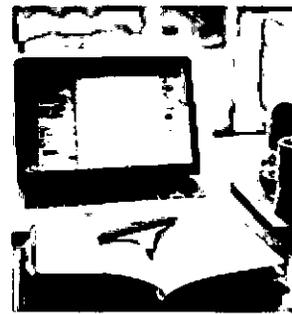




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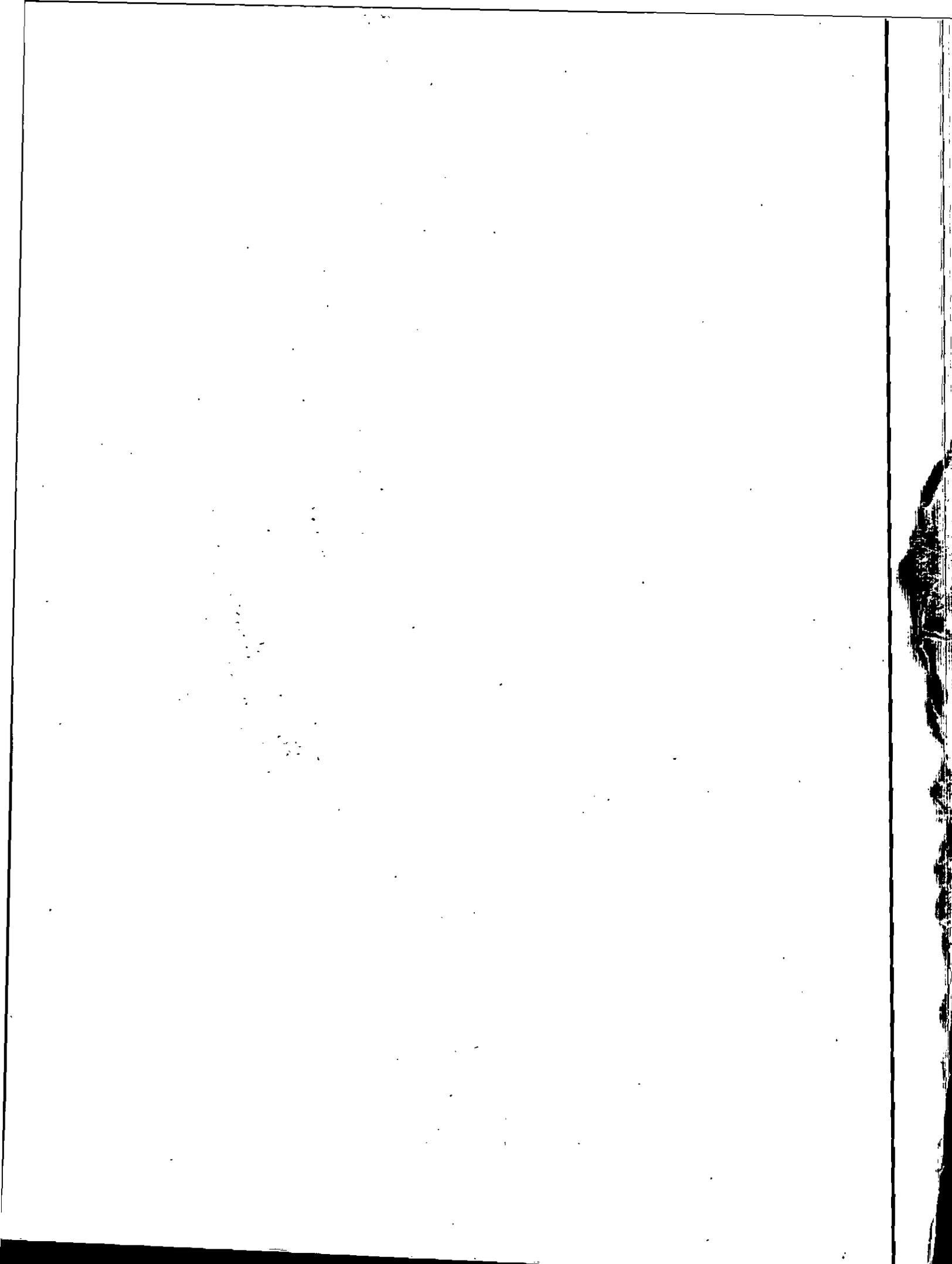
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The Pathways To Higher Studies

Chemistry

Class-XII



CHEMISTRY

CLASS 12

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1

**ATOMS, MOLECULES AND
CHEMICAL ARITHMETIC**

- Understand the concept of Atoms.
- Understand the concept of Chemical Arithmetic.
- Discuss the scope of Molecules.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of atoms and molecules so that the fundamentals of atoms and molecules can be learned.

Introduction

Chemistry - the Centre of Life 'Unna unavu, udukka udai, irukka idam' - in Tamil classical language means food to eat, cloth to wear and place to live. These are the three basic needs of human life. Chemistry plays a major role in providing these needs and also helps us to improve the quality of life. Chemistry has produced many compounds such as fertilizers, insecticides etc. that could enhance the agricultural production. We build better and stronger buildings that sustain different weather conditions with modern cements, concrete mixtures and better-quality steel. We also have better quality fabrics.

Chemistry is everywhere in the world around us. Even our body is made up of chemicals. Continuous bio-chemical reactions occurring in our body are responsible for human activities. Chemistry touches almost every aspect of our lives, culture and environment. The world in which we are living is constantly changing, and the science of chemistry continues to expand and evolve to meet the challenges of our modern world. Chemical industries manufacture a broad range of new and useful materials that are used in everyday life.

Examples : polymers, dyes, alloys, lifesaving drugs etc.

When HIV/AIDS epidemic began in early 1980s, patients rarely lived longer than a few years. But now many effective medicines are available to fight the infection, and people with HIV infection have longer and better life.

The understanding of chemical principles enabled us to replace the non-eco-friendly compounds such as CFCs in refrigerators with appropriate equivalents and increasing number of green processes. There are many researchers working in different fields of chemistry to develop new drugs, environment friendly materials, synthetic polymers etc. for the betterment of the society.

As chemistry plays an important role in our day-to-day life, it becomes essential to understand the basic principles of chemistry in order to address the mounting challenges in our developing country.



Notes

What is an Atom?

Atoms are defined as “the basic building blocks of matter”.

