin{matrix} CH_2-Br \\ | \\ CH_2-Br \end{matrix} + Zn \xrightarrow{\text{Ethyl alcohol}} \underset{\text{Ethene}}{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}} + ZnBr_2$$

(b) Ethyne can be prepared by the following processes.

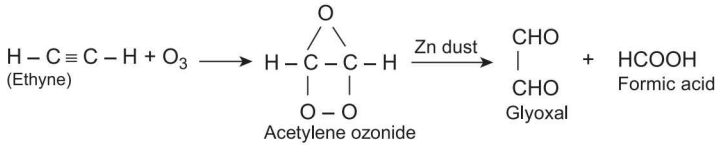
(i) From calcium carbide: Calcium carbide on hydrolysis forms acteylene or ethyne.

$$CaC_2 + 2H_2O \rightarrow \underset{\text{Ethyne}}{C_2H_2} + Ca(OH)_2$$

(ii) From 1, 1, 2, 2 – Tetrabromoethane: Zinc dust when added to a mixture of 1, 1, 2, 2 – Tetrabromoethane and 95% ethyl alcohol produces acetylene gas (ethyne) and zinc bromide.

$$\begin{matrix} H-C-C-H \\ | \quad | \\ Br \quad Br \end{matrix} \begin{matrix} Br \quad Br \\ | \quad | \end{matrix} + 2Zn \xrightarrow[\text{alcohol}]{\text{Ethyl}} \underset{\text{Ethyne}}{H-C\equiv C-H} + 2ZnBr_2$$

(c) Reaction of acetylene with ozone: Acetylene or ethyne on reaction with ozone at room temperature, forms acetylene ozonide which on further hydrolysis with zinc dust gives glyoxal and formic acid.



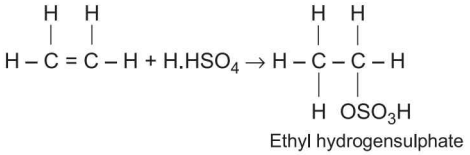
EXAMPLE

How does ethene react with the following compounds? Write the names of all reactants and products.

(a) H_2SO_4 **(b)** HCl **(c)** H_2 **(d)** O_3 **(e)** Cl_2

SOLUTION

(a) Ethene on reaction with H_2SO_4 at room temperature forms ethyl hydrogen sulphate.



(b) Ethene reacts with hydrochloric acid to form additive compound that is 1, 1 – Dichloroethane.

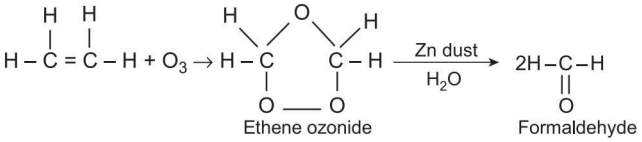
$H_2C = CHCl + HCl \rightarrow H_3C - CHCl_2$

1, 1 – Dichloroethane

(c) Ethene on reaction with hydrogen forms ethane. $C_2H_4 + H_2 \rightarrow C_2H_6$

Ethane

(d) Ethene gas reacts with ozone at room temperature to form ethene ozonide which on hydrolysis in the presence of zinc dust gives two molecules of formaldehyde.



(e) Ethene on reaction with chlorine gives 1, 2-Dichloroethane.

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

1, 2–Dichloroethane

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. Which characteristics of carbon are responsible for the existence of a large number of organic compounds?

2. Urea, an _____ compound, was manufactured from ammonium cyanate, which is an _____ compound.

3. Differentiate the ground state and excited state electronic configuration of carbon atom.

4. Why are oxides and carbonates of carbon considered to be inorganic compounds?

5. Which property of carbon gives rise to the structural isomerism of organic compounds?

6. Organic compounds having the same molecular formula, but different structural formulae are called _____.

7. Compare the structure of straight chain, branched chain and closed chain of carbon.

8. What is the difference between structural formula and condensed formula of organic molecules? Which of the two is more helpful to predict the chemical reaction?

9. What are hydrocarbon derivatives?

10. Position isomers differ in the position of _____.

11. Give the products obtained on decarboxylation of sodium ethanoate and sodium propanoate.

12. C_2H_6 and C_6H_6 are both hydrocarbons. What is the difference between them?

13. Saturated compound obtained by treating acetylene with HBr is _____.

14. Ethylene when subjected to hydroxylation in the presence of Baeyer's reagent gets oxidized to_____.

15. _____ can form a red precipitate when it passes through ammonical cuprous chloride solution.

16. What do you mean by an alkyl group?

17. Observe the molecular formulae and classify the following hydrocarbons into alkanes, alkenes and alkynes.

(i) C_2H_4 (ii) C_2H_6
(iii) C_4H_{10} (iv) CH_4
(v) C_3H_6 (vi) C_3H_8
(vii) C_4H_8 (viii) C_5H_{10}
(ix) C_7H_{14} (x) C_6H_{14}

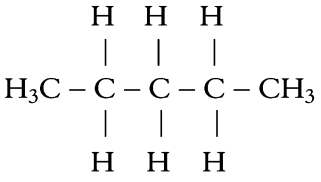
18. n-propane does not exhibit chain isomerism. Why?

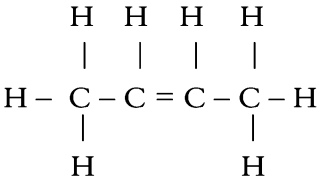
19. 1-Pentene and 3-Methyl-1-Butene are _____ isomers.

20. The hydrocarbon obtained by treating sodium ethanoate with soda lime is _____.

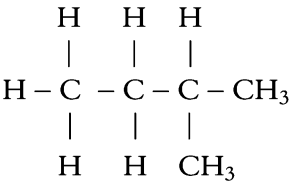
21. What is pyrolysis of methane? What is the use of this reaction?

22. Name the following compounds:

(i)


(ii)


(iii) $H_3C - C = CH$

(iv)


(v) $H_3C - C = C - CH_3$

23. Write the structural formula of the third compound of homologous series of alkane.

24. Complete the structures of following hydrocarbons by placing hydrogens only

(i) $C - C = C - C$ (ii) $C = C - C - C$ (with C branch)

(iii) $C - C - C - C$ (with C branch) (iv) $C = C - C$

(v) $C - C - C - C - C$

25. How is the position of alkyl group determined from the IUPAC name of the hydrocarbon?

PRACTICE QUESTIONS

26. Polymerization of ethylene gives _____.
27. Draw the structural formulae of n-Pentane and isopentane.
28. How can we understand the position of a double bond or triple bond from the name of the hydrocarbon?
29. Saturated compound obtained by the addition of halogen to acetylene is _____.
30. Draw the structural formula of the second compound of the homologous series of alkene.

Short Answer Type Questions

31. Write the structural reactions for the laboratory preparation of methane and ethane with a brief description.
32. Give the structural formulae of first four homologues of alkanes and alkenes.
33. Explain hydroxylation of ethene.
34. Describe the formation of ethyl alcohol from ethane.
35. Write the different products obtained by the chlorination of ethane.
36. What is chain isomerism? How many structural isomers are possible for the compound with molecular formula C_4H_{10}?
37. Give the two reactions of acetylene which are used to distinguish it from alkenes.
38. Which reagents oxidize ethyl alcohol to acetaldehyde and acetic acid? Why are two different reagents required for these conversions?
39. Describe the process by which methane converts to formaldehyde.
40. Write the laboratory preparation of ethyne gas in brief.
41. Describe the halogenation of acetylene gas.
42. How is acetylene gas produced from 1, 1, 2, 2-Tetrabromoethane?
43. Give the reactions representing the combustion of methane, ethane and ethyne.
44. Why do alkenes and alkynes undergo addition reaction while alkanes do not?
45. Describe the catalytic hydrogenation of ethene gas.

Essay Type Questions

46. Compare ozonolysis of ethene and ethyne in detail along with the reactions.
47. What is polymerization? Describe the polymerization of ethene and explain how it is useful.
48. Describe the different addition reactions of ethene.
49. (i) Describe in detail one test to distinguish saturated hydrocarbon from unsaturated hydrocarbon.
    (ii) Describe in detail one test to distinguish ethene and acetylene.
50. Describe the following conversions:
    (i) ethene to acetic acid
    (ii) acetylene to acetaldehyde
    (iii) methane to formic acid

CONCEPT APPLICATION

Level 1

***Directions for questions from 1 to 7*: State whether the following statements are true or false.**

1. Both alkenes and cycloalkanes both can be represented by the same general formula.
2. The general formula C_nH_{2n} is valid for any alkene with any number of multiple bonds.
3. Acetone is the common name of propanone.
4. The number of carbons present in isopentane and 2-Methylpentane are same.
5. 1, 2-Dibromoethane gives corresponding alkyne by treating with Zn dust under suitable conditions.

6. Isomers always show same chemical properties.

7. Ethylene when subjected to hydroxylation in the presence of Baeyer's reagent gets oxidized to glyoxal.

***Directions for questions from 8 to 14*: Fill in the blanks.**

8. When methane is mixed with excess chlorine and the mixture is exposed to sunlight, the final product is _____.

9. The compound formed when ethyl alcohol is treated with conc. H_2SO_4 at 170°C is _____.

10. By treating alkylchloride with aq. KOH _____ is produced along with KCl.

11. Pyrolysis of methane takes place in _____ of air and the products are _____ and _____.

12. Decolourization of $KMnO_4$ solution takes place when it reacts with ethene. The final product of this reaction which is used as an anti-freeze is _____.

13. Difference in molecular weight between two successive compounds in alkane homologous series is _____.

14. C_6H_{12} and C_6H_6 are the examples of _____ and _____ hydrocarbons, respectively.

***Directions for question 15*: Match the entries in column A with the appropriate ones in column B.**

15.

Column A		Column B
A. Unsaturated hydrocarbon	( )	a. C_6H_6
B. Aromatic hydrocarbon	( )	b. CH_4
C. Saturated hydrocarbon derivative	( )	c. $CHCl_3$
D. Sugar in water	( )	d. C_4H_8
E. Action of water on aluminium carbide	( )	e. $(CH_3)_2CHCH_2CH_3$

***Directions for questions from 16 to 45*: For each of the questions, four choices have been provided. Select the correct alternative.**

16. Controlled hydrogenation of ethyne gives which of the following compounds?
(a) rthane (b) ethene
(c) methane (d) none of these

17. Which of the following compound can be used to prepare ethene from ethyl alcohol?
(a) Al_2O_3 (b) H_2SO_4
(c) CaO (d) both (1) and (2)

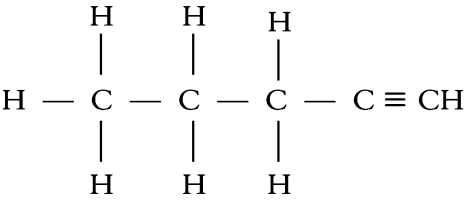
18. Catalytic hydrogenation of ethene produces _____.
(a) ethane (b) acetylene
(c) methane (d) ethyne

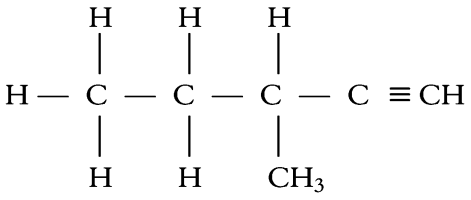
19. Number of moles of oxygen required for the combustion of one mole of an alkane is equal to
(a) n + 1 (b) $\frac{n+1}{2}$
(c) $\frac{3n+1}{2}$ (d) n

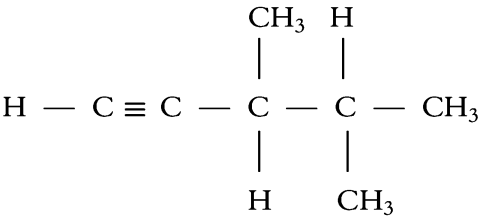
20. The ratio of the difference between number of hydrogens present in propane and propyne, propane and propene is
(a) 1 : 2 (b) 2 : 1
(c) 3 : 2 (d) 2 : 3

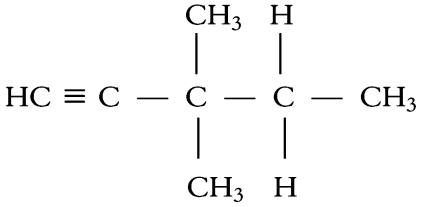
21. Which of the following groups consists of triple bond?
(a) $-C_3H_7$ (b) $-C_4H_7$
(c) $-C_5H_7$ (d) $-C_5H_{11}$

22. What is the correct structural formula of 3-Methyl-1-Pentyne?

(a)


(b)


(c)


(d)


PRACTICE QUESTIONS

23. Which of the following compounds cannot exhibit chain isomerism?
(a) propane (b) butane
(c) pentane (d) hexane

24. Polymerization of acetylene gives rise to _____.
(a) polyethylene (b) polyacetylene
(c) benzene (d) polypropene

25. Which of the following hydrocarbons can decolourize the alkaline potassium permanganate solution?
(a) C_2H_6 (b) C_3H_8
(c) C_5H_{12} (d) C_3H_6

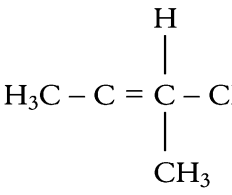
26. Identify the organic compound which can react with only one mole of sodium metal in the presence of strong base.
(a) propyne (b) ethyne
(c) 2-Butyne (d) ethene

27. Ethylene glycol is used as
(a) an anti-freezer
(b) a fuel
(c) a refrigerant
(d) an agent for ripening of fruits

28. Which of the following components is present in major proportions in LPG and why?
(a) Methane because it is easily liquefiable.
(b) n-butane because it is easily liquefiable.
(c) Isooctane because it reduces knocking property.
(d) n-propane because it has high calorific value.

29. A molecule of hydrocarbon "X" can add upon two molecules of Br_2. "X" on ozonolysis gives two different products which cannot be further oxidized. Identify "X."
(a) $H_2C = CH - CH = CH_2$
(b) $HC \equiv CH$
(c) $H_3C - C \equiv CH$
(d) $H_3C - CH = CH - CH_3$

30. Products obtained at the end of the reaction when



is subjected to ozonolysis are
(a) acetaldehyde
(b) propanaldehyde
(c) acetone, acetaldehyde
(d) acetone, formaldehyde

31. The various steps for writing IUPAC name of an organic compound are given below. Arrange the steps in the correct order.
(1) numbering of carbon chain
(2) identification of primary suffix
(3) selection of the longest chain
(4) identification of secondary suffix
(5) identification of number and nature of alkyl groups attached to carbon chain
(a) 3 1 2 4 5 (b) 3 1 5 2 4
(c) 3 2 4 1 5 (d) 1 3 2 4 5

32. Hexane exhibits chain isomerism. One of its isomers possesses two tertiary carbon atoms. Arrange the following steps in a proper sequence to write IUPAC name for the respective isomer.
(1) Identification of number of carbon atoms in the main chain.
(2) Writing the structure of respective isomer of hexane.
(3) Numbering of carbon chain.
(4) Giving position numbers for the alkyl groups attached to main chain.
(5) Identification of nature of tertiary carbon atom.
(a) 2 1 3 5 4 (b) 5 1 2 3 4
(c) 2 5 3 1 4 (d) 5 2 1 3 4

33. Arrange the following hydrocarbons in the increasing order of volume of oxygen required for complete combustion per mole under the same conditions.
(1) ethane (2) propyne
(3) ethyne (4) propene
(5) propane (6) ethene
(a) 3 6 1 2 4 5 (b) 5 4 2 1 6 3
(c) 3 2 6 4 1 5 (d) 5 2 4 6 1 3

34. Preceding and succeeding homologues of $C_{10}H_{22}$ respectively are
(a) C_9H_{20}, $C_{11}H_{22}$ (b) C_9H_{20}, $C_{11}H_{24}$
(c) $C_{11}H_{24}$, C_9H_{20} (d) C_8H_{18}, C_9H_{20}

35. Which of the following compounds contains a triple bond?
(a) C_2H_6 (b) C_4H_8
(c) C_5H_8 (d) C_5H_{12}

36. The part of IUPAC name which indicates saturation or unsaturation is
(a) root word (b) primary suffix
(c) secondary suffix (d) prefix

37. Which of the hydrocarbons cannot decolourize the red-coloured solution of bromine in CCl_4?
(a) CH_4 (b) C_2H_4
(c) C_2H_2 (d) C_3H_6

38. Complete hydrogenation of ethyne gives _____
(a) ethane (b) ethane
(c) methane (d) none of these

39. The hydrocarbons obtained by pyrolysis of ethane are _____ and _____.
(a) C_2H_4, C_2H_2 (b) CH_4, C_2H_2
(c) C_2H_4, CH_4 (d) C_2H_2, C_6H_6

40. What is the number of hydrogen atoms present in the hydrocarbon formed by the hydrogenation of ethylene?
(a) 4 (b) 6
(c) 8 (d) 2

41. Which of the following compounds on hydrolysis produces methane?
(a) $CaCN_2$ (b) CaC_2
(c) Al_4C_3 (d) SiC

42. How many grams of hydrogen is required to saturate one mole of acetylene?
(a) 3 g (b) 6 g
(c) 10 g (d) 4 g

43. Which of the following molecular formulae corresponds to an unsaturated hydrocarbon with triple bond?
(a) C_4H_8 (b) C_4H_6
(c) C_4H_{10} (d) C_6H_{12}

44. **Assertion (A)**: Unsaturated hydrocarbons decolourize the red coloured bromine water.

Reason (R): Unsaturated hydrocarbon undergoes substitution reaction with bromine water.
(a) Both A and R are correct and R is the correct explanation of A.
(b) Both A and R are correct but R is not the correct explanation of A.
(c) A is correct and R is wrong.
(d) A is wrong and R is correct.

45. Arrange the following in a proper sequence for writing the structural formula from the given IUPAC name 4-Methyl-4-Nonene.
(1) Locate the primary suffix and insert at the given position.
(2) Identify the substituent and insert at the given position.
(3) Add suitable number of hydrogen atoms to satisfy the valencies of each carbon atom.
(4) Identify the root word and write down the parent carbon chain.
(a) 4 1 3 2 (b) 2 4 1 3
(c) 4 1 2 3 (d) 4 2 3 1

Level 2

1. Is it possible to separate isomeric n-alkane and isoalkane by fractional distillation? Explain with appropriate reasons.

2. How do you effect the following conversions?
(a) ethane to methane
(b) ethyne to ethyl alcohol

3. Higher alkanes, i.e., hexadecane (an alkane with 16 carbon atoms) are used as lubricant oils. Justify the statement with appropriate reasons.

4. (i) $A + Br_2 \xrightarrow[Zn]{CCl_4} \underset{\|}{\overset{HC-Br}{HC-Br}} + Br_2 \longrightarrow C$

(ii) $CH_3I \xrightarrow[\text{ethyl alcohol}]{Zn/Cu} A + Cl_2 \xrightarrow{bv} C \xrightarrow[\text{water}]{KOH} D$

Give IUPAC names of A, C and D in both (i) and (ii) set of reactions.

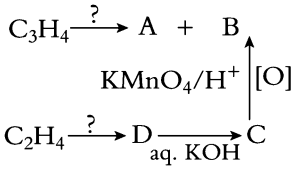
5. Compared to other hydrocarbons, methane is more effective as a fuel in a gas turbine or steam boiler for electricity generation. Give reasons.

6. Give the role of the following reagents in the respective reactions.
(a) quicklime in decarboxylation of salts of carboxylic acids
(b) zinc dust in ozonolysis

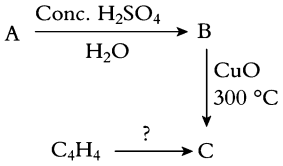
PRACTICE QUESTIONS

7. Identify A, B, C and D in the given following conversions and write their structural formulae.

(i)



(ii)



8. Why is the dipole moment of all alkanes zero?

9. Both methane and ethane can be used as fuels. By giving the balanced equations corresponding to the reactions responsible for the above use, justify which is a better fuel.

10. $CH_4 + Cl_2 \xrightarrow{?} CH_3Cl + HCl$. Is it possible to carry out the reaction under incandescent bulb? Justify.

11. How is polyvinyl chloride obtained from acetylene?

12. The first homologue of the series with general formula C_nH_{2n} on oxidation with alkaline $KMnO_4$ gives a compound is added to water which is used as a coolant in automobiles. Identify the compound and explain the purpose of its addition to water.

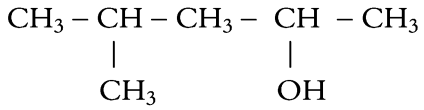
13. Methanol and ethane have almost the same molecular weight. But boiling point of methanol is 65°C and ethane is –89°C. Explain why.

14. Write the possible structural isomers for the compound with molecular formula C_5H_{10} and explain how these isomers can be identified with ozonolysis.

15. What is the role of sunlight in the halogenation of a hydrocarbon?

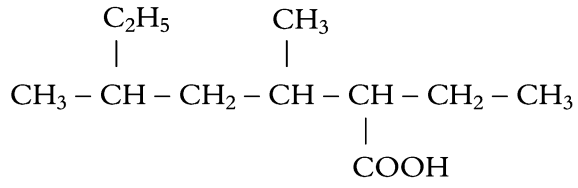
16. In an examination, structures for four organic compounds are given. A student, Jujo, has written the names corresponding to the structures. Identify whether the name is appropriate for the given structure. If not, give a reason and suggest the correct name for the structure.

(a)



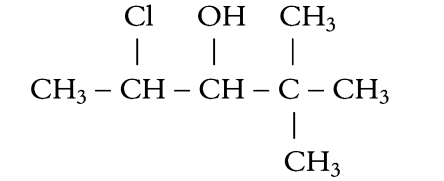
2 – Methyl–4–pentanol

(b)



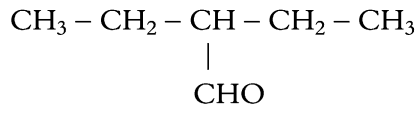
4, 6–Dimethyl–3–octanoic acid

(c)



4 – Chloro –2, 2 – dimethyl–3–pentanol

(d)



3 – Hexanal

17. How many structural isomers can pentene have? Give their structures and IUPAC names.

18. Two metals X and Y have 3 and 2 electrons in their valence shells "M" and "N," respectively. These metals can form binary compounds A and B with the same non-metal carbon. Both A and B can undergo hydrolysis forming hydrocarbons C and D. Identify C and D and write the steps required for the conversion of D to second member of alkanes.

19. How is ozonolysis of unsaturated hydrocarbon used to find out the position of unsaturation? Explain the role of zinc dust used in the reaction.

20. Based on the products of ozonolysis, is it possible to distinguish branched chain and straight chain alkenes? Explain by taking the homologue with vapour density 35.

21. Propane does not exhibit chain isomerism. Why?

22. A hydrocarbon Y decolourizes bromine water. The saturated compound resulted in this reaction, on treatment with Zn dust gives back hydrocarbon Y. Y when passed through a solution of $AgNO_3$ dissolved in NH_4OH gives a white precipitate. The next higher homologue of Y that is X gives ketone

as the product upon addition of water. Identify X and Y and give equations.