It is the smallest constituent unit of matter that possess the properties of the chemical element. Atoms don't exist independently, instead, they form ions and molecules which further combine in large numbers to form matter that we see, feel and touch.

Atoms are much too small to be seen; hence experiments to find out their structure and behaviour have to be conducted with large numbers of them. From the results of these experiments, we may attempt to construct a hypothetical model of an atom that behaves like the true atom.

Molecules consist of one or more atoms bound together by covalent (chemical) bonds. Atoms may be depicted by circle shapes, each of which has a nucleus at the centre (containing protons and neutrons), surrounded by one or more concentric circles representing the ‘shells’ or ‘levels’ in which the electrons surrounding the nucleus of the atom are located and markings indicating the electron. at each level. A molecule is the smallest thing a substance can be divided into while remaining the same substance. It is made up of two or more atoms that are bound together by chemical bonding.

Atoms and Molecules

Atom Definition

The smallest particle of an element, which may or may not have an independent existence but always takes place in a chemical reaction is called an atom. An atom is defined as the smallest unit that retains the properties of an element. An atom is composed of atoms and these cannot be made or destroyed. All atoms of the same element are identical and different elements have different types of atoms. Chemical reactions occur when atoms are rearranged.

Atoms consist of three fundamental types of particles, protons, electrons and neutrons. Neutrons and protons have approximately the same mass and in contrast to this the mass of an electron is negligible. A proton carries a positive charge, a neutron has no charge and an electron is negatively charged. An atom contains equal numbers of protons and electrons and therefore overall an atom has no charge. The nucleus of an atom contains protons and neutrons only, and therefore is positively charged. The electrons occupy the region of space around the nucleus. Therefore, most of the mass is concentrated within the nucleus.

The centre of the atom is called the nucleus. The nucleus contains neutrons and protons that give an atom its weight and positive charges. A neutron carries no charge and has a mass of one unit. A proton carries a single positive charge and also has a mass of one unit, the atomic number of an element is equal to the number of protons or positive charges in the nucleus. The atomic weight of an element is determined by combining the total number of protons and neutrons in the nucleus. An electron carries a single negative charge. If an atom of an element is to have zero charge, it must have the same number of electrons as protons. These electrons are arranged in orbits around the nucleus of the atom like the layers of an anion.

What is the Size of an Atom?

The size of an atom is extremely small, much smaller than our imagination. A layer of an atom as thick as a thin sheet of paper is formed when more than millions of atoms are stacked



together. It is impossible to measure the size of an isolated atom because it's difficult to locate the positions of electrons surrounding the nucleus.

However, the size of an atom can be estimated by assuming that the distance between adjacent atoms is equal to half the radius of an atom. Atomic radius is generally measured in nano metres.

$$1 \text{ m} = 10^9 \text{ nm}$$

Relative Sizes

Examples	Radii (m)
Atom of Hydrogen	10^{-10} m
Molecule of water	10^{-9} m
Molecule of haemoglobin	10^{-8} m
Grain of Sand	10^{-4} m

What are Atoms made of?

An atom is composed of three particles, namely, neutrons, protons and electrons with hydrogen as an exception without neutrons.

Every atom has a nucleus that bounds one or more electrons around it.

The nucleus has typically a similar number of protons and neutrons which are together known as nucleons.

The protons are positively charged, electrons are negatively charged and neutrons are neutral.

What is Atomic Mass?

It is the mass of an atom in a chemical element. It is roughly equivalent to total neutrons and protons present in the atom. It is expressed in atomic mass units (denoted by u). 1amu is equal to the exactly one-twelfth the mass of 1 atom of C-12 and the relative atomic masses of elements is determined with respect to-12 atom.

Atomic masses of Some Elements

Elements	Atomic Mass (u)
Hydrogen	1
Carbon	12
Nitrogen	14
Oxygen	16
Sodium	23
Magnesium	24
Sulphur	32
Chlorine	35.5
Calcium	40

Salient features of Dalton's Atomic Theory

- The matter is composed of minute particles known as atoms.



- Atoms are indivisible particles that can't be destroyed or created through chemical reactions.
- All atoms of an element have identical chemical properties and mass whereas, atoms of different elements have different chemical properties and masses.
- Atoms combine in a ratio of small whole numbers to form compounds.

The matter is anything and everything in our surrounding. It has basic structural and fundamental units. Let us examine the concept of matter with an example. Taking a storybook into consideration and dividing its structure. The book contains many pages, each page consists of paragraphs, and each paragraph has many sentences.

Each sentence will further have many words and each word will have characters. Therefore, we have divided a storybook into characters. This is exactly the same case when we take the matter into account. The matter is made up of substances which contain molecules. The molecules, in turn, are made up of groups of atoms.

Atoms in simple terms are defined as the smallest unit of matter. In ancient times the scientists wondered whether the matter could be further divided or not. Around 500 BC the idea of divisibility of matter evolved in India. A scientist named Maharishi Kanad stated that matter can be divided into smaller and smaller units. The smallest unit of matter after which further division was not possible was known as parmanu.

What is a Molecule?

A molecule is defined as the smallest unit of a compound that contains the chemical properties of the compound. Molecules are made up of groups of atoms. Describing the structure of an atom, an atom is also sub-divided into smaller units. Protons, electrons, and neutrons are sub-particles of an atom. The protons and neutrons are contained inside the nucleus of the atom and electrons revolve around the nucleus.

Protons are positively charged particles whereas electrons are negatively charged particles. Neutrons do not carry any charge. So, we can say that the nucleus is positively charged due to the presence of protons. The nucleus is a bulk mass at the centre of an atom. Atoms are largely vacant.

Every element has a certain atomic number. The atomic number of an element is defined as the number of protons present in its nucleus. It is denoted by Z .

When we talk about the mass of atoms, the mass of its particles is taken into consideration. Electrons have negligible mass. Hence the mass of an atom is the sum of the mass of protons and neutrons. The mass number is denoted by A .

A molecule is the smallest unit (particle) of a compound having the physical and chemical properties of that compound. This does not mean that molecules cannot be broken down into smaller parts, e.g., the atoms from which they are formed or the fragments of the molecule, each consisting of several atoms or parts of atoms.