23. Explain the similarities and dissimilarities between C_2H_4 and C_2H_2 by using the following reagents.
    (a) bromine (Br_2) in presence of CCl_4
    (b) alkaline $KMnO_4$
    (c) ammonical silver nitrate
    (d) ammonical cuprous chloride

24. Write the structural formulae for the following compounds:
    (a) 2-Butanol
    (b) 3, 4, 5-Trimethyl heptane
    (c) 4-Ethyl-2-Methyl heptane
    (d) 2-Ethyl-1-Pentene
    (e) 4-Chloro-5-Methyl 2-Octene

25. The molar ratio of CO_2 and H_2O produced by the combustion of one mole of hydrocarbon X is 5 : 4. Write the balanced equation for the combustion of X, succeeding and preceding homologues of X. Mention the chain isomers of X and their names.

Level 3

1. What is teflon? Why is it used as an electrical insulation?

2. The tendency of halogenation of alkanes decreases in the order $Cl_2 > Br_2 > I_2$. Give a reason and also explain how fluorination of alkanes can be carried out?

3. Why is tetrachloroethene extensively used for the purpose of dry cleaning?

4. Methane is made to react with chlorine and iodine in closed containers in two separate reactions in presence of sunlight. The yield of CH_3I was much less when compared to the yield of CH_3Cl. Give a reason. However, if the reaction is carried out in presence of HNO_3 or HIO_3, the yield of CH_3I is found to increase. How do you account for this?

5. Propane and butane are used as propellants in aerosol sprays. Why?

***Directions for questions from 6 to 10*: Application-Based Questions**

6. The first and second members of alkynes necessarily show acetylide formation. Do the later members necessarily show the same behaviour? Justify by taking the simplest homologue as an example.

7. Why are alkanes hydrophobic in nature?

8. Identify the molecular formula of an alkane which has only three chain isomers. Suggest a suitable method of separation of these isomers and draw a comparison of their dipole moments.

9. Three hydrocarbons X, Y and Z have carbon which combine with hydrogen in the ratio of 3 : 2 : 1, respectively. Comment on their characteristic reactions.

10. How do you effect the following conversions?
    (a) ethane to methane
    (b) ethyne to ethyl alcohol

PRACTICE QUESTIONS

CONCEPT APPLICATION

Level 1

True or false

1. True
2. False
3. True
4. False
5. False
6. False
7. False

Fill in the blanks

8. CCl_4
9. ethene
10. alcohol
11. absence of C, H_2
12. ethylene glycol
13. 14
14. aliphatic, aromatic

Match the following

15. A : d B : a C : e D : c E : b

Multiple choice questions

16. b
17. d
18. a
19. c
20. b
21. c
22. b
23. a
24. c
25. d
26. a
27. b
28. b
29. c
30. c

31. (i) Selection of the longest chain
    (ii) Numbering of carbon chain
    (iii) Identification of primary suffix
    (iv) Identification of secondary suffix
    (v) Identification of number and nature of alkyl groups attached to carbon chain

32. (i) Writing the structure of respective isomer of hexane
    (ii) Identification of nature of tertiary carbon atom
    (iii) Numbering of carbon chain
    (iv) Identification of number of carbon atoms in the main chain
    (v) Giving position numbers for the alkyl groups attached to main chain

33. (i) Ethyne
    (ii) Ethene
    (iii) Ethane
    (iv) Propyne
    (v) Propene
    (vi) Propane

34. Preceding homologue of $C_{10}H_{22}$ is C_9H_{20} and succeeding homologue of $C_{10}H_{22}$ is $C_{11}H_{24}$

35. Formula C_5H_8 corresponds to C_nH_{2n-2} and is an alkyne. It contains a triple bond.

36. Primary suffix indicates saturation or unsaturation

37. Saturated hydrocarbons (methane) cannot decolourize red-coloured solution of bromine in CCl_4.

38. $HC \equiv CH + 2H_2 \xrightarrow{Ni} H_3C - CH_3$.
    Ethane is formed

39. $3C_2H_6 \xrightarrow{450°C} 2C_2H_4 + CH_4 + H_2$

40. Ethylene on hydrogenation gives ethane. Ethane has six hydrogen atoms.

41. Aluminium carbide on hydrolysis produces methane.

42. One mole of acetylene requires 2 moles of hydrogen to give ethane. Two moles of hydrogen corresponds to 4 g.

43. C_4H_6 corresponds to general molecular formula C_nH_{2n-2}. which possesses one triple bond.

44. Since unsaturated hydrocarbons are reactive they decolourize reddish brown bromine water by forming additions compound by addition reaction and not by substitution reaction.

45. (a) Identify the root word and write down the parent carbon chain.

(b) Locate the primary suffix and insert.

(c) Identify the substituent and insert.

(d) Add suitable number of hydrogen atoms to satisfy the valencies of each carbon atom.

Level 3

1. (i) Principle of fractional distillation.

(ii) Comparison of structure of isomeric alkanes.

(iii) Effect of structure on boiling points. The type of bond breakage in the reaction.

2. (a) (i) Different reactions involved in conversions.

(ii) Identification of reaction and reagents associated with decrease in number of carbon atoms.

(b) (i) Identification of reactant which can give ethyl alcohol.

(ii) Identification of respective steps involved in getting the reactant from the unsaturated hydrocarbon (ethyne).

3. (i) State and nature of higher alkanes

(ii) Structure of higher alkanes

(iii) Requisite for lubricant oil

(iv) Relation of structure with boiling point

4. (i) Identification of nature of the compounds A, C and D

(ii) Identification of A based on type of product formed and reagents used

(iii) Identification of C

(iv) Identification of from D with the given specific reagent.

5. (i) Comparison of combustion of methane and other hydrocarbons

(ii) Comparison of calorific value of methane with other hydrocarbons

(iii) Relation of calorific value with fuel efficiency

6. (a) Nature of CaO, Zn dust

(b) (i) Chemical equation corresponding to decarboxylation of salts of carboxylic acids

(ii) Products and by-products obtained

(iii) Effect of by-products on the purity of the main product in cancelling the above effect

(iv) Nature and role of quick lime

(c) (i) Nature of the by-product formed upon ozonolysis

(ii) Effect of the by-product on the main products formed

(iii) Nature and role of zinc dust in compensating the above effect

7. (a) Identification of A, B, C and D based on reactants and reagents given

(b) (i) Identification of functional groups in C and B based on the given reagents

(ii) Identification of D and the reagent used for getting D

(iii) Identification of the nature of initial hydrocarbon

(iv) Identification of reagent which can give "B" from the given hydrocarbon

(c) (i) Identification of functional groups in B and C from the reagent used

(ii) Identification of nature of hydrocarbon (C_4H_8)

(iii) Identification of reagent for the conversion of C_4H_8 to C

(iv) Identification of "A" on the basis of given reagent and functional group of "B."

8. (i) Structure of alkanes

(ii) Effect of structure on dipole moment

9. (i) Comparison of ΔH values of the two equations

(ii) Comparison of percentage composition of hydrogen in methane and ethane

(iii) Relation between percentage of hydrogen and calorific value

(iv) Balanced chemical equations for combustion of methane and ethane

(v) Comparison of ΔH values

(vi) Calculation of amount of energy released per gram of methane and ethane from ΔH values

(vii) Relation between amount of energy released and the efficiency of the fuel

(viii) Comparison of amount of harmful product formed per unit weight of hydrocarbon

10. (i) Conditions required to carry out the reaction

(ii) Relation between the conditions and the process taking place in the reaction

(iii) Heat produced by incandescent bulb

(iv) Comparison of heat produced by incandescent bulb and the actual conditions required for reaction

11. (i) Formula of polyvinyl chloride

(ii) Identification of a characteristic reaction which leads to the formation of PVC

(iii) Identifications of reagent, for the conversion of acetylene to the corresponding monomer of PVC

12. (i) Identification of first homologue

(ii) Identification of the product of the first homologue upon oxidation with alk. $KMnO_4$

(iii) Prerequisite of a substance to act as coolant

(iv) Changes that take place in physical properties of water upon addition of the product obtained in (i)

(v) Effect of change in physical property of water on efficiency of its action as coolant

13. (i) Comparison of forces existing among methanol and ethane molecules

(ii) Effect of the extent of intermolecular forces of attraction on boiling points

14. (i) Comparison of the products obtained on ozonolysis

(ii) Identification of nature of hydrocarbon (saturated/unsaturated) from given molecular formula

(iii) Number of possible isomers based on number of carbon atoms, nature of hydrocarbon and arrangement of carbon atoms

(iv) Reactive centres required for addition of O_3

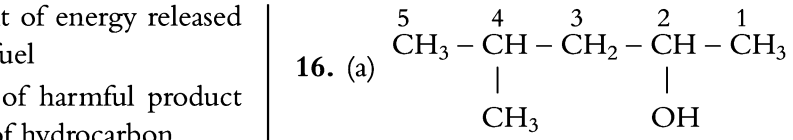
(v) Identification of nature of products obtained by ozonolysis

(vi) Comparison of products of ozonolysis of different isomers

15. (i) Properties of UV rays of sunlight

(ii) Effect of UV rays on the mechanism of reaction

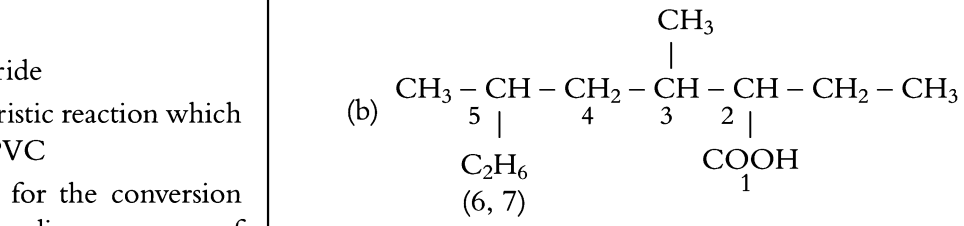
16. (a)



correct name 4-Methyl-2-Pentanol

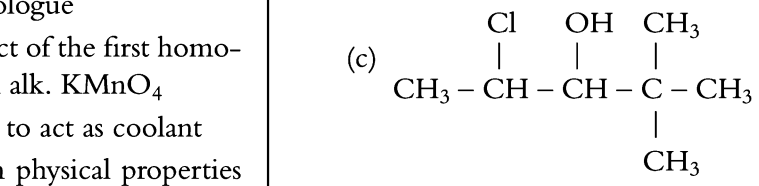
2-Methyl-4-Pentanol is a wrong name. This is because the carbon attached to functional group should get the least position. Between subsistent and functional groups, the functional group gets priority.

(b)



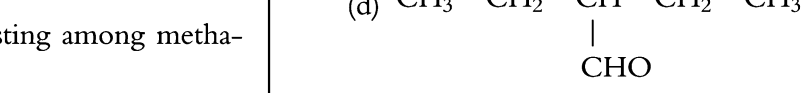
Correct name is 2-Ethyl 3, 5-Dimethyl heptanoic acid

(c)



2-Chloro 4, 4-Dimethyl-3-Pentanol is the correct name. Among alkyl and halo groups, halo group should have the least number.

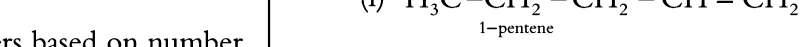
(d)

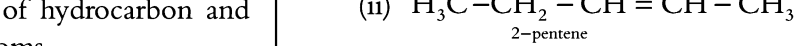


Correct name is 2-Ethyl butanal

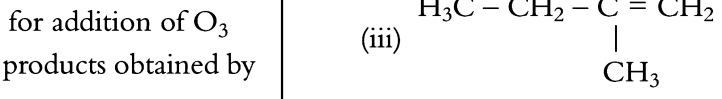
3-Hexanal is the wrong name since the –CHO group is a terminal functional group and should always be taken as a first carbon.

17. Structural isomers for pentene

(i) 

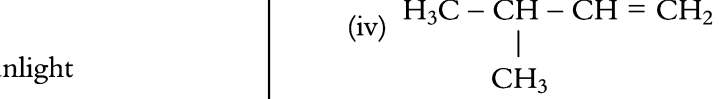
(ii) 

(iii)



2 – methyl – 1– butene

(iv)



3 – methyl – 1– butene

(v) $H_3C - CH = C - CH_3$ with CH_3 branch

2 – methyl – 2– butene

18. The binary inorganic compounds which undergo hydrolysis to form hydrocarbons are aluminium carbide and calcium carbide.

$X \rightarrow 2, 8, 3, Al \rightarrow Al_4C_3$ (A)

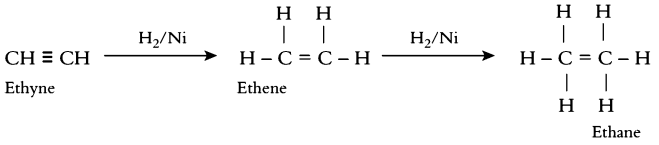
$Y \rightarrow 2, 8, 8, 2, Ca \rightarrow CaC_2$ (B)

$Al_4C_3 + H_2O \rightarrow Al(OH)_3 + CH_4$

(A) (C)

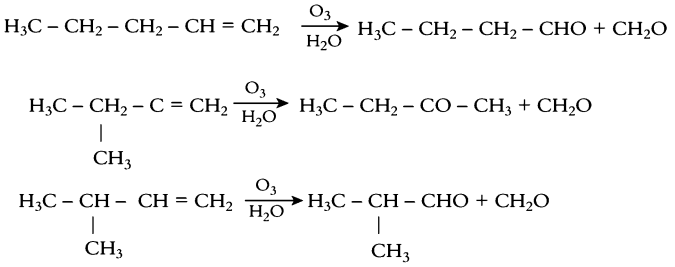
$CaC_2 + H_2O \rightarrow Ca(OH)_2 + C_2H_2$

(B) (D)



19. When ozone reacts with unsaturated hydrocarbon, the pi bond breaks and ozonide formation takes place at the point of unsaturation and hydrolysis of ozonide gives respective hydrocarbon derivatives. Depending on the structure of the hydrocarbon derivative the position of unsaturation can be determined. If Zn dust is not used H_2O_2 would be formed which oxidizes the aldehydes and ketones further to acids. Hence, Zn dust prevents oxidation.

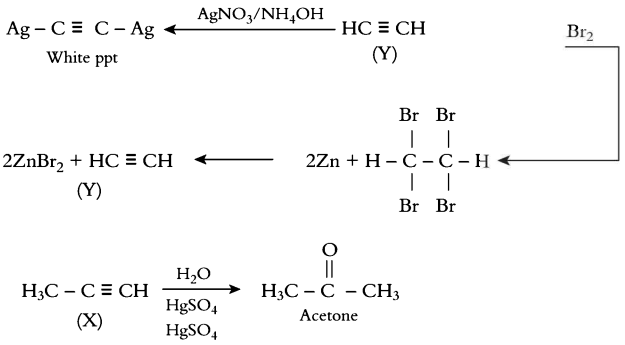
20. Alkene with vapour density 35 is C_5H_{10} (M. Wt = 70). Chain isomers of pentene are



n-alkenes on ozonolysis give straight chain aldehydes only. Among branched chain alkenes, if the alkyl chain is attached to double-bonded carbon, one of the ozonolysis products should be ketone. If the branched chain alkene contains alkyl chain on a single-bonded carbon, on ozonolysis, it gives branched chain aldehyde.

21. Propane has only three carbon atoms and hence cannot have a branched chain.

22.

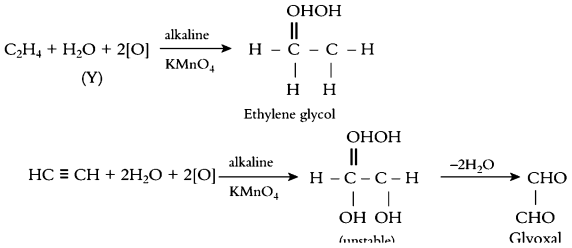


23. (a) Both C_2H_4 and C_2H_2 decolourize bromine (Br_2) in presence of CCl_4 and form dibromo ethane and tetrabromoethane, respectively as the final products:

$$C_2H_4 + Br_2 \xrightarrow{CCl_4} C_2H_4Br_2$$

$$C_2H_2 + Br_2 \xrightarrow{CCl_4} C_2H_2Br_2 \xrightarrow[+Br_2]{CCl_4} C_2H_2Br_4$$

(b) Both C_2H_4 and C_2H_2 decolourize the pink colour of alkaline $KMnO_4$ to colourless and undergo oxidation to form ethylene gylcol and glyoxal, respectively.



(c) C_2H_4 does not react with ammonical silver nitrate, whereas C_2H_2 reacts with ammonical silver nitrate to form a white precipitate of silver acetylide:

$C_2H_4 + AgNO_3 + NH_4OH \rightarrow$ No reaction

$C_2H_2 + 2AgNO_3 + 2NH_4OH \rightarrow Ag–C \rightarrow C – Ag + 2NH_4NO_3 + 2H_2O$

(d) C_2H_4 does not react with ammonical cuprous chloride, whereas C_2H_2 reacts with it and forms a reddish precipitate of cuprous acetylide:

$H_2C = CH_2 + CuCl + NH_4OH \rightarrow$ No reaction

$HC \rightarrow CH + 2CuCl + 2NH_4OH \rightarrow Cu\text{-}C \rightarrow C – Cu + 2NH_4Cl + 2H_2O$

24.

(a) CH_3 with $H_3C – HC – CH – OH_2$

HINTS AND EXPLANATION

(b) $H_3C - H_2C - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH_3$

(c) $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2 - CH - CH_2 - CH_2 - CH_3$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2 - CH_3$

(d) $CH_3 - CH_2 - CH_2 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_2}{|}}{C}} = CH_2$

(e) $H_3C - H_2C - CH_2 - \underset{\underset{CH_3}{|}}{CH} - \underset{\underset{Cl}{|}}{CH} - CH = CH - CH_3$

25. Balanced equation for the combustion of hydrocarbon is

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow x.CO_2 + \frac{y}{2}HO_2$$

The molar ratio of CO_2 and $H_2O = \frac{x}{\frac{y}{2}} = \frac{5}{4}$

$\Rightarrow \frac{2x}{y} = \frac{5}{4} \Rightarrow \frac{x}{y} = \frac{5}{8}$

$\rightarrow$ X is C_5H_8

Succeeding homologue of X is C_6H_{10}

Preceding homologue of X is C_4H_6

$2C_5H_8 + 14O_2 \rightarrow 10CO_2 + 8H_2O$

$2C_6H_{10} + 17O_2 \rightarrow 13CO_2 + 10H_2O$

$2C_4H_6 + 11O_2 \rightarrow 8CO_2 + 6H_2O$

Chain isomers of X (C_5H_8) are

$CH \rightarrow C - CH_2 - CH_2 - CH_3 \rightarrow$ 1-Pentyne

$CH \equiv C - \underset{\underset{CH_3}{|}}{CH} - CH_3 \rightarrow$ 3 – methyl – 1 – butyne

Level 3

1. (i) Comparison of teflon
(ii) Nature of the atoms participating in bond formation
(iii) Strength of the bond
(iv) Influence of this bond on the properties

2. (i) Type of reactions taking place with Cl_2, Br_2 and I_2
(ii) Energy changes involved in multi-step reactions of halogenation
(iii) Identification of the rate-determining step
(iv) Comparison of ΔH values of chlorination, bromination and iodination
(v) Comparison of the factor determining the rate of reaction of chlorination, bromination and iodination
(vi) Energy changes involved when fluorination takes place
(vii) Its effect on reaction
(viii) Conditions to be created for fluorination to proceed in normal way

3. (i) Nature of tetrachloroethene
(ii) Requisites for a solvent used for dry cleaning purpose
(iii) Comparison of properties of tetrachloroethene with dry cleaning solvent
(iv) Intermolecular forces present in tetrachloroethene

4. (i) Comparison of reactions of methane with Cl_2 and I_2.
(ii) Comparison of products obtained from chlorination and iodination
(iii) Comparison of reactivities of by-products produced in above two reactions
(iv) Effect of the by-product produced in iodination on nature and yield of the reaction
(v) Conditions or suitable reagents required to increase the yield

5. (i) Physical properties of propane and butane
(ii) Role of propane and butane as propellants
(iii) Significance of propellant in an aerosol spray

6. The first and second members of alkynes are ethyne and propyne. They have hydrogens attached to "sp" hybrid carbons. "sp" hybrid orbital has greater percentage of "s" character which holds the two carbon atoms more strongly. Due to this C–H bond becomes weaker and the hydrogens become slightly acidic, i.e., replaceable. In case of later members,

1-alkynes possess hydrogens attached to "sp" hybrid carbons. But their position isomers 2-alkynes do not possess such acidic hydrogens. Therefore, they do not form acetylides.

Examples

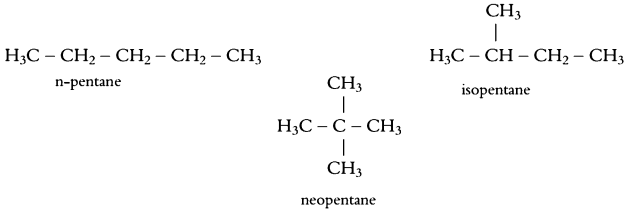
$$H_3C-CH_2-C\equiv CH + AgNO_3 \xrightarrow{NH_4OH} H_3C-CH_2-C\equiv CAg.$$

1 – butyne

$$H_3C-C\equiv C-CH_3 + AgNO_3 \xrightarrow{NH_4OH} \text{No reaction}$$

7. Alkane molecules do not have any resultant dipole moment due to the presence of symmetrical bond that is symmetrical structure. Hence, they neither ionize in water nor form H-bonding. Since no attractive force acts between water and methane molecules, they try to maintain minimum area of contact. Therefore, alkanes are hydrophobic.

8. C_5H_{12} (pentane) is the molecular formula of alkane which can give three chain isomers. When n-pentane, isopentane and neopentane are compared, the increase in branching decreases the surface area of the molecule. Therefore, the intermolecular forces of attraction decrease with increase in branching. As a result, the boiling points decrease. Further, n-alkanes have the highest boiling points, isoalkanes have low boiling points and neoalkanes have least boiling points. Therefore, they can be separated by fractional distillation.

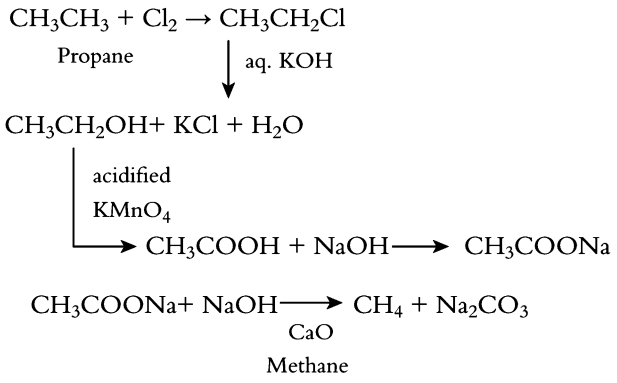


Alkanes have regular tetrahedral structure at each carbon because of sp^3 hybridization and hence the vectorial sum of the dipole moments of the bonds add up to zero even though the hydrogens are replaced by alkyl groups.

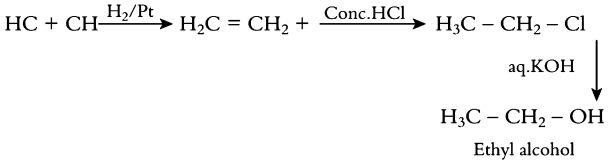
9. The hydrocarbons X, Y and Z respectively as per given data are C_2H_6, C_2H_4 and C_2H_2. Alkanes do not undergo addition reactions because of no double bond. They undergo substitution reactions. In alkenes and alkynes, one or more π bonds are present between carbons which are susceptible to addition reactions.