A molecule is defined as the smallest unit of a compound that contains the chemical properties of the compound. Molecules are made up of groups of atoms. Describing the structure of an atom, an atom is also sub-divided into smaller units. Proton, electrons, and neutrons are sub-particles of an atom. The protons and neutrons are contained inside the nucleus of the atom and electrons revolve around the nucleus.

Protons are known to be positively charged subatomic particles. On the other hand, electrons are subatomic particles that are negatively charged. Neutrons are subatomic



particles that do not carry any charge. Therefore, it can be understood that the nucleus is positively charged due to the presence of protons. The nucleus is a bulk mass at the centre of an atom. Atoms are known to be mostly vacant. Every element has a certain atomic number. The atomic number of an element is defined as the number of protons present in its nucleus. It is denoted by the symbol 'Z'.

When we talk about the mass of atoms, the mass of its particles is taken into consideration. Electrons have negligible mass. Hence the mass of an atom is the sum of the mass of protons and neutrons. The mass number is denoted by A.

Forces between Atoms and Molecules

The simplest forces between atoms are those which arise as a result of electron transfer. A simple example is that of say sodium fluoride. The sodium atom has a nuclear charge of +11, with 2 electrons in the K shell, 8 in the L shell and 1 in the M shell. The fluorine atom has a nuclear charge of 9 with 2 electrons in the K shell and 7 in the L shell.

The outermost electron in the sodium atom may transfer readily to the fluorine atom; both atoms then have a complete shell but the sodium now has a net charge of +1 and the fluorine a net charge of -1. These ions, therefore, attract one another by direct coulombic interaction. The force between them is strong it varies as x^{-2} , where x is the distance between the ions, and it acts in the direction of the line joining the ions.

Furthermore, it is unsaturated – one positive ion can attract several negative ions around it and the force exerted by the positive ion on each negative ion is not affected by the presence of other negative ions. Of course, the negative ions will also repel one another.

Chemical Arithmetic

Element: An element consists of only one type of atom. We know that an atom is the smallest electrically neutral particle, being made up of fundamental particles, namely electrons, protons and neutrons.

Element can exist as monatomic or polyatomic units. The polyatomic elements are called molecules.

Example : Monatomic unit - Gold (Au), Copper (Cu); Polyatomic unit - Hydrogen (H_2), Phosphorous (P_4) and Sulphur (S_8)

Compound: Compounds are made up of molecules which contain two or more atoms of different elements.

Example : Carbon dioxide (CO_2), Glucose ($C_6H_{12}O_6$), Hydrogen Sulphide (H_2S), Sodium Chloride ($NaCl$)

Properties of compounds are different from those of their constituent elements. For example, sodium is a shiny metal, and chlorine is an irritating gas. But the compound formed from these two elements, sodium chloride, shows different characteristics as it is a crystalline solid, vital for biological functions

Atomic Masses

How much does an individual atom weigh? As atoms are too small with diameter of 10–10 m and weigh approximately 10–27 kg, it is not possible to measure their mass directly. Hence it is proposed to have relative scale based on a standard atom.

The C-12 atom is considered as standard by the IUPAC (International Union of Pure and



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Applied Chemistry), and its mass is fixed as 12 amu (or) u. The amu (or) unified atomic mass is defined as one twelfth of the mass of a Carbon-12 atom in its ground state.

i.e., 1 amu (or) 1u $\approx 1.6605 \times 10^{-27}$ kg.

In this scale, the relative atomic mass is defined as the ratio of the average atomic mass factor to the unified atomic mass unit.

Relative atomic mass (A_r)

Relative atomic mass (A_r)

$$= \frac{\text{Average mass of the atom}}{\text{Unified atomic mass}}$$

For example,

Relative atomic mass of hydrogen (A_r)H

$$= \frac{\text{Average mass of H-atom (in kg)}}{1.6605 \times 10^{-27} \text{ kg}}$$

$$= \frac{1.6736 \times 10^{-27} \text{ kg}}{1.6605 \times 10^{-27} \text{ kg}}$$

$$= 1.0078 \approx 1.008 \text{ u.}$$

Since most of the elements consist of isotopes that differ in mass, we use average atomic mass. Average atomic mass is defined as the average of the atomic masses of all atoms in their naturally occurring isotopes. For example, chlorine consists of two naturally occurring isotopes ^{35}Cl and ^{37}Cl in the ratio 77 : 23, the average relative atomic mass of chlorine is

$$= \frac{(35 \times 77) + (37 \times 23)}{100}$$

$$= 35.46 \text{ u}$$

Molecular Mass

Similar to relative atomic mass, relative molecular mass is defined as the ratio of the mass of a molecule to the unified atomic mass unit. The relative molecular mass of any compound can be calculated by adding the relative atomic masses of its constituent atoms.

For example,

i) Relative molecular mass of hydrogen molecule (H_2)

$$= 2 \times (\text{relative atomic mass of hydrogen atom})$$

$$= 2 \times 1.008 \text{ u}$$

$$= 2.016 \text{ u.}$$

ii) Relative molecular mass of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)

$$= (6 \times 12) + (12 \times 1.008) + (6 \times 16)$$

$$= 72 + 12.096 + 96$$

$$= 180.096 \text{ u}$$

Table 1.1 Relative atomic masses of some elements

Table 1.1 Relative atomic masses of some elements

Element	Relative atomic mass	Element	Relative atomic mass
H	1.008	Cl	35.45
C	12	K	39.10
N	14	Ca	40.08
O	16	Cr	51.9
Na	23	Mn	54.94
Mg	24.3	Fe	55.85
S	32.07	Cu	63.55



Notes

Mole Concept

Often, we use special names to express the quantity of individual items for our convenience. For example, a dozen roses means 12 roses and one quire paper means 25 single sheets. We can extend this analogy to understand the concept of mole that is used for quantifying atoms and molecules in chemistry. Mole is the SI unit to represent a specific amount of a substance.

To understand the mole concept, let's calculate the total number of atoms present in 12 g of carbon-12 isotope or molecules in 158.03 g of potassium permanganate and 294.18 g of potassium dichromate.