10.

(a)



(b)



HINTS AND EXPLANATION

Chapter

11

Organic Chemistry–II

Remember

Before beginning this chapter, you should be able to:

- understand the primary classification of organic compounds
- study the nomenclature of organic compounds
- understand the preparation and properties of simple alkanes, alkenes and alkynes

Key Ideas

After completing this chapter, you should be able to:

- understand the preparation and properties of alcohols, carbonyl compounds and carboxylic acids
- study about carbohydrates, proteins, nucleic acids, oils, fats, hormones.
- learn the importance of organic chemistry in polymers cosmetics, dyes, drugs, soaps, detergents, etc.

INTRODUCTION

Organic chemistry is the branch of chemistry which profoundly influences the human society. This is because it plays a major role in all walks of our lives. Carbon forms millions of compounds though it combines only with few elements like hydrogen, oxygen, nitrogen, halogens and sulphur. The compounds containing only carbon and hydrogen are called hydrocarbons. The compounds which possess other elements in addition to carbon and hydrogen are called organic compounds with heteroatoms. The atom or group of atoms present in a molecule of an organic compound which is responsible for the characteristic properties of the compound is called functional group. The organic compounds containing each type of heteroatoms can be further classified on the basis of the nature of the functional group.

Our daily needs of life such as food, clothing, soaps and detergents, medicines, etc., owe their origin from organic compounds. Some of them are very essential for sustenance of life while some others tremendously contribute to improve the quality of life. The special significance of organic chemistry owes not only to the uniqueness of carbon to form innumerable compounds, more astonishingly, with a limited number of elements but also to the immense industrial importance associated with the organic compounds.

NOMENCLATURE OF ORGANIC COMPOUNDS

According to the IUPAC system, which follows the same pattern for all families of organic compounds, the name of an organic compound can be divided into three major parts, namely:

(i) Root word

(ii) Primary suffix

(iii) Secondary suffix

Thus, for the organic compounds with functional groups corresponding secondary suffix is added along with root word and primary suffix.

Secondary Suffix

This is the part of the name which follows the primary suffix. It represents the functional group attached to the carbon chain. "e" of the primary suffix is replaced by the corresponding secondary suffix.

Functional groups	Classes of the compound	Secondary suffixes	IUPAC names
–OH (hydroxyl)	Alcohol	–ol	Alkanol
–CHO	Aldehyde	–al	Alkanal
$>C = O$	Ketone	–one	Alkanone
–COOH	Carboxylic acid	–oic acid	Alkanoic acid

Rules for IUPAC Nomenclature of Organic Compounds

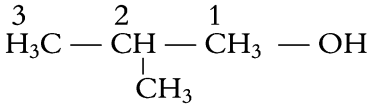
(i) At first, the longest continuous carbon chain which includes the "functional group" is selected. Then the carbon chain is numbered from the end nearer to the functional group. The carbon bearing the functional group should get the least number.

Example

$$\overset{3}{H_3C} - \overset{2}{CH_2} - \overset{1}{CH_2} - OH$$

1 – Propanol

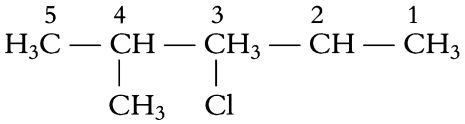
(ii) If both the functional group and the alkyl substituent are present in an organic compound, the numbering of the parent carbon chain is given from the end nearer to functional group (the carbon atom bearing functional group should get the least number in preference to the substituent).



2 – Methyl propanol

(iii) If both the alkyl substituent and the halogen group are present in an organic compound, then the carbon chain is numbered from the end nearer to halogen group (the carbon bearing the halogen group should get the least number).

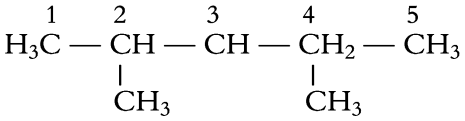
The prefixes (of both alkyl and halogen group) are to be arranged in alphabetical order while writing the name of the compound.



2 – Chloro – 4 – methyl pentane

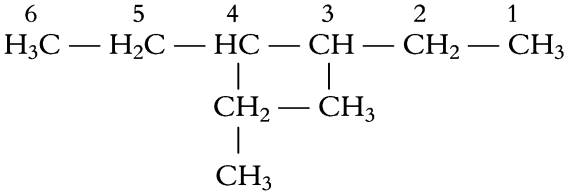
When the substituent like alkyl group is present in an organic compound, the corresponding prefix "alkyl" is used and when the heteroatom like halogen is present the corresponding prefix "halo" (like chloro, bromo, iodo, etc.) is used and the corresponding IUPAC name is "haloalkane."

(iv) When more than one alkyl substituent is present on the parent carbon chain, then the numbering is given in such a way that the "sum of the locants" is the least.



2, 3 – dimethyl pentane.

(v) If "sum of the locants" is equal, then the numbering of carbon chain starts from the end nearer to the smaller alkyl group.



4 – Ethyl – 3 – methylhexane

IUPAC Nomenclature for Esters and Ethers

The IUPAC names of majority of the organic compounds with different functional groups are given by following the above rules. But the IUPAC nomenclature of some functional groups such as ethers and esters follows a slightly different trend.

Ethers

Ethers are a class of compounds which contain an oxygen atom bonded to two alkyl groups.

General molecular formula $C_nH_{2n+2}O$.

Functional group — O —

General formula R^1 — O — R (R, R^1 — same or different alkyl groups)

Nomenclature

The first name is given "alkoxy" for the smaller alkyl group ("R") attached to "O" and is followed by a second name "alkane," for the larger alkyl group (R^1) attached to "O."

Thus, the general IUPAC name for ethers is "alkoxy alkane."

Examples

H_3C — O — CH_3 Methoxy methane

H_3C — O — CH_2 — CH_3 Methoxy ethane

Esters

These are derivatives of carboxylic acids where carboxylate group is attached to two alkyl groups.

General molecular formula $C_nH_{2n}O_2$

Functional group —C(=O)—O—

General formula R^1—C(=O)—O—R

(R^1— H or alkyl group R — alkyl group)

Esters are functional derivatives of carboxylic acids since they contain the common "acyloxy" group namely 'R—C(=O)—O—' $\left(R^1\text{—}\overset{\overset{O}{\|}}{C}\text{—O—R}\right)$ is given the first name as

Nomenclature: The "R" group attached to "O" corresponding "alkyl" and the remaining structure is given the second name "alkanoate."

Thus, the IUPAC name for esters is "alkyl alkanoate."

Example

$H\text{—}\overset{\overset{O}{\|}}{C}\text{—O—}CH_3$ Methyl methanoate

$H_3C\text{—}\overset{\overset{O}{\|}}{C}\text{—O—}CH_3$ Methyl ethanoate

Isomerism

Just like hydrocarbons, organic compounds with any functional group can exhibit chain isomerism. Position isomerism in these compounds arises due to the difference in the position of functional group on the carbon chain. In addition to these two types, some of these compounds also exhibit other types of isomerism namely functional isomerism and metamerism.

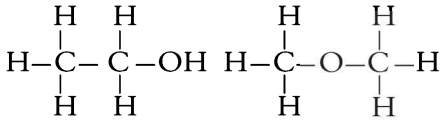
(i) Functional isomerism: Compounds with the same molecular formula but different functional groups are called functional isomers and this phenomenon is called functional isomerism.

Example

Two functional isomers are possible with the molecular formulae C_2H_6O.

One isomer with an alcoholic functional group (R—OH) and the other with an ether linkage or functional group (R—O—R)

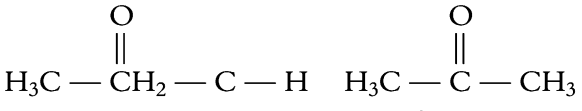
(a) Molecular formula: C_2H_6O



Ethyl aclohol Dimethyl ether

IUPAC : Ethanol UPAC : Methoxy methane

(b) Molecular formula: C_3H_6O



Propanaldehyde Acetone

IUPAC : Propanal IUPAC : Propanone

Two functional isomers namely propionaldehyde and acetone are possible for the molecular formulae.

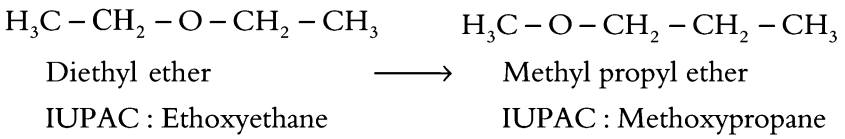
C_3H_6O, one with aldehydic functional group ($R-\overset{\overset{O}{\|}}{C}-H$) and the other with the ketone functional group ($R-\overset{\overset{O}{\|}}{C}-H$).

(ii) Metamerism: The isomers in which there is an unequal distribution of carbon chain or atoms on either side of the functional group are called metamers and this phenomenon is termed "metamerism." Thus metamers differ in the size of an alkyl group or chain on either side of the functional group.

This is exhibited by compounds having divalent functional groups.

Example

Molecular formula: $C_4H_{10}O$



Diethyl ether ⟶ Methyl propyl ether

IUPAC : Ethoxyethane IUPAC : Methoxypropane

Functional groups containing Oxygen

Alcohols

The class of compounds where the alkyl chain is attached to –OH group is called alcohols. They are represented as R-OH where "R" stands for alkyl group. The general formula of alcohols is $C_nH_{2n+1}OH$. The common names for alcohols are given by using the name of the alkyl radical. The IUPAC name of alcohols is alkanols.

Example

$H_3C - CH_2 - OH$

Common name is ethyl alcohol

IUPAC name: eth + ane + ol — ethanol

Homologous Series of Alcohols

Alkanes	Formulas of alkane	Formulas of alcohol	Common names	IUPAC names
Methane	CH_4	$CH_3–OH$	Methyl alcohol	Methanol
Ethane	$H_3C–CH_3$	$H_3C–CH_2–OH$	Ethyl alcohol	Ethanol
Propane	$H_3C–CH_2–CH_3$	$H_3C–CH_2–CH_2–OH$	Propyl alcohol	1-Propanol
Butane	$H_3C–CH_2–CH_2–CH_3$	$H_3C–CH_2–CH_2–CH_2–OH$	n-butyl alcohol	1-Butanol

Methyl Alcohol and Ethyl Alcohol

Methyl alcohol is also known as wood alcohol since it can be prepared by destructive distillation of wood. Ethyl alcohol is also known as grain alcohol.

Methods of Preparation

Methyl alcohol	Ethyl alcohol
Hydrolysis of alkyl halides	
Boiling methyl halides with aqueous sodium hydroxide or aqueous potassium hydroxide.	Boiling ethyl halides with aqueous sodium hydroxide or aqueous potassium hydroxide.
$CH_3Cl + NaOH\ (aq) \rightarrow CH_3OH + NaCl$	$C_2H_5Cl + NaOH\ (aq) \rightarrow C_2H_5OH + NaCl$
Industrial methods	
From water gas: Water gas when mixed with hydrogen and passed over heated catalyst like chromic oxide or zinc oxide at 350°C gives methyl alcohol: $[CO_2 + H_2] + H_2 \xrightarrow[350°C]{Cr_2O_3/ZnO} CH_3OH$	**From ethene:** Ethene on reaction with conc. H_2SO_4 at very high pressure and at 80°C gives ethyl hydrogen sulphate which on boiling with water gives ethyl alcohol: $H_2C = CH_2 + H_2SO_4 \rightarrow CH_3 - CH_2 - HSO_4$ $CH_3 \cdot CH_2 \cdot HSO_4 + H_2O \xrightarrow{70–80°C} H_3C - CH_2 - OH + H_2SO_4$

On a large scale, ethyl alcohol can be manufactured by fermentation of molasses or starch.

Fermentation of Molasses

Fermentation is the process of decomposition of a complex organic compound into simpler compounds by means of microorganisms. Molasses is the mother liquor left after the crystallization of cane sugar from sugar cane juice.

Principle

Dilute solution of molasses which contains sucrose on standing for few days after the addition of yeast cells undergoes decomposition to form ethyl alcohol. This is due to the presence of enzymes such as invertase and zymase in the yeast cells.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[30°C]{Invertse} C_6H_{12}O_6 + C_6H_{12}O_6$$

Sucrose — Glucose — Fructose

$$C_6H_{12}O_6 \xrightarrow[30°C]{Zymse} {}_2H_5OH + 2CO_2$$

Ethyl alcohol

Process of Fermentation

Molasses contains 30%–40% uncrystallized sugar. This is diluted by adding water and the percentage of sugar is brought down to 10%. Sulphuric acid is then added to maintain the pH of the solution at 4. Salts like ammonium sulphate or ammonium phosphate are added to this solution. These salts act as food for the yeast cells.

Yeast is added to the solution and the solution is allowed to stand as such for 24–72 h. The temperature is maintained at 30°C. The fermented liquor is known as wash. It contains 15%–20% ethyl alcohol. When this is subjected to fractional distillation, 93%–95% ethyl alcohol is obtained. This is called **rectified spirit**. However, 100% ethyl alcohol can be obtained by adding anhydrous CaO to the rectified spirit. Further, 100% ethyl alcohol is known as **absolute alcohol**. For industrial use, 5% methyl alcohol is added to ethyl alcohol. This is called **denatured spirit**.

Fractional distillation of wash gives 96% ethyl alcohol known as rectified spirit. The remaining water also can be removed by the treatment of rectified spirit with quick lime. Further, 100% ethyl alcohol is called absolute alcohol.

Uses of Ethyl Alcohol

(i) Industrial solvent: Since a wide range of organic compounds are soluble in ethyl alcohol, it is the most common industrial solvent. To discourage its misuse as beverage, 5% methyl alcohol is added to this, thus making it unfit for drinking. This is called denatured spirit.

(ii) In medicines: Many medicines contain alcohol as one of the constituents in small quantities.

(iii) As beverage: Different brands of alcoholic beverages contain different percentages of alcohol.

Alcoholic beverages	Percentage of alcohol
Beer	3–5
Cider	2–4
Wine	8–10
Gin, brandy, whisky and rum	35–40

From Starch

Instead of molasses, starch can also be taken as the starting material for the manufacture of ethyl alcohol. Starch is warmed with freshly germinated barley called malt at 50°C for 1 h. Malt contains diastase enzyme. Starch is converted to maltose sugar by hydrolysis in the presence of diastase. The remaining process continues in the same manner as in molasses, except that the enzyme maltase carries out the fermentation process of sugar which is in the form of maltose:

$$(C_6H_{10}O_5)_n + \frac{n}{2}H_2O \xrightarrow{\text{diastase}} \frac{n}{2}C_{12}H_{22}O_{11}$$

starch maltose

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{maltase}} 2C_6H_{12}O_6$$

Glucose

$$C_6H_{12}O_6 + H_2O \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Spurious Alcohol

Manufactured ethyl alcohol is available cheaply. But heavy excise duty and taxes are imposed on the alcohol in order to discourage people from getting addicted to drinking alcohol. The industrial alcohol is not taxed heavily. Since this is available at cheaper rates, this is diluted and sold as alcohol

for drinking purpose. As this contains toxic substances like methyl alcohol, pyridine or copper sulphate, etc., the alcohol also becomes toxic. This is called spurious alcohol. Spurious alcohol can also be made by subjecting jaggery to fermentation. During this process, methyl alcohol and acetaldehyde are also formed. These impurities impart toxic effect to ethyl alcohol.

Physical Properties

Methyl alcohol	Ethyl alcohol
Colourless liquid	Colourless liquid
Strong odour	Sweet smell
Inflammable	Inflammable
Highly toxic	Less toxic with a burning taste
Soluble in water and organic solvents	Soluble in water and organic solvents
Boiling point 64.5°C	Boiling point 78.1°C
Consumption can cause blindness and even death.	Consumption for long period can cause damage of liver, kidneys, etc.

Chemical Properties

Methyl alcohol	Ethyl alcohol
Reaction with active metals	
With sodium, products are sodium methoxide and hydrogen: $2CH_3OH + 2Na \rightarrow 2CH_3ONa + H_2$ Sodium methoxide	With sodium, products are sodium ethoxide and hydrogen: $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$ Sodium ethoxide
Reaction with PCl	
Products are methyl chloride and phosphorous acid. $3CH_3OH + PCl_3 \rightarrow 3CH_3Cl + H_3PO_3$ Chloromethane	Products are ethyl chloride and phosphorous acid. $3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$ Chloroethane
Reaction with acetic acid (esterification)	
Product formed is methyl acetate: $CH_3OH + CH_3COOH \rightarrow CH_3COOCH_3$ methylacetate $+H_2O$	Product formed is ethyl acetate: $C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$ ethyl acetate
Reaction with conc. H_2SO_4 (dehydration)	
Product is dimethyl ether obtained at 140°C: $2CH_3OH \xrightarrow[140°C]{\text{conc. } H_2SO_4} CH_3OCH_3 + H_2O$	Product depends upon the temperature. At 140°C diethyl ether is obtained and at 170°C ethane is obtained: $2C_2H_5OH \xrightarrow[140°C]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$ Diethyl ether $C_2H_5OH \xrightarrow[170°C]{\text{conc. } H_2SO_4} H_2C = CH_2 + H_2O$ ethene

Methyl alcohol	Ethyl alcohol
Oxidation	
Passing methyl alcohol vapour over hot copper gives formaldehyde or methanol: $CH_3OH \xrightarrow[300°C]{Cu} HCHO + H_2$ methanol On treating with alkaline $KMnO_4$, the product formed is formic acid: $CH_3OH + [O] \xrightarrow[\text{or acidified } K_2Cr_2O_7]{\text{alk.}KMnO_4} HCOOH$ methanoic acid	On passing ethyl alcohol vapours over hot copper catalyst at 300°C gives acetaldehyde or ethanol: $C_2H_5OH \xrightarrow[300°C]{Cu} CH_3CHO + H_2$ On treating with alkaline $KMnO_4$, the product obtained is acetic acid or ethanoic acid: $C_2H_5OH + [O] \xrightarrow[\text{or acidified } K_2Cr_2O_7]{\text{alk.}KMnO_4} CH_3COOH$ ethanoic acid

Uses

Methyl alcohol	Ethyl alcohol
Used as a solvent Used in paints and varnishes In the manufacture of other industrially useful organic compounds ***Examples*** (i) Formic acid – antiseptic and tanning of leather (ii) Formaldehyde – preservative for biological specimens For making industrial alcohol.	Used as a solvent for many organic compounds Pure and dilute alcohol is used as a beverage. In the manufacture of many organic compounds including dyes, synthetic rubber, varnishes, paints, perfumes, antiseptics, etc.

Isomerism in Alcohols

Alcohols exhibit three types of isomerism as listed hereunder:

(i) Chain isomerism

(ii) Position isomerism

(iii) Functional isomerism

(i) Chain isomerism: These isomers differ in the arrangement of carbon atoms in the chain.

Example

n-butyl alcohol and isobutyl alcohol

Molecular formula: $C_4H_{10}O$

Structural formulae:

$$CH_3 — CH_2 — CH_2 — CH_2OH$$

1 – Butanol

$$CH_3 — \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} — CH_2OH$$

2-Methyl-1-proponal

(ii) Position isomerism: The isomers differ in the position of functional group (–"OH" group) on the carbon chain.

Example

1-Propanol and 2-Propanol

Molecular formula: C_3H_8O

Structural formulae:

$$CH_3 — CH_2 — CH_2OH$$

1 – Propanol

$$CH_3 — \underset{\displaystyle OH}{\underset{|}{CH}} — CH_3$$

2 – Propanol

(iii) Functional isomerism: These are the isomers which differ in the nature of functional groups.

Example

C_2H_6O:

	$H_3C — CH_2 — OH$	$H_3C — O — CH_3$
Common name:	Ethanol	Methoxy methane
IUPAC:	Ethyl alcohol	Dimethyl ether

Aldehydes and Ketones

The classes of compounds in which there is a $\diagdown C =$ group are called carbonyl compounds. The general formula of the carbonyl compounds is $C_nH_{2n}O$. If the carbonyl compound contains $\diagdown C = O$ group linked to hydrogen on one side and alkyl group on the other side, that class of compounds is called aldehydes. If the carbonyl group is linked to two same or different alkyl groups on either side, the class of compounds is called ketones.

Aldehydes are represented by a general formula, $\begin{matrix} H \diagdown \\ \quad\quad C = O \\ R \diagup \end{matrix}$

Ketones are represented by a general formula, $\begin{matrix} R \diagdown \\ \quad\quad C = O \\ R' \diagup \end{matrix}$

The IUPAC names of aldehydes are "alkanals" and those of ketones are "alkanones."

Example

CH_3CHO	H_3CCOCH_3
Common name: Acetaldehyde	Acetone
IUPAC name: –ethanal	–Propanone

Homologous Series of Aldehydes/Ketones

Formulas of aldehyde/ketone	Common names	IUPAC names
HCHO	Formaldehyde	Methanol
CH_3CHO	Acetaldehyde	Ethanol
CH_3CH_2CHO	Propanaldehyde	Propanol
CH_3COCH_3	Acetone (dimethyl ketone)	Propanone
$CH_3CH_2COCH_3$	Ethyl methyl ketone	Butanone

Formaldehyde (methanol)

Preparation: Methyl alcohol on controlled oxidation in the presence of a catalyst gives formaldehyde:

$$2CH_3OH \xrightarrow[900k]{Cu} HCHO + 2H_2O$$

Physical Properties

Parameters	Characteristics
Colour	Colourless
State	Gas
Odour	Strong smell
Boiling point	252 K
Solubility	Highly soluble in water

Chemical Properties

(i) Oxidation: Methanol on oxidation in presence of oxidizing agents such as HNO_3 or acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ gives formic acid (methanoic acid):

$$HCHO + [O] \rightarrow HCOOH$$

(ii) Oxidation in presence of Tollen's reagent (ammonical silver nitrate solution):

Formaldehyde on heating with Tollen's reagent gets oxidized to formic acid. Ag^+ ions get reduced to metallic silver. As a result of this, a shining silver mirror is formed along the inner walls of the test tube.

$$HCHO + AgNO_3 \xrightarrow[[O]]{HN_4OH} HCOOH + NH_4NO_3 + NH_3 + Ag + H_2O$$

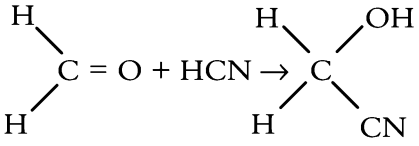
(iii) Oxidation in presence of Fehling's reagent: Fehling's reagent is an alkaline cupric salt solution dissolved in sodium potassium tartarate (Rochelle salt). Formaldehyde on heating with Fehling's reagent in hot water gives a red precipitate of cuprous oxide. Methanol gets oxidized to methanoic acid.

$$HCHO + 2Cu(OH)_2 + NaOH \xrightarrow{\Delta} HCOONa + Cu_2O + 3H_2$$

(iv) Reduction: Methanol on reduction in the presence of palladium gives methyl alcohol:

$$HCHO + H \xrightarrow[[H]]{Pd} CH_3OH$$

(v) Addition of HCN: A double bond is present between carbon and oxygen in formaldehyde. The π-bond can be broken during addition of another molecule. On the addition of HCN to the double bond, hydrogen is added to oxygen and cyanide is added to carbon thereby giving an addition compound cyanohydrin.