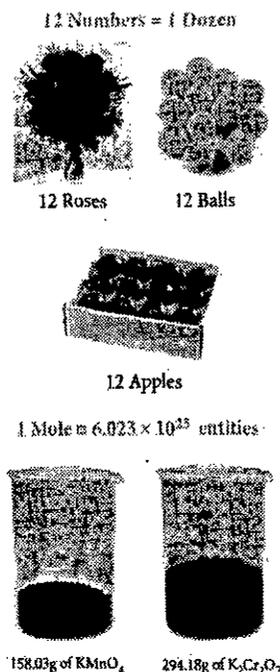


Fig. 1.2 Mole Concept



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Table 1.2 Calculation of number of entities in one mole of substance.

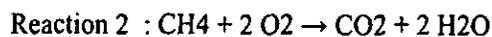
S. No.	Name of substance	Mass of the substance taken (gram)	Mass of single atom or molecule (gram)	No. of atoms or molecules = $\frac{\text{Mass of substance}}{\text{Mass of single atom or molecule}}$
	(1)	(2)	(3)	(2)÷(3)
1.	Elemental Carbon (C-12)	12	1.9926×10^{-23}	$\frac{12}{1.9926 \times 10^{-23}} = 6.022 \times 10^{23}$
2.	Glucose ($C_6H_{12}O_6$)	180	29.89×10^{-23}	$\frac{180}{29.89 \times 10^{-23}} = 6.022 \times 10^{23}$
3.	Potassium dichromate ($K_2Cr_2O_7$)	294.18	48.851×10^{-23}	$\frac{294.18}{48.851 \times 10^{-23}} = 6.022 \times 10^{23}$
4.	Potassium permanganate ($KMnO_4$)	158.03	26.242×10^{-23}	$\frac{158.03}{26.242 \times 10^{-23}} = 6.022 \times 10^{23}$

From the calculations we come to know that 12 g of carbon-12 contains 6.022×10^{23} carbon atoms and same numbers of molecules are present in 158.03 g of potassium permanganate and 294.18 g of potassium dichromate. Similar to the way we use the term 'dozen' to represent 12 entities, we can use the term 'mole' to represent 6.022×10^{23} entities (atoms or molecules or ions)

One mole is the amount of substance of a system, which contains as many elementary particles as there are atoms in 12 g of carbon-12 isotope. The elementary particles can be molecules, atoms, ions, electrons or any other specified particles.

Avogadro Number: The total number of entities present in one mole of any substance is equal to 6.022×10^{23} . This number is called Avogadro number which is named after the Italian physicist Amedeo Avogadro who proposed that equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecules. Avogadro number does not have any unit.

In a chemical reaction, atoms or molecules react in a specific ratio. Let us consider the following examples



In the first reaction, one carbon atom reacts with one oxygen molecule to give one carbon dioxide molecule. In the second reaction, one molecule of methane burns with two molecules of oxygen to give one molecule of carbon dioxide and two molecules of water. It is clear that the ratio of reactants is based on the number of molecules. Even though the ratio is based on the number of molecules it is practically difficult to count the number of molecules. Because of this reason it is beneficial to use 'mole' concept rather than the actual number of molecules to quantify the reactants and the products. We can explain the first reaction as one mole of carbon reacts with one mole of oxygen to give one mole of carbon dioxide and the second reaction as one mole of methane burns with two moles of oxygen to give one mole of carbon dioxide and two moles of water. When only atoms are involved, scientists also use the term one gram atom instead of one mole.



Molar Mass

Molar mass is defined as the mass of one mole of a substance. The molar mass of a compound is equal to the sum of the relative atomic masses of its constituents expressed in g mol^{-1} .

Examples:

- relative atomic mass of one hydrogen atom = 1.008 u
- molar mass of hydrogen atom = 1.008 g mol^{-1}
- relative molecular mass of glucose = 180 u
- molar mass of glucose = 180 g mol^{-1}

Molar Volume:

The volume occupied by one mole of any substance in the gaseous state at a given temperature and pressure is called molar volume.

Conditions	Volume occupied by one mole of any gaseous substances (in litre)
273 K and 1 bar pressure (STP)	22.71
273 K and 1 atm pressure (SATP)	22.4
298 K and 1 atm pressure (Room Temperature & pressure)	24.5

SUMMARY

Chemistry plays a major role in providing these needs and also helps us to improve the quality of life. Chemistry has produced many compounds such as fertilizers, insecticides etc. that could enhance the agricultural production. We build better and stronger buildings that sustain different weather conditions with modern cements, concrete mixtures and better-quality steel. We also have better quality fabrics. Chemistry is everywhere in the world around us. Even our body is made up of chemicals. Continuous bio-chemical reactions occurring in our body are responsible for human activities. Chemistry touches almost every aspect of our lives, culture and environment. An element consists of only one type of atom. We know that an atom is the smallest electrically neutral particle, being made up of fundamental particles, namely electrons, protons and neutrons. Compounds are made up of molecules which contain two or more atoms of different elements. Properties of compounds are different from those of their constituent elements. For example, sodium is a shiny metal, and chlorine is an irritating gas. But the compound formed from these two elements, sodium chloride, shows different characteristics as it is a crystalline solid, vital for biological functions



6. An element X is divalent and another element Y is tetravalent. The compound formed by these two elements will be:

- (a) XY (b) XY₂
(c) X₂Y (d) XY₄

Answer. (b) XY₂

7. The molecular formula of potassium nitrate is _____.

- (a) KNO₃ (b) KNO
(c) KNO₂ (d) KON

Answer. (a) KNO₃

8. 3.42 g of sucrose are dissolved in 18 g of water in a beaker. The numbers of oxygen atoms in the solution are:

- (a) 6.68×10^{23} (b) 6.09×10^{22}
(c) 6.022×10^{23} (d) 6.022×10^{21}

Answer. (a) 6.68×10^{23}

9. Molecular mass is defined as the:

- (a) Mass of one molecule of any substance compared with the mass of one atom of C - 12
(b) Mass of one atom compared with the mass of one atom of hydrogen
(c) Mass of one atom compared with the mass of one molecule
(d) None of the above

Answer. (a) Mass of one molecule of any substance compared with the mass of one atom of C - 12

10. A change in the physical state can be brought about

- (a) only when energy is given to the system
(b) only when energy is taken out from the system
(c) When energy is either given to, or taken out from the system
(d) Without any energy change

Answer. (c) When energy is either given to, or taken out from the system

Review Question

1. Define atoms?
2. Define molecules?
3. What is chemical arithmetic?
4. Explain the properties of atoms?
5. Explain the properties of molecules?
6. Discuss the laws of atoms?
7. How many atoms are present in a piece of iron that has a mass of 65.0 g/ (atomic mass; Fe = 55.9 amu).