Methanal eyanohydrin

Uses of Methanol

(i) The aqueous solution of methanol is called formalin. It acts as a disinfectant. Hence, it is used for the preservation of biological specimens.

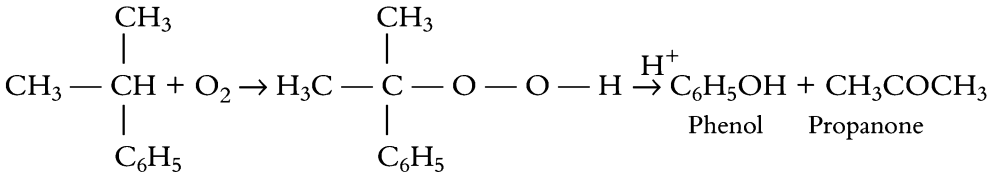
(ii) Methanol is used for the manufacture of a plastic called bakelite which is used for making electric switches.

(iii) Methanol is also taken as a raw material for the manufacture of dyes, medicines, etc.

Acetone or Propanone

Preparation

An aromatic hydrocarbon, cumene on reaction with oxygen gives an intermediate product which on reaction with acid gives propanone along with phenol:



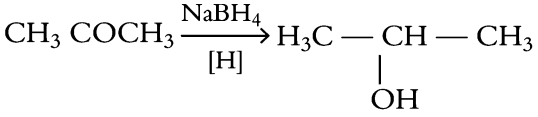
Cumene

Physical Properties

Parameters	Characteristics
Colour	Colourless
Nature	Volatile liquid
Boiling point	329 K
Solubility	Soluble in water

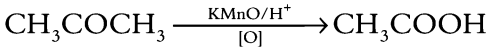
Chemical Properties

(i) Reduction: Propanone on reduction with $LiAlH_4$ or $NaBH_4$ gives 2-Propanol.



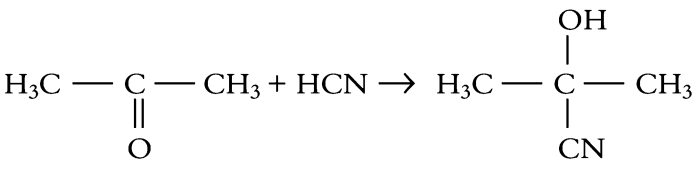
2 - Propanol

(ii) Oxidation: Propanone on oxidation with potassium permanganate in acidic medium gives ethanoic acid:



Ethanoic acid

(iii) Addition of HCN: When HCN is added to the > C = O bond in propanone, hydrogen is added to oxygen and cyanide is added to carbon. This gives propanone cyanohydrin:



Propanone cyanohydrin

Uses of Acetone

(i) An important solvent for organic compounds
(ii) Used in the manufacture of nail polish remover
(iii) Making artificial leather and synthetic resin

Isomerism in Aldehydes and Ketones

(i) Aldehydes exhibit chain isomerism due to the variation in the length of the carbon chain.

Example

n-Butyraldehyde and isobutyraldehyde

$$CH_3 - CH_2 - CH_2 - CHO$$

n – Butyraldehyde

$$\begin{array}{l} \quad CH_3 \\ \quad | \\ CH_3 - CH - CHO \end{array}$$

Isobutyraldehyde

Ketones also exhibit chain isomerism.

Examples

$$\begin{array}{l} \quad\quad\quad O \\ \quad\quad\quad || \\ CH_3 - CH_2 - C - CH_2 - CH_3 \end{array}$$

Diethyl ketone

$$\begin{array}{l} \quad\quad CH_3 \quad O \\ \quad\quad\quad | \quad\quad || \\ CH_3 - CH - C - CH_3 \end{array}$$

Isopropyl methyl ketone

(ii) Aldehydes cannot exhibit position isomerism. This is because –CHO group is a chain-terminating group and it should be always placed in the first position. Ketones exhibit position isomerism due to the location of carbonyl group in different positions.

Examples

$$\begin{array}{l} \quad\quad\quad\

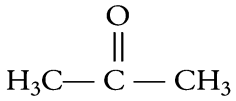
Examples

Propanol and propanone

Molecular formula: C_3H_6O

$CH_3 — CH_2 — CHO$

Propanone



Propanone

Carboxylic Acids

The organic compounds which contain $— \overset{\overset{O}{\|}}{C} — OH$ (carboxyl group) as a functional group are known as carboxylic acids, since this group is a combination of carbonyl group (>C = O) and hydroxyl group (–OH). The general molecular formula of carboxylic acids is "$C_nH_{2n}O_2$." Since they show significant acidity, they are called acids.

Nomenclature

The common names of these acids are mostly derived from the source of their origin.

Examples

Formic acid (Formica – ants)

Acetic acid (Acetum – vinegar)

According to the IUPAC system, these compounds are named by adding a secondary suffix "oic acid" to the corresponding "alkane." These are named as alkanoic acids.

Homologous Series of Carboxylic Acids

Formulas	Common names	IUPAC names
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	Butyric acid	Butanoic acid

Acetic Acid (ethanoic acid)

It is the most important fatty acid which, as a dilute solution, is used as a preservative for foods such as pickles, vegetable sauce, etc.

Methods of Preparation

(i) Ethyl alcohol on oxidation by air in the presence of a bacteria of the genus *Acetobacter*, gives acetic acid:

$$CH_3CH_2OH + [O] \xrightarrow{\text{Acetobacter}} CH_3COOH + H_2O$$

(ii) **Commercial preparation**: Acetic acid can be obtained by the reaction between methyl alcohol and carbon monoxide in presence of iodine and rhodium as catalysts:

$$CH_3OH + CO \xrightarrow{I_2-Rh} CH_3COOH$$

Physical Properties

Parameters	Characteristics
Colour	Colourless liquid
Odour	Pungent smell
Boiling point	391 K
Solubility	Soluble in water

Chemical Properties

(i) Acidic character: When acetic acid reacts with metals/alkalies, the corresponding salt is formed.

Examples

$$2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$$

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

$$CH_3COOH + Na_2CO_3 \longrightarrow CH_3COONa + CO_2 + H_2O$$

(ii) Reaction with alcohols: Acetic acid reacts with alcohols to give the corresponding ester. This reaction is known as esterification.

Examples

$$CH_3COOH + CH_3OH \longrightarrow CH_3COOCH_3 + H_2O$$

Methyl acetate

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

Ethyl acetate

(iii) Decarboxylation: Sodium or potassium salt of acetic acid on reaction with soda lime gives methane due to the removal of CO_2 from the carboxylic acid:

$$CH_3COONa + NaOH \xrightarrow{CaO} CH_4 + Na_2CO_3$$

Uses of Acetic Acid

(i) As a reagent in laboratory
(ii) In the preparation of synthetic vinegar
(iii) For the preparation of white lead

Isomerism in Carboxylic Acids

(i) Just as other compounds, carboxylic acids also exhibit chain isomerism due to the variation in the nature of carbon chain.

Examples

n-butryic acid and isobutryic acid

$$CH_3 — CH_2 — CH_2 — COOH$$

n — Butyric acid

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ CH_3 — CH — COOH \end{array}$$

Isobutyric acid

(ii) Carboxylic acids do not exhibit position isomerism like aldehydes due to the fact that –COOH group is the chain-terminating group.

(iii) Functional isomerism: Carboxylic acids show functional isomerism with esters.

Examples

CH_3CH_2COOH	CH_3COOCH_3
Propanoic acid	Methylacetate

It is quite obvious that the various organic compounds associated with various functional groups are the essential components of biomolecules. However, the biomolecules generally possess high molecular weight organic compounds. This is because they may contain long chains of hydrocarbons as in the case of oils and fats or they may be formed by the polymerization of simpler organic molecules as in the case of carbohydrates and proteins. Hence the study of biomolecules is closely associated with the study of organic chemistry.

EXAMPLE

Two compounds A and B are functional isomers. A has fruity smell and undergoes hydrolysis in presence of acid or base to give C and D, C has same functional group as B. C and B are simultaneously treated with sodium hydroxide. The compounds obtained are treated with soda lime to give two successive homologues E and F which are the first two members of the series. Identify A, B, C, D, E and F.

SOLUTION

CH_3COOCH_3 and $CH_3CH_2COOH \rightarrow$ functional isomers

(A) (B)

$$\underset{(A)}{CH_3COOCH_3} + H_2O \xrightarrow[HCl]{NaOH\ or} \underset{(C)}{CH_3COOH} + \underset{(D)}{CH_3OH}$$

'C' has same functional group as 'B'

$$\underset{(C)}{CH_3COOH} + NaOH \rightarrow CH_3COONa + H_2O$$

$$\underset{(B)}{CH_3CH_2COOH} + NaOH \rightarrow CH_3CH_2COONa + H_2O$$

$$\left.\begin{matrix} CH_3COONa \\ + \\ CH_3CH_2COONa \end{matrix}\right\} \xrightarrow{NaOH} \xrightarrow{CaO} \begin{matrix} \rightarrow CH_4\ (E) \\ \rightarrow C_2H_6\ (F) \end{matrix}$$

CH_4 and C_2H_6 are first two members of alkanes.

EXAMPLE

The first homologue of the series with general formula C_nH_{2n} on oxidation with alkaline $KMnO_4$ gives a compound which is added to water used as a coolant in automobiles. Identify the compound and explain the purpose of its addition to water.

SOLUTION

The first homologue of the series with general formula C_nH_{2n} is ethene.

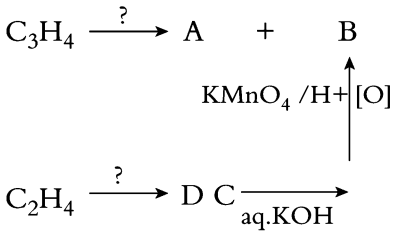
$$H_2C = CH_2 + [O] \xrightarrow{KMnO_4} \underset{\text{Ethene glycol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}}$$

Water is used as a coolant in automobiles because it can absorb large amount of heat from the engine due to high specific heat. However, in cold countries, the water may freeze to ice due to very low temperature. Similarly in summer season water may tend to boil as it absorbs heat. Ethylene glycol is added to water which can prevent freezing as well as boiling. This is because addition of ethylene glycol to water leads to depression in freezing point as well as elevation in boiling point. As a result, water can maintain liquid range over a wide range of temperature.

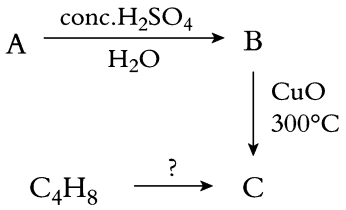
EXAMPLE

Identify A, B, C, D in the following conversions given and write their structural formulae.

(a)

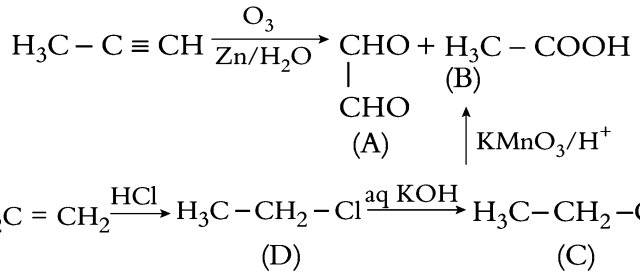


(b)

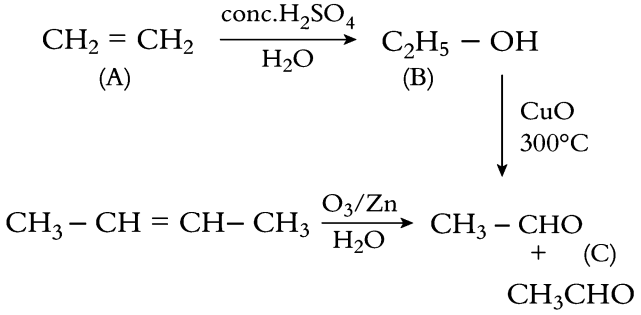


SOLUTION

(a)



(b)



EXAMPLE

Which reagents oxidise ethyl alcohol to acetaldehyde and acetic acid respectively? Why are two different reagents required for these conversions?

SOLUTION

Alkaline $KMnO_4$ oxidises ethyl alcohol to acetic acid and copper at 300°C oxidizes ethyl alcohol to acetaldehyde.

Copper at high temperature removes molecule of hydrogen from ethyl alcohol to form acetaldehyde. It involves only dehydrogenation. Alkaline $KMnO_4$ produces nascent oxygen and oxidises ethyl alcohol to acetic acid.

EXAMPLE

Complete the following reactions.

(a) $CH_3 - CH_2 - CH_2 - COONa + NaOH\ CaSO_3 \rightarrow$ Calcium sulphite

(b) $CH_3 - I\ Zn(NO_2) \rightarrow$ Zinc nitrite **(c)** $C_2H_5Br\ Mg(PO_3)_2 \rightarrow$ Magnesium phosphite

(d) $CO + H_2\ ZnSO_4 \rightarrow$ Zinc sulphate **(e)** $CaC_2 + NaNO_3 \rightarrow$ Sodium nitrate

SOLUTION

(a) $CH_2 - CH_2 - CH_2 - COONa + NaOH \rightarrow CH_3 - CH_2 - CH_3 + Na_2CO_3$

Sodium salt of butanoic acid Propane

(b) $CH_3 - I\ AlPO_4 \rightarrow$ Aluminium phosphate $CH_4 + HI$

Iodomethane Methane

(c) $C_2H_5Br\ V \propto \frac{1}{P}\ (T = \text{constant})\ C_2H_5{-}OH + KBr$

Bromoethane Ethanol

(d) $[CO + H_2] + H_2\ V = \frac{K}{P} CH_3 - OH$ **(e)** $CaC_2 + H_2O \rightarrow CH \equiv CH + Ca(OH)_2$

Water gas Methanol Ethyne

EXAMPLE

How do you bring about the following conversions?

(a) Mthane to methyl alcohol. **(b)** Ethyl chloride to methane **(c)** Ethane to benzene

SOLUTION

(a) Step 1: Methane on chlorination in presence of sunlight produces methyl chloride.

$$CH_4 + Cl_2 \xrightarrow[\text{Pressure (P)}]{1} CH_3Cl + HCl$$

Step 2: Methyl chloride on reaction with aqueous potassium hydroxide gives methyl alcohol.

$$CH_3Cl + KOH_{(aq)} \rightarrow \underset{\text{Methanol}}{CH_3OH} + KCl$$

(b) Ethyl chloride to methane

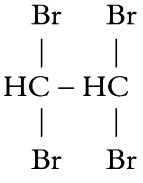
$$C_2H_5Cl + NaOH\ (aq) \rightarrow C_2H_5OH + NaCl$$

$$C_2H_5OH + [O] \xrightarrow[P_1 = 2\,atm]{V_1 = 5\ell} CH_3COOH$$

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

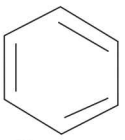
$$CH_3COONa + 2NaOH \xrightarrow[P_2 = ?]{V_2 = 1.6\ell} CH_4 + Na_2CO_3 + H_2O$$

(c) (1) $H_3C - CH_3 + 2Br_2 \xrightarrow{\text{Sunlight}}$



Tetrabromoethane

(2) $\begin{matrix} Br & Br \\ | & | \\ CH - & CH \\ | & | \\ Br & Br \end{matrix} + 2Zn \longrightarrow HC \equiv CH.$

(3) $HC \equiv CH \xrightarrow[\text{300°C}]{\text{red hot 'Cu' tube}}$ 

Benzene

EXAMPLE

ol, al, one

(a) From the box given above, name

(i) a compound with –CHO as the part of its structure.

(ii) a compound with –OH as the part of its structure.

(iii) A compound with $R - \overset{\overset{O}{\|}}{C} - R$ as the part of its structure.

(b) Write the equations for the following laboratory preparations.

(i) Ethanol from iodoethane (ii) Ethene from chloroethane

(iii) Ethane from sodium salt of propanoic acid (iv) Acetic acid from ethanol.

SOLUTION

(a) (i) The name of the compound with – CHO as part of its structure ends with al.

(ii) The name of the compound with –OH as part of its structure ends with ol.

(iii) The name of the compound with $R - \overset{\overset{O}{\|}}{C} - R$ as part of its structure ends with one.

(b) (i) Ethanol from iodoethane can be prepared by treating with aqueous KOH.

$C_2H_5 - I + KOH_{(aq)} \rightarrow C_2H_5 - OH + KI$

(ii) Chloroethane on treatment with alcoholic KOH gives ethene

$C_2H_5 - Cl + KOH_{(alk)} \rightarrow C_2H_4 + KCl + H_2O$

(iii) Sodium salt of propanoic acid on treatment with NaOH gives ethane.

$CH_3 - CH_2 - COONa + NaOH \rightarrow CH_3 - CH_3 + Na_2CO_3$

(iv) Ethanol on oxidation in presence of $H^+/K_2Cr_2O_7$, gives acetic acid.

$C_2H_5 - OH \;\; P_1V_1 = P_2V_2 \;\; CH_3 - COOH$

Carbohydrates (Biomolecules)

Carbohydrates are the ultimate source of most of our food materials. Apart from this, they are mostly present in cotton and wood in the form of cellulose. Therefore, carbohydrates provide us with all basic necessities of life like food, clothing and shelter. Since carbohydrates are produced during the process of photosynthesis and consumed by animals as a source of energy, the study of carbohydrates, in addition to giving an understanding of the commodities of daily use, also gives scope for understanding the various biochemical processes involving their formation and usage.

These are an important class of organic molecules containing carbon, hydrogen and oxygen and defined as polyhydroxyaldehydes, polydroxyketones or compounds which produce these on hydrolysis. They are so named since they were considered to be hydrates of carbon with the general formula $C_x(H_2O)_y$. They are also called saccharides due to the similarity in taste to sugar which is known as saccharum.

Classification

Carbohydrates are broadly classified on the basis of the products formed on hydrolysis. The three main categories of carbohydrates are listed hereunder:

(i) Monosaccharides

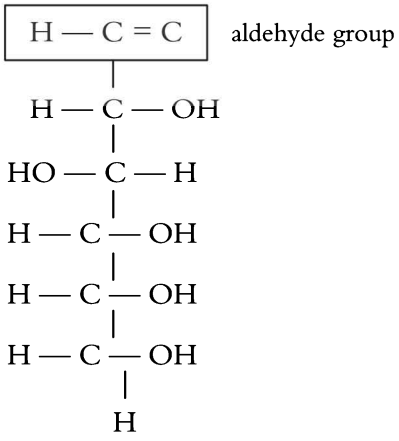
(ii) Oligosaccharides

(iii) Polysaccharides

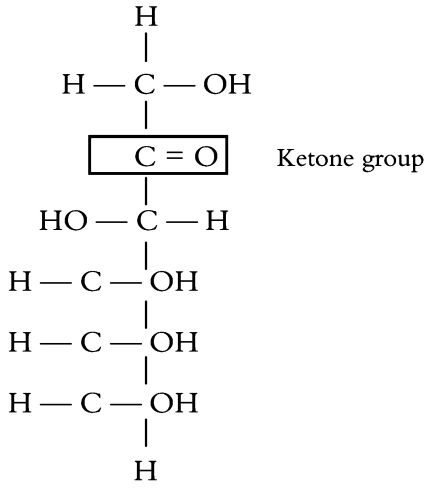
Monosaccharides

The class of carbohydrates which cannot be hydrolysed into simpler saccharide units are called monosaccharides. They may contain chains of 3–10 carbon atoms and can be represented by a general formula $(CH_2O)_n$. Since they contain one carbonyl group and remaining are hydroxyl groups, they are termed as polyhydroxy aldehydes or ketones. Monosaccharides are further classified into "aldoses" and "ketoses," which contain "aldehyde" and "ketone" functional groups, respectively.

Structure of Glucose and Fructose



Glucose (aldose)



Frutose (ketose)

Depending on the number of carbon atoms in the chain, they are further classified into various types as shown hereunder:

Number of carbon atoms	Classes	Examples
3	Trioses	Glyceraldehyde
4	Tetroses	Erythrose
5	Pentoses	Arabinose, ribulose, etc.
6	Hexoses	Glucose, fructose, galactose, mannose, etc.

Oligosaccharides

The class of carbohydrates which on hydrolysis gives 2–9 monosaccharide units are called oligosaccharides. Most common oligosaccharides give two or three or four monosaccharide units on hydrolysis and are named as disaccharides, trisaccharides and tetrasaccharides, respectively.

In the case of oligosaccharides, the different monosaccharide units are joined by means of glycoside bonds. A glycoside bond is a bond formed by the loss of one water molecule between the carbonyl group and hydroxyl group of the monosaccharide units.

Classes	Examples	Formulas	Products of hydrolysis
Disaccharide	Sucrose	$C_{12}H_{22}O_{11}$	Glucose, fructose
Disaccharide	Maltose	$C_{12}H_{22}O_{11}$	Glucose, glucose
Disaccharide	Lactose	$C_{12}H_{22}O_{11}$	Glucose, galactose
Trisaccharide	Raffinose	$C_{18}H_{32}O_{16}$	Glucose, fructose, galactose
Tetrasaccharide	Stachyose	$C_{24}H_{42}O_{21}$	Glucose, fructose and two moles of galactose

Polysaccharides

Polysaccharides represent the class of carbohydrates which can be hydrolysed into a number of monosaccharide units. The number of units can range from hundreds to thousands also. They can be further classified on the basis of the kind of monosaccharide units formed by hydrolysis. They are represented by a general formula $C_n(H_2O)_{n-1}$ or $(C_6H_{10}O_5)_n$.

The polysaccharides which on hydrolysis give only one kind of monosaccharides are called homopolysaccharides and those which give different kinds of monosaccharides are called heteropolysaccharides.

In contrast to monosaccharides and disaccharides which are called sugars, polysaccharides are called nonsugars due to their bland taste.

Sweetness of a carbohydrate results from the interaction of the hydroxyl groups with the taste receptors on the tongue. The various carbohydrates differ in their relative sweetness for which sucrose is taken as the standard.

Comparative Study of Various Simple Carbohydrates

Classes	Examples	Formulas	Functional groups or types of bond	Sources	Characteristic properties	Relative sweetness
Monosaccharides	Glucose (grape sugar)	$C_6H_{12}O_6$	–CHO group (aldehyde)	Honey, ripe grapes, some fruits, blood and urine of mammals	Soluble in water, give reactions of aldehydes and are called reducing sugars	74
	Fructose (fruit sugar)	$C_6H_{12}O_6$	$R\diagdown\!\!\diagup C=O$ group, R (keto group)	Fruits, honey	Soluble in water, non-reducing sugars	173 (maximum)
Disaccharides	Sucrose (table sugar) or (cane sugar)	$C_{12}H_{22}O_{11}$	Glycoside bond between one glucose unit and one fructose unit	Sugar cane and beet root	Soluble in water, non-reducing sugars	100
	Maltose	$C_{12}H_{22}O_{11}$	Glycoside bond between two glucose units	Germinating cereals	Soluble in water, reducing sugars	32
	Lactose	$C_{12}H_{22}O_{11}$	Glycoside bond between one glucose unit and one galactose unit	Milk	Soluble in water. Non-reducing sugar	16

Identification Tests for Some Carbohydrates

Carbohydrates that reduce Tollen's, Fehling's and Benedict's reagent are called reducing sugars. All monosaccharides (aldose or ketose) are reducing sugars.

Both glucose and fructose (monosaccharides) give positive result for Tollen's, Benedict's and Fehling's test.