CLASS-12

Chemistry



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8. A piece of phosphorus has a mass of 99.2 g. How many moles of phosphorus, P₄ are present in it? (atomic mass, P = 31.0 amu)
9. Mass of 8.46×10^{24} atoms of fluorine is 266.95 g. Calculate the atomic mass of fluorine. 10. A sample of magnesium consists of 1.92×10^{22} Mg atoms. What is the mass of the sample in grams? (atomic mass = 24.3 amu)
11. Calculate the molar mass in g mol⁻¹ for each of the following:
 - (i) Sodium hydroxide, NaOH
 - (ii) Copper Sulphate CuSO₄ .5H₂O.
 - (iii) Sodium Carbonate, Na₂CO₃ .10H₂O
12. For 150-gram sample of phosphorus trichloride (PCl₃), calculate each of the following:
 - (i) Mass of one PCl₃ molecule.
 - (ii) The number of moles of PCl₃ and Cl in the sample.
 - (iii) The number of grams of Cl atoms in the sample.
 - (iv) The number of molecules of PCl₃ in the sample.
13. Find out the mass of carbon-12, that would contain 1×10^{19} atoms.
14. How many atoms are present in 100 g sample of C-12 atom?
15. How many moles of CaCO₃ would weigh 5 g? 10. If you require 1.0×10^{23} molecules of nitrogen for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$.
 - (i) What is the mass (in grams) of N₂ required?
 - (ii) How many moles of NH₃ would be formed in the above reaction from 1.0×10^{23} molecules of N₂?
 - (iii) What volume would NH₃ gas formed in



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2

ATOMIC STRUCTURE

- Understand the concept of Atomic structure.
- Understand the concept of atomic models.
- Discuss the Dalton's Atomic Theory.
- Understand the Thomson Atomic Model.
- Discuss the Rutherford Atomic Theory.
- Discuss the various Subatomic Particles.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of atomic structure so that the models and theories of atomic structure can be learned.

Introduction

Atomic structure refers to the structure of atom comprising a nucleus (centre) in which the protons (positively charged) and neutrons (neutral) are present. The negatively charged particles called electrons revolve around the centre of the nucleus.

The history of atomic structure and quantum mechanics dates back to the times of Democritus, the man who first proposed that matter is composed of atoms.

The study about the structure of atom gives a great insight into the entire class of chemical reactions, bonds and their physical properties. The first scientific theory of atomic structure was proposed by John Dalton in 1800s.

The advances in atomic structure and quantum mechanics have led to the discovery of other fundamental particles. The discovery of subatomic particles has been the base for many other discoveries and inventions.

What is Atomic Structure?

The atomic structure of an element refers to the constitution of its nucleus and the arrangement of the electrons around it. Primarily, the atomic structure of matter is made up of protons, electrons and neutrons.

The protons and neutrons make up the nucleus of the atom, which is surrounded by the electrons belonging to the atom. The atomic number of an element describes the total number of protons in its nucleus.

Neutral atoms have equal numbers of protons and electrons. However, atoms may gain or lose electrons in order to increase their stability and the resulting charged entity is called an ion.



Atoms of different elements have different atomic structures because they contain different numbers of protons and electrons. This is the reason for the unique characteristics of different elements.

Atomic Models

In the 18th and 19th centuries, many scientists attempted to explain the structure of the atom with the help of atomic models. Each of these models had their own merits and demerits and were pivotal to the development of the modern atomic model. The most notable contributions to the field were by the scientists John Dalton, J.J. Thomson, Ernest Rutherford and Niels Bohr. Their ideas on the structure of the atom are discussed in this subsection.

Dalton's Atomic Theory

The English chemist John Dalton suggested that all matter is made up of atoms, which were indivisible and indestructible. He also stated that all the atoms of an element were exactly the same, but the atoms of different elements differ in size and mass.

Chemical reactions, according to Dalton's atomic theory, involve a rearrangement of atoms to form products. According to the postulates proposed by Dalton, the atomic structure comprised atoms, the smallest particle responsible for the chemical reactions to occur.

The following are the postulates of his theory:

- Every matter is made up of atoms.
- Atoms are indivisible.
- Specific elements have only one type of atoms in them.
- Each atom has its own constant mass that varies from element to element.
- Atoms undergo rearrangement during a chemical reaction.
- Atoms can neither be created nor be destroyed but can be transformed from one form to another.

Dalton's atomic theory successfully explained the Laws of chemical reactions, namely, the Law of conservation of mass, Law of constant properties, Law of multiple proportions and Law of reciprocal proportions.

Demerits of Dalton's Atomic Theory

- The theory was unable to explain the existence of isotopes.
- Nothing about the structure of atom was appropriately explained.
- Later, the scientists discovered particles inside the atom that proved, the atoms are divisible.

The discovery of particles inside atoms led to a better understanding of chemical species, these particles inside the atoms are called subatomic particles. The discovery of various subatomic particles is as follows:

Thomson Atomic Model

The English chemist Sir Joseph John Thomson put forth his model describing the atomic structure in the early 1900s.

He was later awarded the Nobel prize for the discovery of "electrons". His work is based on an experiment called cathode ray experiment. The construction of working of the experiment is as follows:



Cathode Ray Experiment

It has a tube made of glass which has two openings, one for the vacuum pump and the other for the inlet through which a gas is pumped in.

The role of the vacuum pump is to maintain "partial vacuum" inside the glass chamber. A high voltage power supply is connected using electrodes i.e., cathode and Anode is fitted inside the glass tube.

Observations:

When a high voltage power supply is switched on, there were rays emerging from the cathode towards the anode. This was confirmed by the 'Fluorescent spots' on the ZnS screen used. These rays were called "Cathode Rays".

When an external electric field is applied, the cathode rays get deflected towards the positive electrode, but in the absence of electric field, they travel in a straight line.

When rotor Blades are placed in the path of the cathode rays, they seem to rotate. This proves that the cathode rays are made up of particles of a certain mass, so that they have some energy.

With all this evidence, Thomson concluded that cathode rays are made of negatively charged particles called "electrons".

On applying the electric and magnetic field upon the cathode rays (electrons), Thomson found the charge to mass ratio (e/m) of electrons. (e/m) for electron: $17588 \times 10^{11} \text{ e/bg}$.

From this ratio, the charge of the electron was found by Mullikan through oil drop experiment. [Charge of $e^- = 1.6 \times 10^{-16} \text{ C}$ and Mass of $e^- = 9.1093 \times 10^{-31} \text{ kg}$].

Conclusions:

Based on conclusions from his cathode ray experiment, Thomson described the atomic structure as a positively charged sphere into which negatively charged electrons were embedded.

It is commonly referred to as the "plum pudding model" because it can be visualized as a plum pudding dish where the pudding describes the positively charged atom and the plum pieces describe the electrons.

Thomson's atomic structure described atoms as electrically neutral, i.e., the positive and the negative charges were of equal magnitude.

Limitations of Thomson's Atomic Structure: Thomson's atomic model does not clearly explain the stability of an atom. Also, further discoveries of other subatomic particles, couldn't be placed inside his atomic model.

Rutherford Atomic Theory

Rutherford, a student of J. J. Thomson modified the atomic structure with the discovery of another subatomic particle called "Nucleus". His atomic model is based on the Alpha ray scattering experiment.



Alpha Ray Scattering Experiment

Construction:

- A very thin gold foil of 1000 atoms thick is taken.
- Alpha rays (doubly charged Helium He^{2+}) were made to bombard the gold foil.
- Zn S screen is placed behind the gold foil.

Observations:

- Most of the rays just went through the gold foil making scintillations (bright spots) in the ZnS screen.
- A few rays got reflected after hitting the gold foil.
- One in 1000 rays got reflected by an angle of 180° (retraced path) after hitting the gold foil.

Conclusions:

- Since most rays passed through, Rutherford concluded that most of the space inside the atom is empty.
- Few rays got reflected because of the repulsion of its positive with some other positive charge inside the atom.
- 1/1000th of rays got strongly deflected because of a very strong positive charge in the centre of the atom. He called this strong positive charge as "nucleus".
- He said most of the charge and mass of the atom resides in the Nucleus

Rutherford's Structure of Atom

Based on the above observations and conclusions, Rutherford proposed his own atomic structure which is as follows.

- The nucleus is at the centre of an atom, where most of the charge and mass are concentrated.
- Atomic structure is spherical.
- Electrons revolve around the nucleus in a circular orbit, similar to the way planets orbit the sun.

Limitations of Rutherford Atomic Model

If electrons have to revolve around the nucleus, they will spend energy and that too against the strong force of attraction from the nucleus, a lot of energy will be spent by the electrons and eventually, they will lose all their energy and will fall into the nucleus so the stability of atom is not explained.

If electrons continuously revolve around the 'nucleus, the type of spectrum expected is a continuous spectrum. But in reality, what we see is a line spectrum.

Subatomic Particles

Protons

- Protons are positively charged subatomic particles. The charge of a proton is $1e$, which corresponds to approximately 1.602×10^{-19}



- The mass of a proton is approximately 1.672×10^{-24}
- Protons are over 1800 times heavier than electrons.
- The total number of protons in the atoms of an element is always equal to the atomic number of the element.

Neutrons

- The mass of a neutron is almost the same as that of a proton i.e., 1.674×10^{-24}
- Neutrons are electrically neutral particles and carry no charge.
- Different isotopes of an element have the same number of protons but vary in the number of neutrons present in their respective nuclei.

Electrons

- The charge of an electron is $-1e$, which approximates to -1.602×10^{-19}
- The mass of an electron is approximately 9.1×10^{-31} .
- Due to the relatively negligible mass of electrons, they are ignored when calculating the mass of an atom.

Atomic Structure of Isotopes

Nucleons are the components of the nucleus of an atom. A nucleon can either be a proton or a neutron. Each element has a unique number of protons in it, which is described by its unique atomic number. However, several atomic structures of an element can exist, which differ in the total number of nucleons.

These variants of elements having a different nucleon number (also known as the mass number) are called isotopes of the element. Therefore, the isotopes of an element have the same number of protons but differ in the number of neutrons.

The atomic structure of an isotope is described with the help of the chemical symbol of the element, the atomic number of the element, and the mass number of the isotope. For example, there exist three known naturally occurring isotopes of hydrogen, namely, protium, deuterium, and tritium. The atomic structures of these hydrogen isotopes are illustrated below.

The isotopes of an element vary in stability. The half-lives of isotopes also differ. However, they generally have similar chemical behaviour owing to the fact that they hold the same electronic structures.

Atomic Structures of Some Elements

The structure of atom of an element can be simply represented via the total number of protons, electrons, and neutrons present in it. The atomic structures of a few elements are illustrated below.

Hydrogen

The most abundant isotope of hydrogen on the planet Earth is protium. The atomic number and the mass number of this isotope are 1 and 1, respectively.

Structure of Hydrogen atom: This implies that it contains one proton, one electron, and no neutrons (total number of neutrons = mass number – atomic number)



Carbon

Carbon has two stable isotopes – ^{12}C and ^{13}C . Of these isotopes, ^{12}C has an abundance of 98.9%. It contains 6 protons, 6 electrons, and 6 neutrons.

Structure of Carbon atom: The electrons are distributed into two shells and the outermost shell (valence shell) has four electrons. The tetravalency of carbon enables it to form a variety of chemical bonds with various elements.

Oxygen

There exist three stable isotopes of oxygen – ^{18}O , ^{17}O , and ^{16}O . However, oxygen-16 is the most abundant isotope.

Structure of Oxygen atom: Since the atomic number of this isotope is 8 and the mass number is 16, it consists of 8 protons and 8 neutrons. 6 out of the 8 electrons in an oxygen atom lie in the valence shell.

Bohr's Atomic Theory

Neils Bohr put forth his model of the atom in the year 1915. This is the most widely used atomic model to describe the atomic structure of an element which is based on Planck's theory of quantization.

Postulates:

- The electrons inside atoms are placed in discrete orbits called "stationery orbits".
- The energy levels of these shells can be represented via quantum numbers.
- Electrons can jump to higher levels by absorbing energy and move to lower energy levels by losing or emitting its energy.
- As long as, an electron stays in its own stationery, there will be no absorption or emission of energy.
- Electrons revolve around the nucleus in these stationery orbits only.
- The energy of the stationary orbits is quantized.