(i) Tollen's test: A little amount of glucose or fructose is dissolved in water and the solution is taken in a clean dry test tube. In another test tube, a little amount of silver nitrate is dissolved in 5% NaOH solution. A grey precipitate of silver hydroxide is formed. The precipitates are dissolved by adding a few drops of ammonium hydroxide.

Ammonical silver nitrate solution so obtained is called Tollen's reagent. Addition of this reagent to glucose or fructose solution followed by heating in water bath lead to the formation of shining silver mirror on the walls of the test tube due to the reduction of Ag^+ ions to Ag.

(ii) Benedict's test: Measured proportions of sodium citrate and sodium carbonate are dissolved in water. In this solution, copper sulphate is dissolved. The resulting solution is called Benedict's reagent. Addition of Benedict's reagent to glucose or fructose solution followed by heating in water bath results in the formation of a red precipitate. This is due to the reduction of Cu^{+2} to Cu^{+1}.

(iii) Fehling's test: Fehling's reagent is an alkaline solution of cupric ion complexed with sodium or potassium tartarate ions. When this reagent is added to glucose or fructose solution, followed by heating in water bath, results in the formation of a red precipitate due to the formation of cuprous oxide (reduction of Cu^{+2} to Cu^{+1}).

Sucrose, a disaccharide, does not give positive result to Tollen's or Benedict's or Fehling's test. Hence, it is called a non-reducing sugar.

The addition of a few drops of concentrated HCl to the sucrose solution results in the hydrolysis of sucrose to glucose and fructose. Glucose and fructose being reducing sugars gives Tollen's test, Benedict's test and Fehling's test.

Starch, a polysaccharide is insoluble in water. A thick paste can be made with hot water. Further addition of hot water gives a clear solution of starch.

Test for starch: Addition of 1% iodine solution in alcohol or KI solution to starch solution gives blue colour.

Manufacture of Sucrose

The main sources of sucrose being sugarcane and beetroot, sucrose can be manufactured from both the sources. However, sugarcane is the most common source for the manufacture of sucrose.

Principle

Sugarcane contains 10%–15% of sucrose by weight. Sugarcane juice on purification followed by concentration and crystallization results in the formation of colourless crystals of sugar.

To account for this, lime and $Ca(OH)_2$ are added, which is studied under three different headings.

Process: The process of manufacture of sucrose is carried out in four different steps.

(i) Extraction of juice from sugarcane: Sugarcane is subjected to washing and then when put in cutting machines gets chopped into small pieces. These pieces are then sent into roll

crushers where crushing takes place to extract juice from sugarcane. Addition of water in this stage enhances the efficiency of extraction. This process results in the extraction of 93% of the juice. The remaining cane left after extraction is called bagasse. It is considered as a by-product of sucrose manufacture as it can be used as a fuel in some industries for the manufacture of paper, cardboards and generation of electricity.

(ii) Purification of sugarcane juice: The sugarcane juice is slightly acidic in nature and contains some impurities and suspended particles. Acidity should be removed from sugarcane juice before subjecting it to further process. This is because if the juice is acidic, during the process of concentration, some amount of sugar is lost due to hydrolysis.

(a) Defecation: This process involves the addition of calcium hydroxide which neutralizes the juice and also removes the suspended impurities in the form of precipitates.

(b) Carbonation: This step involves the passage of carbon dioxide gas through the juice obtained from the first step. In this process, excess lime is removed as carbonates and some colouring matter and some inorganic salts are removed and settled as mud. The juice is then filtered.

(c) Sulphitation: The juice obtained after filtration in the above step is subjected to treatment with sulphur dioxide. It being a good bleaching agent decolourises the juice. This also serves to neutralize excess of lime carried from the first step. Calcium sulphite so formed is removed by filtration.

The precipitate obtained in the last step is called press mud and is used as a fertilizer.

(iii) Concentration and crystallization of juice: The juice obtained at the end of second stage is called "clarified juice" which contains 85% of water. When it is subjected to evaporation, the percentage of water is reduced to almost half. Further concentration of juice is carried out initially at low pressure and later in vacuum. The concentrated juice is taken in vacuum pans and concentrated till a supersaturated solution is obtained.

(iv) Isolation and drying of crystals: The juice remaining at the end of the third stage contains 10% of water. Since it is a supersaturated solution, sucrose crystals are separated out by a process called centrifugation. The sugar crystals obtained are then exposed to hot air to remove the minor traces of water.

The mother liquor left after the crystallization of sucrose from sugarcane juice is called molasses. This is a very important by-product of sugar industry.

Proteins

Among all biomolecules, proteins are the most important ones. The diverse functions performed by proteins in the biological system make them the most vital substances of life. The name "proteins" has been originated from the Greek word "proteios" which means "of prime importance" as all living cells invariably contain them. Proteins are the most abundant organic molecules to be found in living cells and 50% of their total dry mass is protein.

Due to the diversity of the structure, proteins have a wide range of structural and metabolic activities in the biological systems of various living organisms.

Examples

(i) Proteins in hair–Keratin

(ii) Insulin in pancreas

(iii) Enzymes like cellulase, amylase, etc.

(iv) Blood contains a red pigment called haemoglobin which is also proteinic in nature.

Structure of Protein

Proteins are high polymers or polyamides, (of high molecular mass) where a single protein molecule consists of hundreds to thousands of amino acid units. These units consist of 20 odd amino acids combined in different ways, thus forming a large number of protein molecules. Therefore, amino acids are considered as the basic units of protein molecules.

Basically, there are 25 different amino acids commonly found in proteins. All these amino acids can be synthesized by plants from the basic raw materials like CO_2, water and other inorganic compounds of nitrogen. Animals do not have the ability to synthesize these amino acids on their own. Hence, they depend on plants for these amino acids. Thus they obtain 10 amino acids directly from the food they consume. These amino acids are termed as essential amino acids. By making use of these amino acids, the other amino acids can be synthesized and such amino acids are termed as nonessential amino acids.

This classification of amino acids as essential and nonessential amino acids does not actually reflect their relative significance. Instead, the classification implies the ability of the living systems to synthesize a particular amino acid within the system.

Nomenclature of Amino Acids

The general formula of the amino acid can be given as $\begin{matrix} R-CH-COOH \\ | \\ NH_2 \end{matrix}$ where "R" is an alkyl group.

Amino acids are named as amino carboxylic acids according to the IUPAC system. Their trivial names have generally originated from their sources. They are preferably indicated by a three-letter symbol. While writing genetic code, they are represented by one-letter code. The various amino acids differ in the characteristic feature of the nature of alkyl side chain.

Structure of Amino Acids

Every amino acid molecule has a central carbon atom to which one acidic carboxyl group (COOH) and one basic amino group (—NH_2) are attached. Apart from these two functional groups, the other two valencies of carbon are satisfied by an alkyl group and a hydrogen atom. The uniqueness and specificity of each amino acid can be attributed to the nature of the alkyl group attached.

Some Simple Essential Amino Acids

Nature of alkyl chains	Trivial names	Symbols	Codes
H_3C \ CH / H_3C	Valine	Val	V
H_3C \ $CH-CH_2-$ / H_3C	Leucine	Leu	L

$H_3C-CH_2-CH(CH_3)-$	Isoleucine	Ile	I
$HN=C(NH_2)-NH-(CH_2)_3-$	Arginine	Arg.	R
$H_2N-(CH_2)_4-$	Lysine	Lys	K
$H_3C-CHOH-$	Threonine	Thr	T
$C_6H_5-CH_2-$	Phenylalanine	Phe	F

Some Simple Nonessential Amino Acids

Nature of alkyl chains	Trivial names	Symbols	Codes
—H	Glycine	Gly	G
$-CH_3$	Alanine	Ala	A
$H_2N-C(=O)-CH_2-CH_2$	Glutamine	Gln	Q
$HOOC-CH_2-CH_2-$	Glutamic acid	Glu	E
$H_2N-C(=O)-CH_2-$	Asparagine	Asn	N
$HO-CH_2-$	Serine	Ser	S
$HS-CH_2-$	Cysteine	Cys	C
$HO-C_6H_4-CH_2-$	Tyrosine	Tyr	Y

Properties of Amino Acids

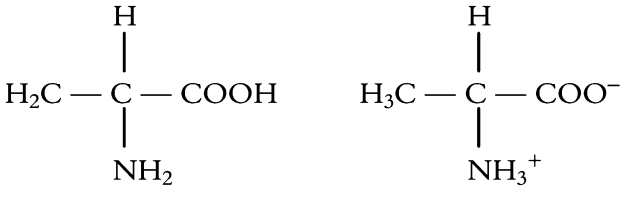
(i) Amino acids are polar covalent compounds.

(ii) They are crystalline substances which are soluble in water.

(iii) They have high melting points.

(iv) Since each molecule of the amino acid contains an acidic —COOH group and a basic —NH_2 parts, they exhibit amphoteric nature. The amino acid has the tendency to transfer the H^+ ion from the —COOH group to the —NH_2 group. As a result of this, the molecule carries a negative charge on one end and positive charge on the other end. It is this charge separation which makes the molecule dipolar and the dipolar ions thus formed are called zwitter ions.

Example

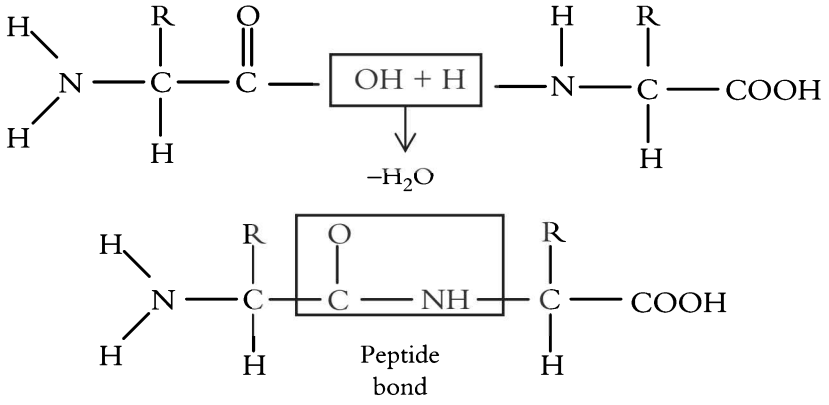


Amino acid

Zwitter ion

(v) Peptide bond formation is the characteristic property of amino acids. Since amino acids have two functional groups, two similar or dissimilar amino acids can combine together by the elimination of a water molecule. The bond hence formed is called a peptide bond. A number of amino acids can join together by means of a number of peptide bonds and the resultant molecule is called a polypeptide.

Formation of the Peptide Bond



Synthesis of Proteins from Amino Acids

Innumerable number of proteins is formed from the 20 odd amino acids available. This is possible because the sequence in which amino acids are linked with each other changes from one protein to the other. The proteins differ in number and sequence of the amino acids. Due to this, the proteins perform different functions in the biological systems. A slight variation in the number or sequence of amino acids in a protein makes the protein ineffective for carrying out the respective function.

Blood contains an important protein called haemoglobin. This protein performs the function of absorbing oxygen to form oxyhaemoglobin which performs important metabolic process. Haemoglobin is made up of 574 amino acids in a specific sequence. Variation of even one amino acid in the sequence makes haemoglobin ineffective for carrying oxygen in the blood. This leads to a disease called "sickle cell anaemia."

A part of normal sequence of haemoglobin: –Val–His–Leu–Thr–Pro–Glu–Glu–Lys

A part of sickle cell anaemia sequence of haemoglobin: –Val–His–Leu–Thr–Pro–Val–Glu–Lys

Significance of Carbohydrates and Proteins

Energy Cycle

The chemistry of biomolecules is closely associated with the sources of energy in plants and animals. These sources of energy being carbohydrates, the energy cycle involves the various steps associated with the production and consumption of these nutrients.

Solar energy is the primary source of energy for all natural processes. Green plants trap the solar energy and carry out the process of photosynthesis which is highly endoergic process of conversion of carbon dioxide and water vapour to glucose and oxygen. The oxygen so liberated during the process of photosynthesis is taken up by the animals by means of respiration. Carbohydrates which are consumed by the animals are subjected to oxidation in the living cells with the help of oxygen present in blood. The energy liberated during the above process is stored in living cells in adenosine triphosphate (ATP) molecules. Each ATP molecule hydrolyses to give adenosine diphosphate and

HPO_4^- with the liberation of 36 k cal of energy. This energy is utilized for various metabolic activities.

$$ATP + H_2O \rightarrow ADP + HPO_4^- + \text{energy}$$

Each ATP molecule can store 36 k cal of energy. In the absence of metabolic activities in the living system, the energy remains stored in the ATP molecules. During the process of metabolism, these ATP molecules undergo hydrolysis, thereby, releasing the required amount of energy.

All these processes involve the role of enzymes which are biocatalysts. Enzymes as well as ATP molecules are constituted by proteins.

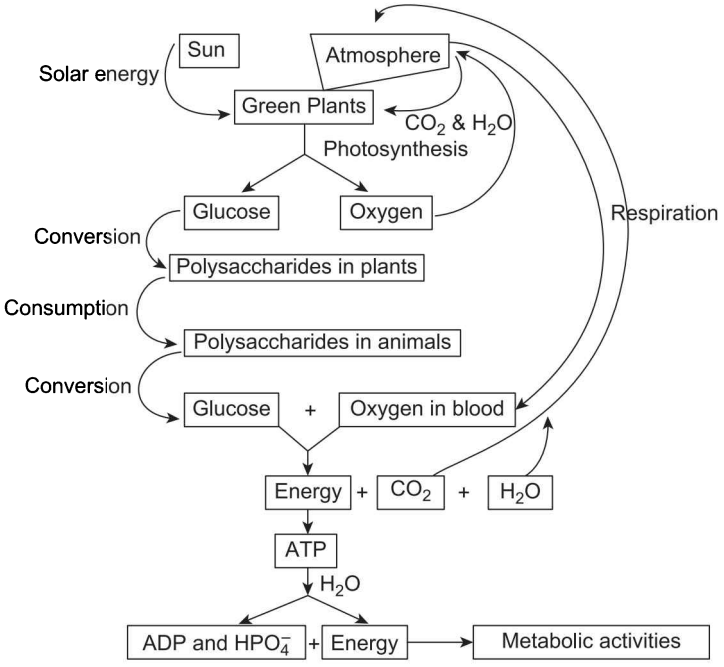


Figure 11.1 Energy cycle

Food Stuffs Rich in Carbohydrates and Proteins

The various food materials contain varying amounts of carbohydrates and proteins. The amount of energy released in kilocalories by the combustion of one gram of the food is called calorific value. Depending on the amount of carbohydrates present in various food stuffs, they differ in their calorific values. For example, the calorific value of glucose is 3.81 cal/g. The nutritive value of the food material ultimately depends on its calorific value. The calorific value of the same food item also varies for the cooked and the uncooked state of food.

Cooked food items	Calorific values	Uncooked food items	Calorific values
Rice	110	Egg	173
Paratha	360	Milk	85
Green vegetables	130	Butter	730
Bread	245	Oil/ghee	900
Pulses	345	Chocolate bar	545

Activities	Calories required
Walking	228
Golf	300
Bicycling	414

Swimming	420
Tennis	426
Running	870

The amount of energy so released is utilized for doing various anabolic activities. Just as the various stuffs have different calorific values, the various anabolic activities also require variable amounts of calories. The quantity and the quality of the food material to be consumed depend not only on the nutritive values of the food stuffs but also on the regular activities performed by the individuals.

Oils and Fats

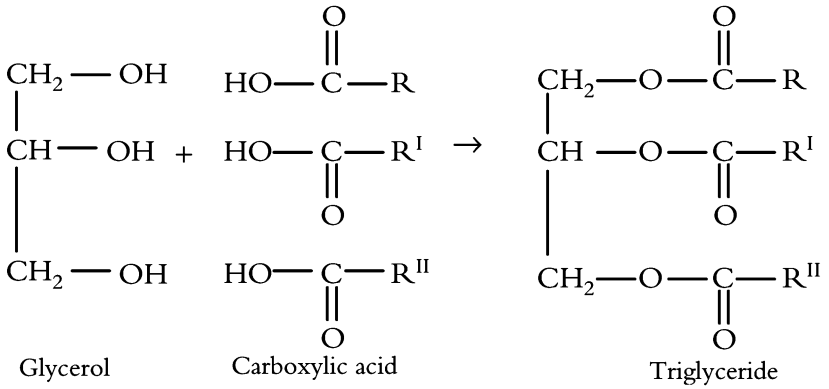
In addition to carbohydrates and proteins, oils and fats form another important class of nutrients. Carbohydrates are considered as immediate sources of energy and proteins are responsible for structural and metabolic activities, whereas oils and fats act as the most important reservoirs of energy. In addition to being rich in nutritive value, oils and fats serve as important raw materials for the manufacture of soaps, vanaspathi ghee, paints and varnishes. Seeds of plants are the sources of vegetable oils, rich sources of essential fatty acids. Animal sources of fats are milk, ghee, eggs, fish and meat.

Structure and Chemical Composition of Oils and Fats

With respect to chemical composition, oils and fats are known as triesters of glycerol or triacylglyerol associated with long chains of fatty acids.

Glycerols are trihydric alcohols where the three carbon atoms can be attached to three –OH groups. Fatty acids are carboxylic acids with long carbon chains ranging from 14 to 22 carbon atoms. If the fatty acid molecule contains one or more double bonds, it is called an unsaturated fatty acid. Glycerol, which undergoes condensation with three molecules of fatty acids, loses three molecules of water to form corresponding triesters, called as triglyceride or triacylglycerol.

Example



R, R^1 and R^{11} are alkyl groups

Classification of Oils and Fats

The triglycerides which are solids at room temperature are called fats and the triglycerides which are liquids at room temperature are called oils.

This difference in phase in triglycerides depends on the extent of unsaturation present in the fatty acid part of the triglycerides. In the case of fats, the extent of unsaturation is less and hence they exist as solids. In the case of oils, the extent of unsaturation is more and hence they exist as oils.

Saturated oils or fats are glycerides of lauric acid ($C_{11}H_{23}COOH$) and stearic acid ($C_{17}H_{35}COOH$) which are saturated fatty acids.

Examples: Coconut oil, butter – lauric acid

Animal fat – stearic acid

Unsaturated oils are glycerides of unsaturated fatty acids like oleic acid ($C_{17}H_{33}COOH$) or linoleic acid ($C_{17}H_{33}COOH$).

Examples: Cotton seed oil, animal fat – oleic acid

Linseed oil – linoleic acid

They can be solidified by converting the unsaturated fatty acid into the corresponding saturated fatty acids. This can be done by subjecting the oils to a process called hydrogenation.

Generally, the term "oils" can be applicable to both unsaturated oils and saturated oils. However, the term "fats" is confined to saturated oils only.

Hydrogenation of Oils

The process involves the passage of hydrogen gas through the unsaturated oil at 200°C temperature and 5 atm pressure in the presence of nickel catalyst. The carbon–carbon double bonds in the fatty acids are broken due to the addition of hydrogen to these bonds. Therefore, the unsaturated oils get converted to saturated fats, thereby leading to solidification. The solidified fat thus formed has a higher melting point.

Hence, this process is also called hardening of oils. The process of hydrogenation carried out is generally partial since complete hydrogenation gives very hard fats unsuitable for cooking purposes. Fats so obtained are more resistant to spoilage in addition to having a better taste and odour.

$$\underset{\text{(Unsaturated)}}{\text{Oil}} + H_2 \xrightarrow[(200^\circ C,\ 5\ \text{atm})]{\text{Ni}} \underset{\text{(saturated)}}{\text{Fat}}$$

Physical Properties of Oils and Fats

(i) Generally odourless and tasteless

(ii) Immiscible with water and lighter than water

(iii) Highly soluble in organic solvents

Uses

(i) Various vegetable oils such as groundnut oil, coconut oil, sunflower oil, etc., are used for cooking.

(ii) The hydrogenated oils such as dalda, vanaspathi, ghee, etc., are also used for cooking purposes.

(iii) Some oils like coconut oil, mustard oil, olive oil, etc., are used for cosmetic purposes.

(iv) Cod liver oil and eucalyptus oil have medicinal value.

(v) Oils and fats find industrial applications in the manufacture of soaps, paints, varnishes, detergents, etc.

EXAMPLE

Why does starch form a thick paste when it is boiled with water?

SOLUTION

Starch is composed of two units namely amylose unit and amylopectin unit. Amylose is water soluble and amylopectin is water insoluble. On heating with water, amylose dissolves and amylopectin remains as such. Therefore starch becomes partially soluble and forms paste.

EXAMPLE

How is glucose tested in human blood?

SOLUTION

Glucose is formed by the degradation of food in the human body. This glucose so formed enters blood and a certain level of glucose is always maintained in blood. If the concentration of glucose in the blood exceeds a certain limit, it leads to 'diabetes'. For the diagnosis of diabetes, the amount of glucose in blood has to be estimated. Glucose contains aldehyde group. It gives all the reactions given by the normal aldehydes. The test is based on the principle that aldehydes reduce cupric ions to cuprous ions. Benedict's reagent is the solution of copper sulphate in an aqueous solution of a mixture of citric acid and sodium carbonate. A red precipitate of cuprous oxide is formed which shows the presence of glucose. The amount of ferrous oxide formed gives an estimation of the amount of glucose in blood.

Important Applications of Organic Chemistry

There are many organic compounds which are useful for various purposes in our daily life. They include plastics, rubber, synthetic fibres, dyes, medicines, cosmetics, petroleum products, etc. Among these, plastics and synthetic fibres are made up of synthetic polymers which are obtained from simple organic molecules. "Polymers" as the name itself suggests are giant organic molecules made up of many simpler units which may be identical or not. The simple compounds which join together to give polymers are called monomers. Polymers are otherwise called macromolecules. The process of formation of polymers from the corresponding simple monomer molecules is called **polymerization**. Polymers can be naturally occurring or they may be man-made.

Synthetic Polymers

Some of the natural polymers such as starch, proteins, nucleic acids, rubber, silk, etc., are available in living systems, whereas many polymers can be prepared in a laboratory from simple organic compounds. These are called synthetic polymers in order to distinguish them from natural polymers.

There are two types of polymerizations as listed hereunder:

(i) addition polymerization and

(ii) condensation polymerization.

(i) Addition polymerization: This reaction involves joining the individual organic molecules by breaking of π-bonds and adding the molecules together.

The macromolecules formed are called addition polymers.

Example

$$2H_2C = CH_2 \xrightarrow[\text{or HCl}]{H_2SO_4} CH_2 — CH_2 — CH_2 — CH_2 —$$

$$\underset{\substack{\text{ethylene or}\\\text{ethene}}}{nCH_2 = CH_2} \xrightarrow{H_2SO_4} \underset{\substack{\text{polyethylene or}\\\text{polythene}}}{\{CH_2 — CH_2\}_n}$$

Some Examples of Addition Polymers

Name of monomers	Formulae	Names of polymer	Formulas	Uses
Ethene	$H_2C=CH_2$	Polyethene	$\{CH_2—CH_2\}_n$	Toys, pipes, bags, containers
Vinyl chloride	$CH_2=CH—Cl$	PVC (polyvinyl chloride)	$\{CH_2 — CH(Cl)\}_n$	Floor tiles, toys, rain coats
Tetrafluoroethene	$CF_2=CF_2$	Teflon	$\{CF_2—CF_2\}_n$	Nonstick cookware coating
Propene	$CH_2 — CH=CH_2$	Polyprene	$\{CH_2 — CH(Cl)\}_n$	Fibres for carpets, fishing nets
Isoprene	$H_2C=C(CH_3)–CH=CH_2$	Natural rubber	$\{CH_2 — C(CH_3)=CH — CH_2\}_n$	Water proof materials sheets, balls, tyres, shoes
1, 3-Butadiene	$H_2C=CHCH=CH_2$	Synthetic rubber, Buna–s	$\{CH_2—CH = CH—CH_2\}_n$	Same as natural rubber
Chloroprene	$H_2C=C(Cl) —CH=CH_2$	Neoprene	$\{CH_2 — C(Cl)=CH — CH_2\}_n$	Insulating material, conveyor belts in mines, synthetic fibre

(ii) Condensation polymerization: A reaction in which the joining of monomer molecules involves a loss of simple molecules such as water or ammonia is called condensation polymerization. The resulting products are called condensation polymers.

This type of polymerization is possible only between the molecules having two reactive sites or functional groups. The classes of organic compounds which involve in this process are generally alcohols, carboxylic acids, amines and amides.

The basic reactions involve the formation of ester group or amide group.

Example

$$RCOOH + HOR^1 \xrightarrow{H_2SO_4} RCOOR^1 + H_2O$$

$$RCOOH + \begin{matrix} H \\ \diagdown \\ N - R^1 \\ \diagup \\ H \end{matrix} \rightarrow RCONHR^1 + H_2O$$

(R & R^1 → alkyl groups)

Some Examples of Condensation Polymers

Names of monomers	Formulae of monomers	Names of the polymer	Uses
Ethylene glycol + Dimethyl terephthalate	CH_2OH (—) CH_2OH + C_4H_4 (—) $COOCH_3$, $COOCH_3$	Terylene (or) (polyester) Dacron	Manufacture of synthetic fabric

Hexamethylene diamine + adipic acid	$H_2N(CH_2)_6NH_2$ + $HOOC-(CH_2)_4-COOH$	Nylon – 6, 6 (polyamide)	Manufacture of synthetic fabric

Classification of Polymers

Polymers can be classified into three types depending on the structure and physical properties. They are listed hereunder:

(i) elastomers,

(ii) fibres and

(iii) plastics.

(i) Elastomers/Rubber: Elastomers are polymers which exhibit the unique property of high elasticity. They can be stretched to 5 to 10 times their original length under tension and their original dimension can be reversed back on the release of the load. Thus, elasticity is the characteristic property.

Elastomer/rubber is an addition polymer. Naturally available rubber can be formed from latex of rubber trees. The basic monomer units in rubber are isoprene units. This polymer is highly elastic in nature. This natural rubber is subjected to a process called vulcanization which makes the rubber temperature resistant. Vulcanization is the process of heating of natural rubber with sulphur which improves the elasticity as well as reduces the sticky nature of rubber. During this process, different isoprene units are joined together by C–S–S–C bonds. Synthetic rubbers are also addition polymers.

Examples

Buna–S, thiokol, etc.

Elastomers can be of two types—natural and synthetic elastomers.

Natural rubber is the example of natural elastomer and examples of synthetic elastomers are Buna-S rubber and neoprene.

Characteristics

(a) The material is soft.

(b) It can withstand very high strain.

(ii) Fibres

Fibres are polymers which have the characteristic property of high tensile strength and can be elongated into long thin threads.

Examples

Cellulose is a natural polymer, a main constituent, present in natural fibres such as cotton, wool and silk. Synthetic fibres are nylon, polyester, terylene, orlon, rayon, etc.

Characteristics

(a) High tensile strength

(b) Ability to withstand pressure and temperature (sunlight and ironing)

(c) Resistance to chemical reactions with alkalis and solvents of dry cleaning

(d) Resistance to aerial oxidation

Preparation of Synthetic Fibre

From a polymeric material, the synthetic fibre can be obtained by spinning. Spinning of fibre can be of various types as discussed hereunder.

(i) Melt spinning: The molten polymer when pumped through a porous spinneret jet followed by cooling gives fibre.

Examples: Nylon and dacron

(ii) Dry spinning: The polymer is made to dissolve in an organic solvent that has a low boiling point. It is pumped through the spinneret. The solvent is evaporated by sending hot air around the spinneret. Thus, a fibre is obtained.

Examples: Cellulose acetate and Orlon

(iii) Plastics

The polymers which can be extended as sheets or pipes or which when dissolved in suitable solvents form paints and emulsions or which can be moulded into various shapes are called plastics. For making various types of plastics, small amounts of other compounds are added to the polymeric organic compound. These compounds which are added are called fillers, plasticizers and lubricants.

Monomers	Polymers	Uses
Styrene	Polystyrene	Insulating materials, packing, TV, refrigerator lining
Vinyl chloride	Polyvinyl chloride (PVC)	Pipes, floor coverings, gramophone records

Characteristics

(a) Tough and hard materials

(b) High resistance to chemical reactions with water, heat and pressure, atmosphere

(c) Ease of fabrication

(d) Ease of colour mixing

(e) Resistance to corrosion

Adhesives

The substance which is used for attaching materials at their surfaces is called an adhesive.

(i) Natural adhesives: Natural adhesives are made from bones of animals and fish, milk protein casein, vegetable protein, egg albumin, blood albumin, starch, etc.

Examples: Gum-Arabica, shellac, glue, etc.

(ii) Synthetic adhesives: Synthetic adhesives can be obtained from derivatives of cellulose. The additional materials such as wetting agents, fillers and preservatives are added to adhesives.

Examples: Epoxy resins, silicones, phenol–urea formaldehyde resin, polyvinyls, polystyrenes, polyamides, etc.

Characteristics

(i) It should be capable of holding the material together by surface attachment.

(ii) It should dry at a faster rate.

(iii) The solvents should not react with the material to which the adhesive is applied.

Cosmetics

Cosmetics is a class of materials used for cleaning or beautification of a person. They include creams, talcum powders, cleaning lotions, nail polishes, etc.

(i) Cold creams: They are emulsions of oil in water used to protect skin from external effects.

Characteristics

(a) Should melt at body temperature

(b) Should easily spread over the skin

(c) Should not be sticky and greasy

(d) Should act as a shield to hot sun, cold weather and wind

Ingredients of a cold cream: Almond oil, bees wax, rose water, butter, olive oil, borax and paraffin wax.

(ii) Nail polish: It is a polymeric resin applied on nails for cosmetic purpose.

Characteristics

(a) Nontoxic in nature

(b) Faster evaporation of solvents and faster drying

(c) Water insoluble in nature

(d) Should be available in attractive colours

Ingredients of nail polish: Organic polymer, a plasticizer, colouring pigments, perfume, low boiling solvent. The polymeric resin may be a derivative of nitrocellulose. Plasticizer can be castor oil. The low boiling solvents can be alcohols, benzene, etc.

Dyes

These substances are organic colouring materials which can impart colours to various fibres.

Characteristics

(i) Resistance to sunlight

(ii) Resistance to soaps and detergents

(iii) Ability to spread uniformly over the fabric

(iv) Resistance to water

(v) Resistance to heat and temperature

(vi) Ability of easy drying

Structural aspects of the ingredients of dyes

All dyes are basically aromatic organic compounds. The unsaturated group of the organic molecule which imparts colour to the fabric is called **chromophores**.

Example: $-NO_2$, – NO, – N = N –, C = O, C = S groups. The other part of the molecule intensifies the colour of the dye. In addition to this, it is this part which forms bonds with the fibre. These are called **auxochromes**.

Example: -COOH, -OH, $-SO_3H$, $-NH_2$, -NHR groups

Classification of Dyes

On the basis of the nature of chromophore present in the dye, the dyes are classified into various types. Some of these types of dyes are discussed hereunder:

Chromophores	Types of dye	Examples
$-NO_2$	Nitro dye	Martius yellow
–NO	Nitroso dye	Naphthol green
–N≡N	Azo dye	Methyl orange, Bismarck brown
–C=O	Quinone dye	Indigo

Dyes can be classified into various types on the basis of the method of application as discussed hereunder:

Types of dye	(Method of application) Media required	Examples
Acid dye	Acid medium	Orange I
Basic dye	Basic medium	Malachite green
Direct dye	Neutral medium	Martius yellow
Mordant dye	Insoluble and applied along with soluble dye	Alizarin
Vat dyes	Reduced form	Indigo

(i) Acid dyes

These are water soluble anionic dyes that are applied to fibre such as silk, wool and nylon. Attachment to the fibre is attributed to salt formation between anionic groups in the dye and cationic group of the fibre.

(ii) Basic dyes

Basic dyes are water soluble cationic dyes. Those are mainly applied to acrylic fibres, but find some use for wool and silk also. Basic dyes are also used for the colouration of paper.

(iii) Direct dyes

The dying with direct dyes is normally carried out in neutral or slightly alkaline dye bath at or near boiling point, with the addition of NaCl or Na_2SO_4. Direct dyes are used for cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators.

(iv) Mordant dyes

These dyes cannot dye the fabric directly. When some substances called mordants are added to these dyes, they can produce wash-fast colours. The mordants include salts of some metals like aluminium, iron and chromium. Acidic dyes require basic mordants and basic dyes require acidic mordants.

Example: Alizarin

(v) Vat dyes

These are a kind of developed dyes. The actual dye is colourless. On application to the fabric, it gets oxidized and converted to the coloured form. The colourless form is called leuco form.

Example: Indigo

Drugs

The word "drug" is derived from the French word "drogue" which means a dry herb. This is because, in ancient times, drugs were extracted from various plant parts.

A drug can be defined as a substance which is used for prevention, diagnosis, treatment or cure of a disease in human beings or animals.

Characteristics of an Ideal Drug

(i) Localized site of action

(ii) Efficient in action

(iii) Should have negligible side effects

(iv) Should not cause any damage to host tissues

(v) Should not acquire tolerance on prolonged usage

Therapeutic Action of Drugs

It is the effect of a particular drug on localized site to produce a desired action on the desired physiological process. Based on the physiological action or therapeutic action, drugs are classified into six types as listed hereunder:

(i) Drugs acting on central nervous system

(ii) Drugs acting on peripheral nervous system

(iii) Cardiovascular drugs

(iv) Chemotherapeutic drugs

(v) Vitamins

(vi) Hormones

(i) Drugs acting on central nervous system: These drugs work either to stimulate or depress the action of brain and spinal cord. These are also called **tranquilizers**.

Examples: Meprobamate, amytal (barbiturates), etc.

(ii) Drugs acting on peripheral nervous system: These drugs act to stimulate or block temporarily the action of body nerves. These are also called **analgesics**.

Examples: Aspirin, paracetamol, benadryl, etc.

(iii) Cardiovascular drugs: These drugs act on the blood vessels and on the functioning of heart. That means, they may be cardiotonic, antihypertensive and hypocholestemics. Some drugs also act on renal system and they are called diuretics.

Examples: Aspirin, naproxen, etc.

(iv) Chemotherapeutic drugs: Treating the disease by chemical substances is called chemotherapy. Chemotherapy is the use of drugs to kill an invading microorganism present in the body cells without causing any damage to the host cells. These are further classified into various types based on their action on the type of microorganism.

(a) Antimalarial drugs

Example: Chloroquine

(b) Antiseptics

Examples: Dettol, boric acid, etc.

(c) Antifungals

Example: Sulphadiazine

(d) Antibiotics

Examples: Erythromycin, tetracycline, chloramphenicol, penicillin, etc.

(e) Antiviral drugs

Example: Aureomycin

(f) Anti-tuberculosis drugs

Examples: Rifampicin, cycloserine, etc.

Vitamins

These are compounds which are required by the animals in small quantities for their metabolic activities and for the maintenance of normal health. They form part of the food materials consumed. However, their deficiency causes various diseases. Hence, the supplementation of vitamins to the body in the form of drugs is essential in times of need.

Vitamins	Chemical names	Deficiency disorders
A	Retinol	Night blindness
B_1	Thiamine	Beriberi
B_2	Riboflavin	Tongue sores and sores at mouth corner
B_3	Nicotinic acid	Pellagra
B_5	Pantothenic acid	No deficiency symptoms reported
B_6	Pyridoxine	Convulsions
B_{12}	Cyanocobalamin	Anaemia
C	Ascorbic acid	Scurvy

D	Calciferol	Rickets
E	Tocoferol	Infertility
K	Phyloquinone	Bleeding or haemorrhage

Hormones

These are chemical substances produced by endocrine glands inside the human or animal body. They control the metabolic rate, and hence act as metabolic catalysts. E.g., insulin secreted by pancreas controls the glucose levels in blood. But deficiency of these hormones in the body results in physiological disorders or disease. In order to cure these disorders, the hormones should be given externally as a drug. These drugs also form the part of anti-fertility drugs and are known as contraceptives.

Pharmaceutical Formulations

Pharmaceutical formulations are the various forms in which drugs are given to the patients. A drug cannot be directly consumed by a patient due to its unpleasant taste, smell and appearance. Above all, the drug when passing through the system may show harmful effects on the various parts of the body. It has to be released at its site of action in required amounts at regular intervals.

Due to these reasons, a drug is mixed with other ingredients and modified into various forms like tablets, capsules, syrups, tonics, ointments, injections, powders, etc.

(i) Tablets: To the powdered drug, suitable gum is added, dose is determined and then moulded into solid form called "tablets."

Mode of Preparation

(a) Dry method: All ingredients are granulated and screened through a mesh sieve. The dry granules are compressed and packed.

(b) Wet method: The granulated drug and other ingredients are dispersed in a binder excipient uniformly and screened through a mesh sieve. The granules are dried on trays in hot air ovens and compressed to get tablets and the tablets are packed.

(ii) Capsules: When the drug is bitter or when it causes harm to the intestinal walls or when the drug is to be absorbed slowly, it is made into a capsule form. These are also prepared in the same manner as the drug in the form of powder or granules is filled in an outer covering.

(iii) Syrups and tonics: The drug is dissolved in a suitable solvent and made into a colloid or suspension. Flavouring agents and colours are also added to these to give them good taste, odour and appearance. Most of the paediatric drugs are in these formulations.

(iv) Injections: When the drug action is required immediately, drug formulations are introduced directly into the body fluids such as injections.

The drug is made to dissolve in a suitable solvent to form a solution. These are the formulations where the drug is directly injected into the muscles or nerves.

Soaps and Detergents

Soaps

Soap is the sodium or potassium salt of a long chain of fatty acids.

Principle

Hydrolysis of triglycerides in the presence of alkali gives salts of the corresponding fatty acids and glycerol. This reaction is known as saponification of ester.

$$\underset{\text{Triglyceride}}{R\,COOR^1} + NaOH \xrightarrow{H_2O} \underset{\text{Soap}}{RCOONa} + \underset{\text{Glycerol}}{R^1OH}$$

Process: The process of manufacture of a soap is carried out in three steps as discussed hereunder:

(i) Hydrolysis

This step is carried out in a stainless steel tower. Coconut oil or cotton seed oil or animal fat is taken in the tower. Superheated steam is passed through the oil at 240–250°C under a pressure of 4.1 mega pascals for 2–3 h in presence of zinc oxide or calcium oxide catalyst. The oil gets hydrolysed to give a mixture of fatty acids and glycerol. Glycerol, being highly soluble in water, is separated by distillation, leaving behind fatty acids.

(ii) Separation

The fatty acids obtained are used further for the preparation of the soap. In this step the mixture of fatty acids is separated and required fatty acid is used for further process. The mixture is dried and separated by fractional distillation. The fatty acids required are chosen, mixed in required ratios (this dictates the quality of soap) and sent for neutralization.

(iii) Neutralization

The fatty acids are neutralized by using bases. The type of base used depends on the type of soap to be manufactured. Different salts of fatty acids have different uses in soaps.

$$\underset{\text{glyceride}}{\begin{array}{l}CH_2\text{–}O\text{–}COC_{17}H_{33}\\ |\\ CH_2\text{–}O\text{–}COC_{17}H_{33}\\ |\\ CH_2\text{–}O\text{–}COC_{17}H_{33}\end{array}} + 3NaOH \longrightarrow \underset{\text{glycerol}}{\begin{array}{l}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}} + \underset{\text{soap}}{3C_{17}H_{35}COONa}$$

Types of soap	Bases used for neutralization
Toilet soap	KOH
Laundry soap	NaOH
Water proof texture	$Ca(OH)_2$, $Al(OH)_3$
Dry cleaning	Triethanol ammonium hydroxide

Certain other additives are also added to the soap to give them certain extra features.

Soap/Features	Additives added
Deodorant soap	3, 4, 5-Tribromosalicylanilide
Shaving soap/Slow drying lather	Stearic acid
Transparent soap	Glycerine
All soaps	Perfumes, soda ash, sodium bicarbonate

A large variety of soaps is available in the market for various purposes. The best quality soap is the one which gives maximum lather with water. Soap, however, does not form lather with hard water.

Detergents

Detergents are sodium salts of alkyl benzene sulphonate or fatty alcohol sulphates.

Manufacture of Detergents

Manufacture of detergents also involves three stages as discussed hereunder:

(i) Treating alkyl benzene or fatty alcohol with oleum, (H_2SO_4 + SO_3) gives alkyl benzene sulphonate or fatty alcohol sulphate, respectively.

(ii) Alkyl benzene sulphonate and fatty alcohol sulphate are acids and are treated with sodium hydroxide. Sodium salt of alkyl benzene sulphonate and fatty alcohol sulphate are formed.

(iii) In this step, builders like salt, soda ash and sodium bicarbonate are added to the sodium salt of alkyl benzene sulphonate or fatty alcohol sulphate to give detergents.

$$\underset{\text{Lautyl alcohol}}{nC_{11}H_{33}CH_2OH} \xrightarrow{H_2SO_4} nC_{11}H_{23}CH_2OSO_3H \xrightarrow{NaOH} \underset{\text{Sodium laurylsulphate}}{nC_{11}H_{23}CH_2OSO_3^-Na^+}$$

A wide variety of detergents is manufactured and hence available with different trade names in the market.

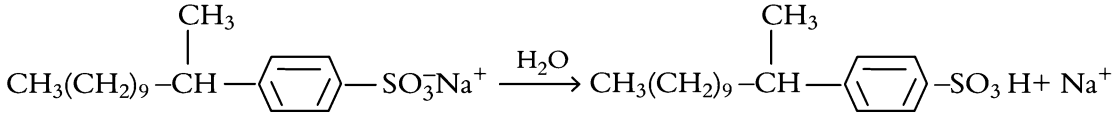
Cleansing Action of Soaps and Detergents

The basic principle behind the working of soaps and detergents is the same. Soap, being a sodium or potassium salt of stearic acid, can be ionized into stearate ions and Na^+ or K^+ ions. The stearate ion is hydrophobic in nature which consists of long chain of hydrocarbon which forms the tail part and carboxylic acid which is hydrophilic in nature and forms the head part.

$$\underset{\text{Soap}}{CH_3(CH_2)_{15}CH_2COONa} \xrightarrow{H_2O} \underset{\text{Stearate ion}}{CH_3(CH_2)_{15}CH_2COO^-} + Na^+$$

$$CH_3(CH_2)_{15}CH_2COO^- \Rightarrow CH_3(CH_2)_{15}CH_2 \text{ hydrophobic tail}$$

COO^- hydrophilic head



Sodium salt of alkyl benzene sulphonic acid

(detergent)

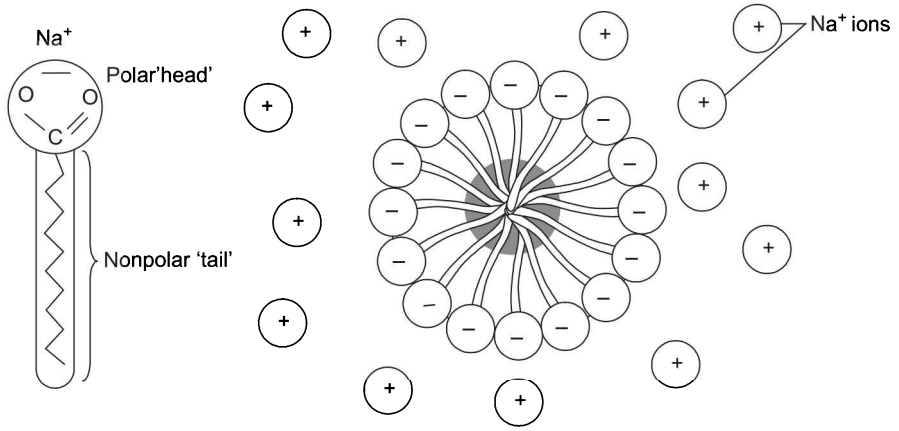
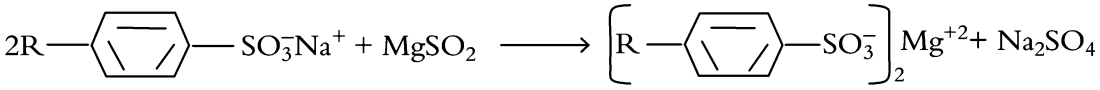


Figure 11.2 (a) A soap molecule (b) Cross section of a soap micelle in water

Advantage of Detergents Over Soap

Detergents are sodium or potassium salts of alkyl sulphonic acids. The hydrocarbon tail part remains the same as is soap, whereas the head part contains $-SO_3^-$ end instead of COO^- end. Cleansing action of detergents is the same as that of a soap.

$$2RCOO^-Na^+ + \underset{\text{(Hard water)}}{MgSO_4} \rightarrow (RCOO)_2^-Mg^{+2} + Na_2SO_4$$



Soaps are efficient in action only when they are used with soft water. But when they are used with hard water, they cannot work efficiently. Hard water contains Ca^{+2} and Mg^{+2} ions. When soap dissolves in hard water, these ions form insoluble salts with stearate ions of soap. Thus, the stearate ion concentration available for micelle formation gets reduced.

Detergents are more efficient than soaps since the calcium or magnesium salts of sulphonic acid formed are soluble in hard water and, therefore, do not cause any precipitation.

Disadvantages of Using Detergents

Though detergents are more efficient than soaps, they are disadvantageous as they add to water pollution. This is because of the fact that the branched chain of hydrocarbon parts of detergent molecules is resistant to degradation and persist for a longer time in the environment.

This difficulty could be overcome by reducing the extent of branching to minimum thus rendering faster degradation of detergent molecules. These are termed as biodegradable detergents.

Petroleum and Petrochemicals

Petroleum is a dark viscous oily liquid with unpleasant odour, which originates at depths of thousands of feet below the earth's surface. It is also called rock oil (Petra means rock and oleum means oil) or crude oil.

Composition

Petroleum mainly consists of a complex mixture of hydrocarbons, predominantly alkanes (straight and branched chain $-C_1$ to C_{40}) and cycloalkanes. Further, aromatic hydrocarbons are present in considerable amounts in the same petroleum deposits. In addition to these, compounds of oxygen, nitrogen and sulphur are also found in petroleum in minor proportions. However, the composition of petroleum is variable depending upon the place of its origin.

Extraction of Petroleum

All crude oil deposits contain a gaseous mixture of lower alkanes called natural gas. Methane is the major constituent of natural gas. Petroleum is found floating on the layer of salt. Petroleum can be obtained by drilling a deep well through the various layers under the earth's surface till the oil-bearing strata are reached. During the process of drilling, pressure created in the underground reservoir allows the gases to fizz out of solution pushing crude oil to the surface. Pipes are introduced up to the oil level through which the crude oil can be drawn out. But by this method only 20% of the crude oil gushes out. To draw more petroleum out, either water or compressed air is pumped through the outer pipe and oil is drawn out through the inner pipe.