Limitations of Bohr's Atomic Theory:

- Bohr's atomic structure works only for single electron species such as H, He^+ , Li^{2+} , Be^{3+} ,
- When the emission spectrum of hydrogen was observed under a more accurate spectrometer, each line spectrum was seen to be a combination of no of smaller discrete lines.
- Both Stark and Zeeman effects couldn't be explain using Bohr's theory.

Heisenberg's uncertainty principle: Heisenberg stated that no two conjugate physical quantities can be measured simultaneously with 100% accuracy. These will always be some error or uncertainty in the measurement.

Drawback: Position and momentum are two such conjugate quantities which were measured accurately by Bohr (theoretically).

Stark effect: Phenomenon of deflection of electrons in the presence of an electric field.

Zeeman effect: Phenomenon of deflection of electrons in the presence of a magnetic field.



Dual Nature of Matter

The electrons which were treated to be particles, the evidence of photoelectric effect shows they also have wave nature. This was proved by Thomas young with the help of his double slit experiment.

De-Broglie concluded that since nature is symmetrical, so should be light or any other matter wave.

Quantum Numbers

Principal Quantum number (n): It denotes the orbital number or shell number of electrons.

Azimuthal Quantum numbers (l): It denotes the orbital (sub-orbit) of the electron.

Magnetic Quantum number: It denotes the number of energy states in each orbit.

Spin Quantum number(s): It denotes the direction of spin, $S = -\frac{1}{2}$ = Anticlockwise and $\frac{1}{2}$ = Clockwise.

Electronic Configuration of an Atom

The electrons have to be filled in the s, p, d, f in accordance with the following rule.

1. Aufbau's principle: The filling of electrons should take place in accordance with the ascending order of energy of orbitals: Lower energy orbital should be filled first and higher energy levels.

The energy of orbital $\propto (n + l)$ value if two orbitals have same $(n + l)$ value, $E \propto n$

Ascending order of energy 1s, 2s, 2p, 3s, 3p, 4s, 3d, . . .

2. Pauli's exclusion principle: No two electrons can have all the four quantum numbers to be the same or, if two electrons have to place in an energy state they should be placed with opposite spins.
3. Hund's rule of maximum multiplicity: In case of filling degenerate (same energy) orbitals, all the degenerate orbitals have to be singly filled first and then only pairing has to happen.

SUMMARY

Atomic structure refers to the structure of atom comprising a nucleus (centre) in which the protons (positively charged) and neutrons (neutral) are present. The negatively charged particles called electrons revolve around the centre of the nucleus. The advances in atomic structure and quantum mechanics have led to the discovery of other fundamental particles. The discovery of subatomic particles has been the base for many other discoveries and inventions. The atomic structure of an element refers to the constitution of its nucleus and the arrangement of the electrons around it. Primarily, the atomic structure of matter is made up of protons, electrons and neutrons. Nucleons are the components of the nucleus of an atom. A nucleon can either be a proton or a neutron. Each element has a unique number of protons in it, which is described by its unique atomic number. However, several atomic structures of an element can exist, which differ in the total number of nucleons. These variants of elements having a different nucleon number (also known as the mass number) are called isotopes of the element. Therefore, the isotopes of an element have the same



number of protons but differ in the number of neutrons. The atomic structure of an isotope is described with the help of the chemical symbol of the element, the atomic number of the element, and the mass number of the isotope. For example, there exist three known naturally occurring isotopes of hydrogen, namely, protium, deuterium, and tritium.

EXERCISE

MCQ

1. How many orbitals can have the following set of quantum numbers, $n = 3, l = 1, m_l = 0$?

- (a) 3 (b) 1
(c) 4 (d) 2

Answer: (b)

2. Electronic configuration of the outer shell of the element Gd with atomic number 64 is

- (a) $4f^4 5d^5 6s^1$ (b) $4f^3 5d^5 6s^2$
(c) $4f^5 5d^4 6s^1$ (d) $4f^7 5d^1 6s^2$

Answer: (d)

3. Maximum number of electrons in a subshell can be

- (a) $4l + 2$ (b) $4l - 2$
(c) $2n^2$ (d) $2l + 1$

Answer: (a)

4. The orientation of atomic orbitals depends on their

- (a) spin quantum number (b) magnetic quantum number
(c) azimuthal quantum number (d) principal quantum number

Answer: (b)

5. A gas X has C_p and C_v ratio as 1.4, at NTP 11.2 L of gas X will contain _____ number of atoms

- (a) 1.2×10^{23} (b) 3.01×10^{23}
(c) 2.01×10^{23} (d) 6.02×10^{23}

Answer: (d)

6. Number of unpaired electrons in N_2^+

- (a) 3 (b) 1
(c) 2 (d) 0

Answer: (b)



7. The excitation energy of a hydrogen atom from its ground state to its third excited state is

- (a) 12.75 eV
- (b) 0.85 eV
- (c) 10.2 eV
- (d) 12.1 eV

Answer: (a)

8. 3p orbital has _____ radial nodes

- (a) three
- (b) two
- (c) one
- (d) none

Answer: (c)

9. A 0.66 kg ball is moving with a speed of 100 m/s. Find its wavelength

- (a) 6.6×10^{-34} m
- (b) 6.6×10^{-32} m
- (c) 1.0×10^{-32} m
- (d) 1.0×10^{-35} m

Answer: (d)

10. Orbital angular momentum of p electrons is

Review Questions

1. (a) What are the three fundamental particles that constitute an atom? (b) Compare the charge and mass of an electron and of a proton.
2. What do you think is the most significant contribution of Rutherford to the development of atomic structure?
3. What experimental evidence shows the dual nature of light?
 - (a) Compute the energy of a FM radio signal transmitted at a frequency of 100 MHz.
 - (b) What is the energy of a wave of red light with $\lambda = 670$ nm?
4. In what way was the Bohr's model better than the Rutherford's model?
5. What are the drawbacks of Bohr's Model?
6. What led to the development of Wave Mechanical Model of the atom?
7. What do you understand by an orbital? Draw the shapes of s and p orbitals.
8. Explain the Hund's rule of maximum multiplicity with the help of an example.