Processing of Petroleum

The crude oil extracted from the earth's crust contains a lot of impurities. It has to be first processed in oil refineries. The petroleum drawn out by the process of drilling is transported through pipes to the oil refineries and distilled. This oil is of two kinds. One is heavy oil or lubricating oil which is used as such. The second one is light oil which must be subjected to a series of operations for purification and separation.

The Purification of Crude Oil Involves Two Major Steps

1st step: Removal of impurities: Since crude oil is present with a layer of salt beneath earth's surface, it contains salt water as the major impurity. This water can be removed by passing the crude oil sample between two highly charged electrodes. Water droplets are attracted towards the electrodes and separated out. The oil so obtained is devoid of water and is subjected to treatment with copper oxide. The sulphur compounds present in the oil react with copper oxide forming copper sulphide which is removed by filtration.

2nd step: Fractional distillation: After the removal of impurities, the crude oil obtained is a pure mixture of hydrocarbons. This method involves heating of the mixture over a specific range of temperature in a fractionating column with a long tube. This allows separation of various components of the mixture according to their boiling points.

The crude oil is taken in an iron retort and heated up to 350°C–400°C. The various components in the oil evaporate at this temperature. The vapours so obtained are passed through a fractionating column. The fractionating column consists of a number of horizontal stainless steel trays in a tall cylindrical tower. The vapours when passed through this column cool down and get condensed. The condensation takes place at different heights of the fractionating column. The high boiling components get condensed first leaving behind the low boiling components. The liquids formed by condensation are collected in different trays and are collected separately. At the end of the fractional distillation, a cake like solid residue remains in the retort. This is called "asphalt".(crude oil rich in naphthalene).

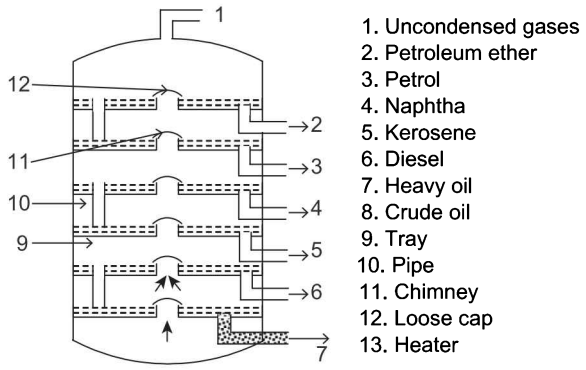


Figure 11.3 Purification of crude oil

The various components obtained at various stages can be used for different purposes. These products which are derived from crude oil by this refining process are used as fuels. Depending on the actual composition of fraction and the purpose for which it is used, these fractions are subjected to further purification. As a result, these products get freed from corrosive constituents and also from unpleasant odours.

Main fractions	Boiling temp. ranges	Composition alkanes	Uses
Petroleum gas	Below 30°C	C_1 to C_4	Fuel, for making carbon black
Crude naphtha	30°C–150°C	(a) Petroleum ether (below 90°C) (C_5–C_7) (b) Gasoline or petrol (90°C–120°C) (C_7–C_9) (c) Benzene (120°C–150°C) (C_9–C_{10})	Solvent Motor fuel Dry cleaning
Kerosene oil	150°C–300°C	C_{10}–C_{16}	Cooking fuel, illuminant oil gas
Fuel oil	300°C–350°C	C_{16}–C_{20} (a) Gas oil (b) Diesel oil (c) Furnace oil	Motor fuel, cracking stock for gasoline
Lubricating oil	350°C–400°C	C_{20}–C_{24}	Paint oil, lubricants
Paraffin wax	Above 400°C	C_{24} and above	Candles, matches, paints, water proofing, ointments, protective paints

Petrol or Gasoline

It is the most important product of petroleum. It is mainly used as a fuel for automobiles. This is also used as a solvent for the dry-cleaning of clothes. The petrol which is directly obtained by fractional distillation of crude oil is called straight-run petrol.

Petrol can also be manufactured by a process of cracking of heavier petroleum products.

Cracking

Cracking is decomposition of long chain hydrocarbons into simple hydrocarbons at high temperature and pressure in presence of catalysts. The petrol so obtained is more efficient than the straight-run petrol.

Cooking Gas/Domestic Gas

Cooking gas is technically called liquefied petroleum gas (LPG). It is a mixture of propane, propene and butane with little amount of ethane. This gaseous mixture when subjected to high pressure gets liquefied. This liquefied mixture is kept in cylinders at high pressure and is used as the cooking fuel and also as motor fuel.

Petrochemicals

Petroleum is an important raw material for the manufacture of industrial chemicals. These products obtained from crude petroleum are called petrochemicals. Petrochemicals find extensive applications in the manufacture of plastics, synthetic fibres, synthetic rubber, pesticides, detergents, dyes, drugs, etc.

Direct	Indirect
Methane	Methyl chloride, methyl alcohol, chloroform, etc.
Ethane	Ethyl chloride, ethyl alcohol, acetic acid, nitroethane, etc.
Ethylene	Glycol, vinyl chloride, 1, 3-Butadiene, etc.
Propane	Nitropropane
Propylene	Allyl alcohol, butadiene, etc.
Butylene	Butyl alcohol, butadiene, etc.

Thus petroleum forms the most important raw material for the manufacture of various fuels. Nevertheless, the significance of petroleum is being shifted to the manufacture of petrochemicals which form the backbone of organic chemical industry. Therefore, researches are going on for development of alternative sources of energy in place of petroleum for a rational and judicious use of this exhaustible natural resource.

EXAMPLE

Cardiac patients are advised to preferably consume unsaturated oils. Justify.

SOLUTION

Saturated oils solidify at body temperature and block blood vessels. Unsaturated oils do not solidify and prevent blockage of blood vessels.

EXAMPLE

"Boiling is preferred process to frying as far as preservation of nutritive values is concerned". Comment on this statement.

SOLUTION

Cooking involves loss of water soluble vitamins whereas frying involves loss of both water soluble and fat soluble vitamins.

EXAMPLE

Explain the cleansing action of soap.

SOLUTION

Soap is sodium or potassium salt of stearic acid. It can be ionised into stearate ions and Na^+ or K^+ ions. Stearate ion is hydrophobic in nature as it consists of long chain hydrocarbon part and carboxylic acid part is hydrophilic in nature. Thus soap micelles are formed and oily dirt goes along with soap water.

TEST YOUR CONCEPTS

Very Short Answer Type Questions

1. What are the different parts of the IUPAC name of an organic compound?
2. Give the IUPAC names for the following:

   (i) $H_3C—O—C_2H_5$

   (ii) $H_2C—CH_2—\overset{\overset{O}{\|}}{C}—CH_3$
3. Give common names for the following:

   (1) HCHO

   (2) CH_3CHO

   (3) $CH_3—\overset{\overset{O}{\|}}{C}—CH_3$
4. Why aldehydes cannot exhibit position isomerism?
5. How is petrol obtained from heavier fractions of petroleum distillation?
6. What is petroleum? Give its composition. Also mention the other names of petroleum.
7. State the functions of the two parts of a dye.
8. What are mordant dyes? Give an example.
9. What are the types of synthetic polymers? Give one example of each.
10. What is meant by pharmaceutical formulations? Name the different types of formulations of a drug.
11. The IUPAC name of ethylmethylketone is _____.
12. What is meant by rectified spirit? How is absolute alcohol different from rectified spirit?
13. How is ethyl alcohol prepared from starch? Give equation.
14. 1-Propanol and 2-Propanol are _____ isomers.
15. Why are carbohydrates called saccharides?
16. What are oligosaccharides? Give some examples.
17. What are the types of isomerism exhibited by ketones?
18. What is the general formula of polysaccharides? Give examples.
19. What is meant by vulcanization?
20. Give the reactions of ethyl alcohol with H_2SO_4.
21. What is absolute alcohol? How is it obtained from rectified spirit?
22. Write the chemical reactions involved in the manufacture of ethyl alcohol form sucrose.
23. Maltose is an example of _____.

    (1) oligosaccharide (2) homopolysaccharide

    (3) heteropolysaccharide (4) monosaccharide
24. What are essential amino acids? In what way are they different from nonessential amino acids?
25. Name some disaccharides. Give the formula.
26. What is zwitter ion? Why do amino acids form zwitter ions?
27. The secondary suffix "al" indicates functional group in the compound.
28. What is a glycoside bond? How is it formed?
29. Give the composition of a denatured spirit.
30. Define the following:

    (a) Soap

    (b) Detergent

    (c) Fats

    (d) Oils

    (e) Unsaturated oils

    (f) Saturated oils

Short Answer Type Questions

31. Give the structures of the following compounds:

    (a) 2-Butanol (b) 3-Bromopentane

    (c) 2-Chloro-2-Propanol (d) 2-Propanone
32. What is secondary suffix? Give the different functional groups with their secondary suffixes.
33. Give equations for the addition of HCN to an aldehyde and a ketone.

PRACTICE QUESTIONS

34. What is meant by spurious alcohol? Why is it fatal?
35. How are carbohydrates classified? Explain.
36. Draw the structures of glucose and fructose.
37. What are Tollen's reagent and Fehling's reagent? How do they help in identification of carbonyl compounds?
38. Give characteristics of synthetic fibres. How do they differ from other types? Give two examples.
39. What are the characteristics of a dye?
40. Define a drug. List out the characteristics of an ideal drug.
41. Explain the cleansing action of a soap.
42. Explain the process of hydrogenation in detail and give its advantages.
43. What is the significance of proteins?
44. What are proteins? How are they formed?
45. What are the products of hydrolysis of sucrose, maltose and lactose?

Essay Type Questions

46. Explain the process of fermentation of molasses.
47. What are reducing and non-reducing sugars? Give examples. What are their sources? How are they distinguished from each other?
48. What are synthetic polymers? How are they classified? Give the characteristics of each type.
49. Write the differences between soap and detergents. List the differences in the process of manufacturing soap and detergents.
50. Explain the refining of crude oil.

CONCEPT APPLICATION

Level 1

***Direction for questions from 1 to 7*: State whether the following statements are true or false.**

1. Ethyl alcohol on oxidation with acidified $K_2Cr_2O_7$ gives ethanol.
2. Propionic acid is the IUPAC name of carboxylic acid with three carbon atoms.
3. The $-\overset{\overset{O}{\|}}{C}-NH-$ bond is called glycoside bond.
4. Proteins are the polymers of amino acids.
5. Antiseptics are a class of chemotherapeutic drugs.
6. Lauric acid and stearic acid are unsaturated fatty acids.
7. Both glucose and sucrose give Fehling's test.

***Direction for questions from 8 to 14*: Fill in the blanks.**

8. The part of IUPAC name of the organic compound which denotes functional group is called _____.
9. Structural formula of methoxypropane is _____.
10. _____ is the additive used in transparent soaps.
11. Diethyl ketone and isopropyl methyl ketone are called _____.
12. The part of the dye molecule which forms bonds with fibre is called _____.
13. The addition compound obtained by treating propanone with hydrogen cyanide is _____.
14. _____ is obtained by the saponification of oils.

***Direction for question 15*: Match the entries in column A with the appropriate ones in column B.**

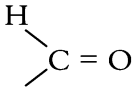
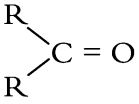
15.

Column A		Column B
A. Chloramphenicol	( )	a. vitamin A
B. Alizarine	( )	b. copolymer
C. Zymase	( )	c. addition polymer
D. Alkyl benzene sulphonate	( )	d. fermentation process
E. Nylon-66		e. antibiotic
F. Polyprene	( )	f. mordant dyes
G. Retinol	( )	g. detergent

PRACTICE QUESTIONS

***Direction for questions from 16 to 45*: For each of the questions, four choices have been provided. Select the correct alternative.**

16. Detergents are less or nonbiodegradable when compared with soaps. For detergents to be biodegradable in nature, the non-polar part of the molecule should
(1) consist of a hydrocarbon with more branching
(2) consist of a hydrocarbon with more number of branches and unsaturation
(3) have straight- or open-chain hydrocarbons
(4) be replaced by aromatic rings substituted by alkyl groups

17. The secondary suffix, "– one" indicates the following functional group in the given compounds.
(1) — COOH (2) 
(3)  (4) — OH

18. In case of oligosaccharides, the monosaccharide units are joined by
(1) glycoside bonds (2) peptide bond
(3) dative bonds (4) covalent bonds

19. When an amino acid solution which is slightly alkaline is subjected to electrolysis, the resulting component migrates towards
(1) cathode due to zwitter ion formation
(2) anode due to the conversion of zwitter ion to positive ion
(3) migrate to cathode due to the conversion to negative ion
(4) one component towards cathode and the other towards anode due to the zwitter ion formation

20. By treating methyl alcohol with conc. H_2SO_4 at 140°C, which of the following products is formed?
(1) ethene (2) dimethyl ether
(3) methyl ethylether (4) ethyne

21. The salt-like structures of amino acids are called
(1) zwitter ions (2) peptide bonds
(3) essential amino acids (4) proteins

22. Which of the following enzymes is used to convert glucose into ethyl alcohol?
(1) diastase (2) maltase
(3) zymase (4) invertase

23. Which of the following carbohydrates is the sweetest sugar?
(1) glucose (2) fructos
(3) cellulose (4) maltose

24. Give the corresponding functional isomer of the product formed when ethanol is treated with ethanoic acid.
(1) propanoic acid (2) ethyl ethanoate
(3) butanoic acid (4) butanone

25. Which of the following is the anti-viral drug?
(1) chloroquine (2) tetracycline
(3) aureomycin (4) sulphadiazine

26. Tollen's reagent contains
(1) silver nitrate
(2) copper nitrate
(3) copper sulphate
(4) ammonical silver nitrate

27. Sucrose doesn't respond to Tollen's test. But it gives a positive result after boiling with conc. HCl. It is due to the
(1) cleavage of glycosidic linkage
(2) formation of glycosidic linkage
(3) formation of a compound containing carboxylic acid group
(4) isomerization to glucose units

28. In deodorant soaps, the additive added in deodorant is
(1) glycerol
(2) stearic acid
(3) potassium bicarbonate
(4) 3, 4, 5-Tribromosalicylaldehyde

29. Which of the following comes under natural adhesives?
(1) epoxyresins (2) polyamides
(3) glue (4) polyvinyls

30. Which among the following is a chromophore of azo dyes?
(1) (2) –NO
(3) –N≡N (4) $-NO_2$

31. Arrange the reactions given below in a proper sequence for the conversion of ethane to methane.
(1) treatment with sodium hydroxide
(2) treatment with aqueous KOH
(3) treatment with NaOH + CaO
(4) halogenation
(5) reaction with acidified $K_2Cr_2O_7$
(a) 5 1 4 2 3 (b) 4 2 5 1 3
(c) 5 3 2 1 4 (d) 4 5 1 2 3

32. Identify the correct sequence of given steps for the conversion of calcium carbide to methyl alcohol.
(1) reaction with aqueous KOH
(2) hydrolysis
(3) reaction with soda lime
(4) reaction with $HgSO_4/H_2SO_4$
(5) reaction with $HgSO_4$
(6) reaction with PCl_5
(a) 2 4 5 3 6 1 (b) 2 4 3 1 6 5
(c) 2 6 4 5 1 3 (d) 4 2 3 5 6 1

33. Arrange the following carbohydrates in the order of number of monosaccharide units formed on hydrolysis.
(1) raffinose (2) fructose
(3) maltose (4) stachyose
(a) 3 2 1 3 (b) 2 3 1 4
(c) 4 1 3 2 (d) 2 1 3 4

34. The IUPAC name of CH_3COOH is
(1) acetic acid (2) formic acid
(3) methanoic acid (4) ethanoic acid

35. Oxidation of ethene with cold alkaline $KMnO_4$ produces
(1) formaldehyde (2) glyoxal
(3) ethene glycol (4) oxalic acid

36. Which of the following compounds on reduction with $NaBH_4$ gives 2-Propanol?
(1) rthyl alcohol (2) acetaldehyde
(3) propanaldehyde (4) acetone

37. Which among the following reactions does not give methyl alcohol?
(1) The reaction of ethylene with H_2SO_4 at 80°C
(2) The reaction of water gas with hydrogen at high temperature
(3) Alkaline hydrolysis of methyl bromide
(4) Both (1) and (2)

38. Which of the following enzymes is required for the conversion of starch to maltose?
(1) diastase (2) maltase
(3) invertase (4) zymase

39. The chemical name of vitamin D is
(1) retinol (2) ferridoxin
(3) calciferol (4) ergosterol

40. In case of natural rubber, the monomeric units are
(1) isoprene (2) propene
(3) 1, 3-butadiene (4) vinyl chloride

41. In deodorant soaps, the additive added is
(1) glycerol
(2) stearic acid
(3) potassium bicarbonate
(4) 3, 4, 5-Tribromo salicylaldehyde

42. Which of the following characteristics is not related to the amphoteric nature of amino acids?
(1) zwitter ion formation
(2) maintenance of pH of body fluids
(3) response of amino acids to electric field
(4) formation of peptide linkage

43. Arrange the following in a proper sequence for the extraction of petroleum.
(1) Processing of crude oil to remove heavy oil.
(2) Heating of the crude oil containing pure mixture of hydrocarbons over a specific range of temperature.
(3) Separation of constituents by fractional distillation.
(4) Purification of crude oil containing salt water.
(5) Drilling of the oil through the various layers under the earth's surface.
(1) 5 2 1 4 3 (2) 5 3 1 2 4
(3) 5 1 4 2 3 (4) 5 1 2 3 4

44. Four oils A, B, C and D have the following values of melting points:
(a) 258 K (b) 273 K
(c) 295 (d) 303 K
Among these, which oil is prohibited from consumption by cardiac patients?
(1) a (2) b
(3) c (4) d

PRACTICE QUESTIONS

45. Which of the following statements is wrong regarding amino acids?

(1) The living systems in plants can synthesize essential amino acids.

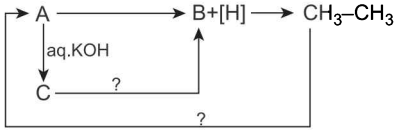
(2) The living systems in animals can synthesize only essential amino acids.

(3) The living systems in animals can synthesize only nonessential amino acids.

(4) The living systems in plants can synthesize nonessential amino acids.

Level 2

1.



Fill up the blanks in the above figure and identify the compounds A, B and C. Also mention the type of reactions involved.

2. Write the possible isomers for the following molecular formulae:

(a) C_4H_8O (b) $C_3H_6O_2$

(c) $C_5H_{12}O$

3. How are the following conversions affected?

(a) ethanol to methanoic acid

(b) ethene to oxalic acid

4. How do you bring about the following conversions?

(a) ethene from ethanol

(b) ethyne to acetic acid

(c) acetylene to oxalic acid

5. A compound "X" has the molecular formula C_4H_8O. Both "X" and its functional isomer "Y" are treated with a solution of $AgNO_3$ dissolved in NH_4OH separately. What observations do you find in both the cases? Justify with equations.

6. Compound "A" on treatment with copper at 300°C gives "B" and a gas "C." It is possible to get back "A" from B and C. In presence of "D," both B and A on treatment with certain reagent gives same compound "E," which on treatment with "A," gives compound F with a fruity smell. Identify the compounds and isomer of "F."

7. What is the working principle of a dye? Why does a dye generally fade?

8. Predict the products formed by the oxidation of glucose with bromine water and concentrated nitric acid respectively.

9. Ethyl alcohol obtained by the fermentation of molasses can be purified by fractional distillation to give 95% ethyl alcohol. Further purification is possible by adding a salt such as potassium acetate to ethyl alcohol and then subjecting to fractional distillation.

10. How can vulcanization improve the quality of rubber?

11. Explain the application of mordant dyes to the fabric.

12. Both sucrose and maltose contain glucose units. But sucrose is a non-reducing sugar and maltose is a reducing sugar. How do you account for this?

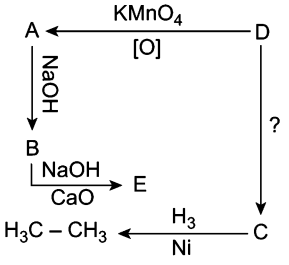
13. Generally, colours of clothes fade away on repeated washing or on exposure to intense sunlight gradually. Explain with a reason.

14. Supplementation with "B" vitamin is more widely recommended than supplementation with any other vitamin. Justify.

15. Among all disaccharides, possessing one or two glucose units, sucrose is the only non-reducing sugar. How do you account for this?

***Directions for questions from 16 to 25*: Application-Based Questions**

16. Complete the blanks by identifying A, B, C, D and E and also specify the reagents for the given reaction.



PRACTICE QUESTIONS

17. (a) Methanol and ethane have almost the same molecular mass. But boiling point of methanol is 65°C while that of ethane is –89°C. Justify.

(b) Acetic acid boils at higher temperature than propyl alcohol though both of them have same molecular mass. Give a reason.

18. How do you bring about the following conversions?

(a) ethyl alcohol to trichloroacetic acid

(b) ethene from ethanol

(c) ethyne to acetic acid

(d) acetylene to oxalic acid

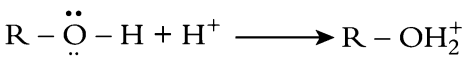
19. Alcohol can act as an acid as well as a base. Justify the statement.

20. Two students were performing some experiments in an organic chemistry laboratory. An unknown compound A which was found to be a hydrocarbon was subjected to the following reactions. A on reaction with chlorine in the presence of light gave compound B which was divided into two parts. To the 1st part aqueous KOH was added and to the second part alcoholic KOH was added. Products C and D were formed, respectively. C was subjected to oxidation to give another compound. The compound formed was same as the compound formed by the ozonolysis product of position isomer of 1-Butene. Identify A, B, C and D.

21. In a revision class in IITF, a chemistry faculty member conducted a quiz in organic chemistry. According to the rules of the quiz, each team has to prepare some questions and ask the other team. Team A asked the following question to team B. "A hydrocarbon has two sp^3 hybrid carbons and two sp^3 hybrid carbons. The compound when subjected to controlled hydrogenation in the presence of catalyst nickel gives another hydrocarbon which decolourises bromine water forming a compound from which both the above hydrocarbons can be regenerated. But the parent hydrocarbon did not give a reddish brown precipitate when passed through ammonical cuprous chloride solution. Identify the hydrocarbon. What would be your answer for the above question and give proper justification for your answer.

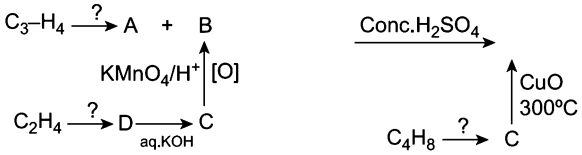
22. A hydrocarbon on ozonolysis gives one mole each of compounds A and B. Both A and B on reduction with sodium borohydride gives compounds C and D belonging to same homologous series. C has no position isomer, whereas D has a position isomer. A and B do not belong to the same homologous series. However, both A and B on oxidation with acidified $KMnO_4$ give the same compound. Identify the hydrocarbon compounds A, B, C and D and write the series of reactions.

23.



Identify X, Y, Z, P and Q. Give the significance of above series of reactions. Also predict whether the position isomer of "X" would give a yellow precipitate or not.

24. Identify A, B, C and D in the following conversions given and write their structural formulae.



25. Paul is a student of IITF. One day, his younger brother who is one year old fell sick. Paul accompanied him to the hospital along with his mother. The doctor gave a medicine which was in the form of a powder and said that water should be added to that powder to prepare a syrup. He said that it has to be consumed within a 5-day period and any leftover syrup should be discarded as it becomes unfit for consumption. On the other hand, when Paul was suffering from high fever, the doctor administered injections. Can you give justification for both the above treatments?

Level 1

1. Explain how proteins help to maintain pH of the body.

2. The amount of ethyl alcohol in blood of a person can be analysed by using a breathalyzer which contains acidified $K_2Cr_2O_7$. Explain the principle involved.

3. What is meant by a copolymer? Why are copolymers preferred to other polymers for various purposes?

4. Three samples of amino acids A, B and C are taken in neutral, acidic and basic mediums, respectively.

PRACTICE QUESTIONS

Comment on the behaviour of these samples when subjected to an electric field and explain how amino acids in the form of proteins help in maintaining the pH of body fluids.

5. Ketones do not respond to Tollen's test or Fehling's test. However, fructose which contains keto group responds to Tollen's test or Fehling's test. How do you account for this?

***Directions for questions from 6 to 10*: Application-Based Questions**

6. Two persons X and Y were caught by policemen at midnight. They had one equipment consisting of a bulb containing acidified $K_2Cr_2O_7$. By using this equipment policemen could identify that "X" has consumed alcohol and "Y" has not. Explain the principle involved and name the instrument used for the above purpose.

7. Though fats and oils have higher calorific values, carbohydrates are consumed in major proportions as the main sources of food. Justify.

8. Why does starch form a thick paste when it is boiled with water?

9. How is glucose tested in human blood?

10. "Boiling is a preferred process to frying as far as preservation of nutritive values is concerned." Comment on this statement.

CONCEPT APPLICATION

Level 1

True or false

1. False
2. False
3. False
4. True
5. True
6. False
7. False

Fill in the blanks

8. secondary suffix
9. $CH_3–O–CH_2–CH_2–CH_3$
10. Glycerol
11. metamers $(H_3C-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3)$
12. auxochrome
13. Propane cyanohydrin
14. Soap

Match the following

15. A : e B : f C : d D : g
    E : b F : c G : a

Multiple choice questions

16. c	17. c	18. a	19. b	20. b
21. a	22. c	23. b	24. c	25. c
26. d	27. a	28. d	29. c	30. c

31. (i) Halogenation
    (ii) Treatment with aqueous KOH
    (iii) Reaction with acidified $K_2Cr_2O_7$
    (iv) Treatment with sodium hydroxide
    (v) Treatment with NaOH + CaO

32. (i) Hydrolysis
    (ii) Reaction with $HgSO_4/H_2SO_4$
    (iii) Reaction with $HgSO_4$
    (iv) Reaction with soda lime
    (v) Reaction with PCl_5
    (vi) Reaction with aqueous KOH

33. (i) Fructose
    (ii) Maltose
    (iii) Raffinose
    (iv) Stachyose

34. CH_3COOH is the given IUPAC name of ethanoic acid.

35. Ethene on oxidation with cold alkaline $KMnO_4$ gives ethene glycol.

36. Acetone on reduction with $NaBH_4$ gives 2-Propanol.

37. Ethylene on treatment with Conc. H_2SO_4 at 80°C gives ethyl hydrogen sulphate.

38. Diastase enzyme is required for the conversion of starch to maltose.

39. Calciferol is the chemical name of vitamin D.

40. Monomer units in natural rubber are isoprene units.

41. 3, 4, 5-Tribromo salicylaldehyde is the additive added to deodorant soaps.

42. Formation of peptide linkage has no relevance to the amphoteric nature of amino acids. All other properties are due to the amphoteric nature of amino acids.

43. (i) Drilling of the oil through the various layers under the earth's surface.

(ii) Processing of crude oil to remove heavy oil
(iii) Purification of crude oil containing salt water
(iv) Heating of the crude oil containing pure mixture of hydrocarbons over a specific range of temperature
(v) Separation of constituents by fractional distillation

44. The oils having higher unsaturation in the fatty acid component have very low melting points. Hence, on the consumption of these oils there is less chance of blockage of blood vessels. The saturated oils have higher melting points and they get solidified easily. Therefore they block the blood vessels and so are prohibited from consumption by cardiac patients. Hence oil D is prohibited from consumption by cardiac patients.

45. Plants can synthesize all amino acids. The living systems in animals can synthesize only nonessential amino acids.

Level 2

1. (i) Type of reaction possible with alcoholic KOH and aqueous KOH
(ii) Identification of "B" based on the product of its hydrogenation
(iii) Identification of the type of reactions possible with alcoholic KOH and aqueous KOH
(iv) Identification of "A" and "C" based on "B."
(v) Identification of the reagent required to convert the given alkane to "A."

2. General formulae and the structural formulae.

3. (a) Identification of the functional group which can be oxidized to –COOH group
(b) Identification of reagent that can oxidize double bond
(c) (i) Identification of immediate corresponding organic compound and reagent from which methanoic acid can be obtained
(ii) Identification of reactant and suitable reagent from which above compound is obtained
(iii) Identification of suitable reagent and conditions for formation of compound from ethanol
(d) (i) Identification of corresponding immediate functional group which can give –COOH group and also the reagent required
(ii) Identification of reaction which can give the compound with the above functional group
(iii) Identification of series of steps involved in the formations of above compound (ii) from ethane

4. (a) Structures and their characteristic chemical reactions
(b) (i) Conversion of ethanol to corresponding alcohol
(ii) Conversion of alcohol to corresponding unsaturated hydrocarbon
(c) (i) Conversion of ethyne to corresponding aldehyde
(ii) Conversion of aldehyde to corresponding acid
(d) (i) Conversion of ethyne to corresponding diol
(ii) Conversion of diol to oxalic acid

5. (i) Identification of the functional group having one oxygen atom in it
(ii) Identification of isomer of organic compound namely X and Y from given molecular formula
(iii) Prediction of functional groups in X and Y on the basis of isomerism
(iv) Nature of the reagent given
(v) Requisite of an organic compound to respond to the reagent given
(vi) Comparison of type of products formed

6. (i) Nature/property of the reagent namely copper at 300°C
(ii) Property exploited by the specific reagent used namely Cu at 300°C
(iii) Prediction of functional groups of A and B from the nature of reagent used
(iv) Identification of "D" based on "B" and "A."
(v) Identification of functional groups of "E" from B and A based on the usage of common specific reagents
(vi) Identification of F from the reaction between E and B
(vii) Prediction of functional isomer of "F" based on nature of functional group and its molecular formula

7. (i) Composition of the dye
(ii) Group responsible for electronic transition

(iii) Type and nature of the dye used for fabric
(iv) Comparison of structure of the dye and detergent
(v) Comparison of affinity of dye to the fabric and detergent

8. (i) Strength of given oxidizing agents
(ii) Conversion of carbonyl group to corresponding acid (by suitable oxidizing agent)
(iii) Conversion of both carbonyl group and hydroxyl group to corresponding acid (by suitable oxidizing agent)

9. (i) Significance of 95% ethyl alcohol wrt fractional distillation
(ii) Nature of ethyl alcohol obtained by fermentation of molasses
(iii) Purpose of fractional distillation
(iv) Physical property of ethyl alcohol exploited for the purpose
(v) Change in physical property when 95% ethyl alcohol is obtained
(vi) Effect of the above change on the state of ethyl alcohol when the process to continued
(vii) Effect of addition of potassium acetate on the above physical property
(viii) Relation between the effect and the process carried out

10. (i) Process of vulcanization
(ii) Type of bonding between the added element and major constituent of rubber
(iii) Effect of these bonds on physical properties of rubber

11. (i) The role of mordants in fixing dye to the fabric
(ii) Working principle of a dye
(iii) Composition of mordants
(iv) The type of association between dye and fabric
(v) Role of mordants in developing the above type of association

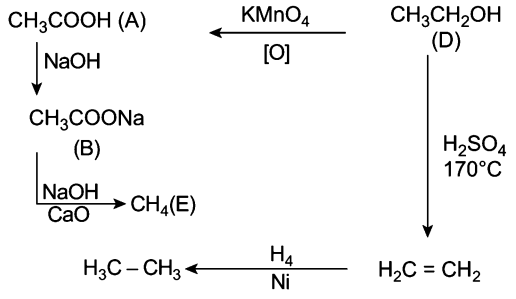
12. (i) Composition and structure of sucrose and maltose
(ii) Functional group responsible for reducing nature
(iii) Type of bonding present in these two sugars
(iv) Effect of oxidizing agents on these molecules

13. (i) The parts of the dye molecule
(ii) Components of a dye molecule
(iii) Requisite for an organic compound to exhibit colour
(iv) Components of dye which impart colour and intensifies colour
(v) Type of attractions between the component of dye molecule and fabric
(vi) Changes that take place in the dye when fabric is washed successively
(vii) Effect of solar radiation on the colour of fabric

14. (i) Nature and relative requirement of vitamin "B."
(ii) Comparison of solubilities of vitamin B with other vitamins.
(iii) Comparison of functions of vitamin B with other vitamins

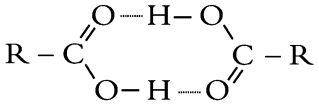
15. (i) Requisite for reducing sugar
(ii) Composition of monosaccharide units present in sucrose
(iii) Type of glycosidic linkage in sucrose
(iv) Requisite of a disaccharide to be a reducing sugar
(v) Comparison of different groups present in other disaccharides
(vi) Comparison of position of glycoside linkage in sucrose and other disaccharides

16.



17. (a) In methanol, intermolecular forces of attraction are more due to the presence of H-bonding, whereas ethane does not have H-bonding. Therefore the boiling point of ethanol is much higher than that of ethane though the molecular weights are almost same.
(b) A carboxylic acid contains –COOH group. Since there are two highly electronegative oxygen's attached to the carbon, they can form two

hydrogen bonds with the –COOH group of adjacent molecule.



Due to the presence of high intensity of hydrogen bonding between carboxylic acids they boil relatively at high temperatures when compared to alcohols with almost same molecular weight. In between acetic acid molecules two hydrogen bonds are present while between two propyl alcohol molecules only one hydrogen bond is present. Hence more energy is required to break two hydrogen bonds in acetic acid when compared to the same molecular weight containing propyl alcohol.

	B. P.
Acetic acid	118°C
Propyl alcohol	97°C

18. (a) $CH_3 - CH_3 - OH \xrightarrow{\text{alk } KMnO_4} CH_3 - COOH \xrightarrow{Cl_2,\ P} CCl_3 - COOH$

(b) Ethene from ethanol

$$CH_3CHO \xrightarrow[[H]]{NaBH_4} CH_3CH_2OH \xrightarrow[170°C]{\text{Conc. } H_2SO_4} H_2C = CH_2 + H_2O$$

(c) $HC \equiv CH + 2H_2O \xrightarrow{Pd} H_3C - CH_3$

$$H_3C - CH_3 + Cl_2 \xrightarrow{\text{Sunlight}} H_3C - CH_2 - Cl + HCl.$$

$$H_3C - CH_2 - Cl + KOH_{(aq)} \rightarrow CH_3 - CH_2 - OH \xrightarrow[KMnO_4]{Alk.} CH_3COOH.$$

(d) $HC \equiv CH + O_3 \xrightarrow[Zndust]{} CHO \xrightarrow[KMnO_4]{\text{alkaline}} COOH$

CHO, COOH

Oxalic acid

19. The polarity of the O–H bond facilitates the removal of positively charged hydrogen thereby forming alkoxide ion. Thus, alcohol acts as an acid in presence of a base.

$$R - O - H \longrightarrow \underset{\text{alkoxide}}{RO^-} + H^+$$

Due to the presence of a lone pair of electrons on oxygen atom, the alcohol molecule can accept a proton (H+ ion) and form protonated alcohol. Thus, alcohol can act as a base in presence of an acid.

$$R - \ddot{\underset{\cdot\cdot}{O}} - H + H^+ \longrightarrow R - OH_2^+$$

20. $H_2C = CH - CH - CH_3$

1 – butene

$$H_3C - HC = CH_3 + O_3 \xrightarrow[Zn]{H_2O} 2CH_3 - CHO$$

2 – butene

$$CH_3CH_2OH + [O] \xrightarrow{CuO} CH_3CHO$$

C

$$CH_3 - CH_2 - Cl \xrightarrow[aq.KOH]{\text{alc. KOH}} \underset{D}{H_2C = CH_3} \quad \underset{C}{CH_3CH_2OH}$$

B

$$H_3C - CH_3 + Cl_2 \xrightarrow{hv} CH_3CH_2Cl$$

B

21. $H_3C - C = C - CH_3 + [H] \xrightarrow[Ni]{} H_3C - CH = CH - CH_3$

$$\overset{sp^3}{H_3C} - \overset{sp}{CH} = \overset{sp}{CH} - \overset{sp^3}{CH_3} + Br_2 \longrightarrow H_3C - \underset{Br}{CH} - \underset{Br}{CH} - CH_3$$

$H_3C - C = C - CH_3 + 2KBr + 2H_3O$; $H_3C - \overset{H}{C} = \overset{H}{C} - CH_3 + ZnBr_3$

22. A and B should be carbonyl compounds since they are ozonolysis products. One should be aldehyde and the other one should be ketone.

$$H_3C - \underset{CH_3}{CH} = C - CH_3 + O_3 \xrightarrow[Zn]{H_2O} \underset{A}{CH_3CHO} + \underset{B}{CH_3COCH_3}$$

A: $\xrightarrow{NaBH_4/[H]} CH_3CH_2OH$ Ethanol C

B: $\xrightarrow{NaBH_4/[H]} CH_3 - \underset{OH}{CH} - CH_3$ 2–propanol D

Position isomer of D $\longrightarrow$ $CH_3CH_2CH_2OH$

1 propanol

CH_3COH Ethanal, CH_3COCH_3 Propanone $\xrightarrow{KMnO_4/H^+}$ CH_3CoOH Ethanoic acid

23.

$$\underset{H}{\overset{Cl}{R - C - CH_3}} \xrightarrow{aq.NaOH} \underset{H}{\overset{OH}{R - C - CH_3}} \xrightarrow{NaOI} R - \overset{O}{\overset{\|}{C}} - CH_3$$

(X)

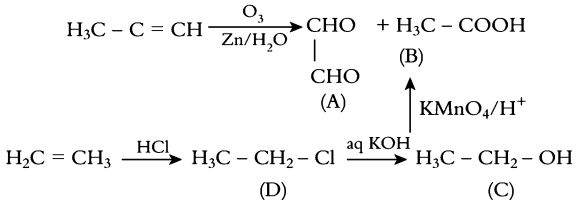
$$R - CH_2 - CH_3 \xrightarrow[Cl_2]{hv} \text{(Q)}$$

(Y) $\xrightarrow{I_2/NaOH}$ $R - \overset{O}{\overset{\|}{C}} - ONa + CHI_3$ (Z) Yellow precipitate

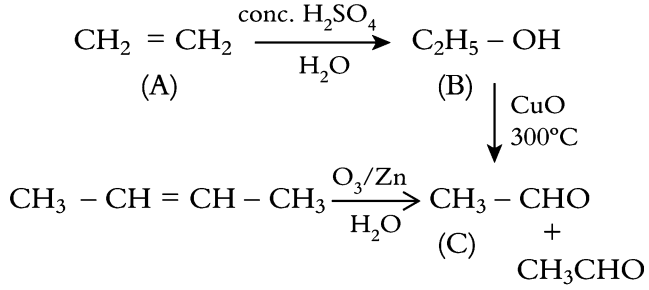
The above reaction helps to identify the particular set of organic compounds with $R-\underset{\underset{H}{|}}{\overset{\overset{X}{|}}{C}}-CH_3$ structure.

(where X = halogen or –OH or $-\overset{\overset{O}{||}}{C}-$) group and thus it helps to identify methyl ketones, 2° and 3° alcohols, alkylhalides, etc., Among 1° alcohols and 1° alkyl halides, only ethyl alcohol and ethyl chloride will respond but not others. This is halo form or iodoform test. The position isomer of 1-Propanol doesn't give a yellow precipitate.

24. (a)



(b)



25. There are some solid forms of medicines which are insoluble in water. At the same time, they cannot be given with organic solvents. Though they cannot form a true solution, they can give suspensions when dissolved in water. Suspensions are the solutions where the particle size is much larger. But suspensions being very less stable cannot be prepared and stored. Hence, the powders have to be made into suspensions with water and then administered. They should be consumed within the stipulated time. Usually, the paediatric medicines are given in such formulations since infants cannot consume tablets. Medicines can be given in different formulations like tablets, capsules, syrups and injections. Tablets, capsules and syrups are taken orally. They contain the drug and drug carrier so that the drug will be released only at the site of action. Before the drug reaches the site of action and gets released there, it has to pass through the system. After it is released, it has to be assimilated into the blood. Hence, the entire process requires some time before it starts its action on the particular organ system. But injections are directly given into the veins where the drug is absorbed by the blood. Being in liquid form, they start action much earlier than the solid form. Therefore, medicines in the form of injections are faster in action than the other formulations.

Level 3

1. (i) Dipolar nature of amino acids of proteins
(ii) Functional groups present in proteins
(iii) Effect of these functional groups on the pH

2. (i) Exhaled air composition of an alcoholic or drunken person
(ii) Composition of exhaled air of alcoholic person
(iii) Nature of substance present in breathalyser
(iv) Changes that take place in breathalyser when the above substance reacts with the component of exhaled air of an alcoholic person
(v) Identification of colours of the reagent and one of the by-products
(vi) Relation between change in colour observed and the nature of product formed

3. (i) Chemical units present in copolymers and other polymers
(ii) Comparison of physical properties of copolymer and other polymers
(iii) Effect of structural units of different polymers on degradation of polymers

4. (i) The functional groups present in amino acid
(ii) Composition and structural formula of amino acid

(iii) Nature of amino acid that exists under neutral conditions

(iv) The constituents of acid and base

(v) Change in structure and nature of amino acids in acidic and basic solutions, respectively

(vi) Effect of change in structure of amino acid on migration to different electrodes respectively

(vii) Relation between the change in structure of amino acid and the change in nature of body fluid

(viii) Effect of the above change on pH

(ix) Significance of maintaining pH of body fluids

5. (i) The requisite for Tollen's test or Fehling's test

(ii) Nature of functional group which responds to the given tests

(iii) Composition, structural formula and functional group of fructose

(iv) Requisite of a monosaccharide to respond to Tollen's or Fehling's test

(v) Changes that take place in fructose upon hydrolysis

(vi) Effect of above change on reactivity of fructose towards Tollen's or Fehling's reagent

6. The instrument used for the detection of alcohol vapours is called breathalyzer. Since it contains acidified $K_2Cr_2O_7$, on exposure of alcohol vapours to this, it oxidizes alcohol to acid. In that process, $K_2Cr_2O_7$ gets reduced to $Cr_2(SO_4)_3$ which is green in colour. This indicates the presence of alcohol in the exhaled air of the person "X." No colour change is observed in case of exhaled air of "Y" indicating that "Y" has not consumed alcohol.

7. Fats and oils are not metabolized and do not serve the purpose of immediate requirement of energy. They are stored for utilization in times of need. Carbohydrates get hydrolysed to give glucose producing energy for immediate requirement.

8. Starch is composed of two units namely amylose unit and amylopectin unit. Amylose is water soluble and amylopectin is water insoluble. On heating with water, amylose dissolves and amylopectin remains as such. Therefore, starch becomes partially soluble and forms paste.

9. Glucose is formed by the degradation of food in the human body. This glucose so formed enters blood and a certain level of glucose is always maintained in blood. If the concentration of glucose in the blood exceeds a certain limit, it leads to "diabetes." For the diagnosis of diabetes, the amount of glucose in blood has to be estimated. Glucose contains an aldehyde group. It gives all the reactions given by the normal aldehydes. The test is based on the principle that aldehydes reduce cupric ions to cuprous ions. Benedict's reagent is the solution of copper sulphate in an aqueous solution of a mixture of citric acid and sodium carbonate. A red precipitate of cuprous oxide is formed which shows the presence of glucose. The amount of ferrous oxide formed gives an estimation of the amount of glucose in blood.

10. Cooking involves loss of water soluble vitamins, whereas frying involves loss of both water soluble and fat soluble vitamins.

6e

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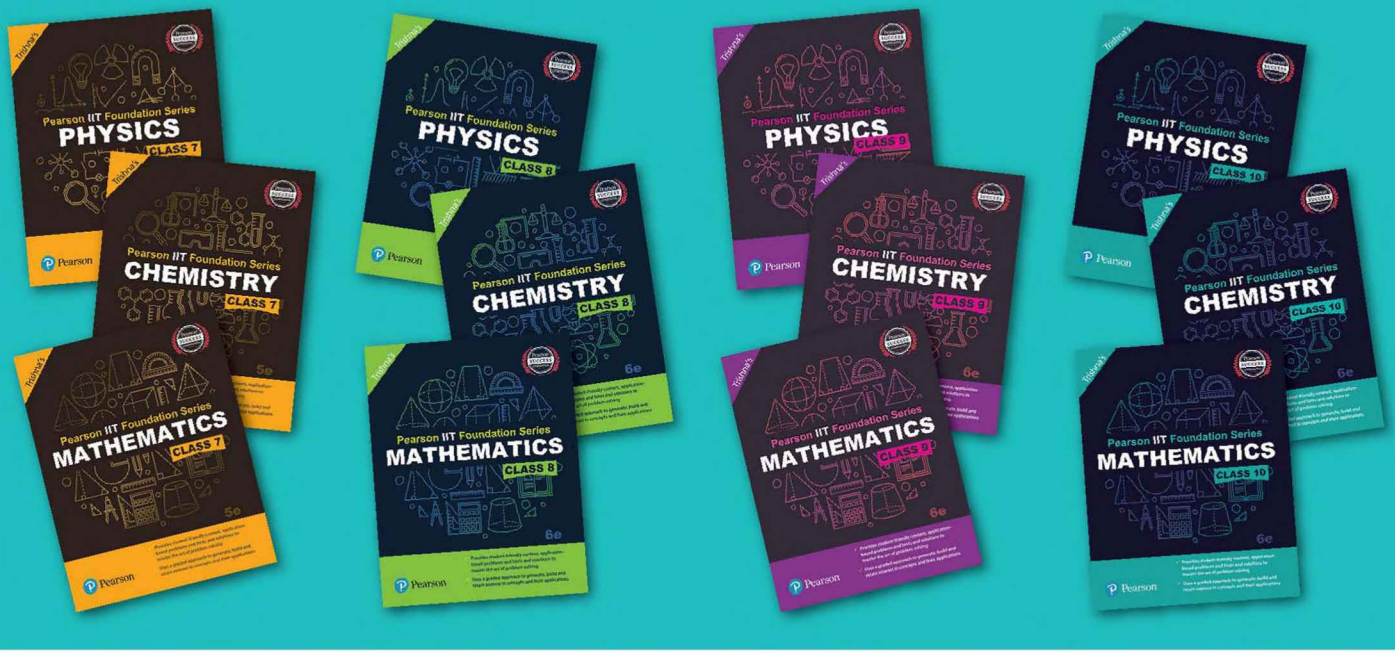

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