Notes



PERIODIC TABLE AND PERIODICITY IN PROPERTIES

- Understand the concept of periodic table.
- Understand the Mendeleev Periodic Table.
- Discuss the properties of periodic table.
- Understand the Periodic properties of elements.
- Discuss the classification of elements.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of periodic table so that the properties of periodic tables can be learned.

Introduction

What is the Periodic Table?

The periodic table is an arrangement of all the elements known to man in accordance with their increasing atomic number and recurring chemical properties. They are assorted in a tabular arrangement wherein a row is a period and a column is a group.

Elements are arranged from left to right and top to bottom in the order of their increasing atomic numbers. Thus,

Elements in the same group will have the same valence electron configuration and hence, similar chemical properties.

Whereas, elements in the same period will have an increasing order of valence electrons. Therefore, as the energy level of the atom increases, the number of energy sub-levels per energy level increases.

The first 94 elements of the periodic table are naturally occurring, while the rest from 95 to 118 have only been synthesized in laboratories or nuclear reactors.

The modern periodic table, the one we use now, is a new and improved version of certain models put forth by scientists in the 19th and 20th century. Dimitri Mendeleev put forward his periodic table based on the findings of some scientists before him like John Newlands and Antoine-Laurent de Lavoisier. However, Mendeleev is given sole credit for his development of the periodic table.

Periodic properties of elements

The basic law governing modern periodic table states that the properties of elements are periodic functions of their atomic number. These properties reappear at regular intervals or



follow a particular trend at regular intervals. This phenomenon is known as the periodicity of elements.

The periodic properties of elements occur due to the recurrence of similar electronic configuration that is having the same number of electrons in the outermost orbit. In a particular group, the number of valence electrons remains the same. On the other hand, the number of valence electrons increases, as we move from left to right across a period. The chemical property of an element depends on the number of electrons in the valence shell.

Periodic Table

Explanation for periodic properties

The periodic properties of an element depend on valency and number of shells in an atom. As we move down a group the number of shells increases successively such that the number of the shell of an element is equal to the number of periods to which it belongs. As we move across a period, the number of shells remains the same. For example, elements of the second period have two shells.

The combining capacity of an atom is known as its valency. It is equal to the number of electrons that an atom can accept or donate in order to complete its octet. As we move down a group, the number of electrons in the valence shell remains the same. Hence, the valency of a group is constant. Valency depends on the number of electrons in the outermost shell of an atom. If the number of electrons is 1, 2, 3, 4 then the respective valences will be 1, 2, 3, 4. If the number of electrons in the outermost shell will be 5, 6, 7 then the valency will be $8 - 5 = 3$, $8 - 6 = 2$ and $8 - 7 = 1$. Valency is the combining capacity of an atom hence will always have a positive value and largely affects the periodic properties.

In a period, the number of electrons increases from left to right. As a result, the number of electrons needed to complete the octet also changes. Hence, the valency successively increases to four in group 14 and then subsequently decreases to 1 in group 17.

Classification of Elements and Periodicity in Properties

Classification of Elements was necessary since many elements were being discovered in the 19th century and the study of these elements individually was proving difficult.

There were many attempts at classifying elements including 'Dobereiner's Triads' and 'Newland's Octaves'.

Dobereiner's Triads

German chemist Johann Wolfgang Dobereiner attempted to classify elements with similar properties into groups of three elements each. These groups were called 'triads'. Dobereiner suggested that in these triads, the atomic mass of the element in the middle would be more or less equal to the mean of the atomic masses of the other two elements in the triad.

An example of such a triad would be one containing lithium, sodium, and potassium. The atomic mass of lithium 6.94 and that of potassium is 39.10. The element in the middle of this triad, sodium, has an atomic mass of 22.99 which is more or less equal to the mean of the atomic masses of lithium and potassium (which is 23.02).



The Limitations of Dobereiner's Triads are :

All the elements known at that time couldn't be classified into triads.

Only four triads were mentioned – (Li,Na,K + Ca,Sr,Ba + Cl,Br,I + S,Se,Te).

Newland's Octaves

English scientist John Newlands arranged the 56 known elements in increasing order of atomic mass in the year 1866. He observed a trend wherein every eighth element exhibited properties similar to the first. This similarity in the properties of every eighth element can be illustrated as follows.

Classification of Elements and Periodicity in Properties – Newland's Octaves

Newland's Law of Octaves states that when the elements are arranged in increasing order of atomic mass, the periodicity in properties of two elements which have an interval of seven elements in between them would be similar.

Limitations of Newland's octaves are:

It was only up till calcium that the classification of elements is done via Newland's Octaves.

The discovery of noble gases added to the limitations of this method since they couldn't be included in this arrangement without disturbing it completely.

Mendeleev's Periodic Table

Russian chemist Dmitri Ivanovich Mendeleev put forth his periodic table in 1869. He observed that the properties of elements, both physical and chemical, were periodically related to the atomic mass of the elements.

The Periodic Law (also referred to as Mendeleev's Law), states that the chemical properties of elements are a periodic function of their atomic weights.

The advantages of Mendeleev's Periodic table are:

The inclusion of these newly discovered elements did not disturb the periodic table. Examples include germanium, gallium, and scandium.

It was used to correct the wrong atomic weights in use at that time.

A variance from the atomic weight order was provided by Mendeleev's table.

The limitations of Mendeleev's Periodic table are:

Hydrogen's position was in the group of alkali metals but hydrogen also exhibited halogen like qualities.

Isotopes were positioned differently since this type of classification of elements was done by considering the atomic weight of the element. Therefore – protium, deuterium, and tritium would occupy varying positions in Mendeleev's table.

An anomalous positioning of a few elements showed that the atomic masses did not increase regularly from one element to the next. An example of this would be the placement of cobalt (atomic mass of 58.9) before nickel (atomic mass of 58.7).



Notes

These methods were the foundation on which the modern periodic table was built. However, the greatest contributor to the modern periodic table was Dmitri Mendeleev. Mendeleev is also known as the Father of the Modern Periodic Table. The modern periodic law is also called Mendeleev's Law to honour him.

SUMMARY OF THE CHAPTER

The periodic table is an arrangement of all the elements known to man in accordance with their increasing atomic number and recurring chemical properties. They are assorted in a tabular arrangement wherein a row is a period and a column is a group. Elements are arranged from left to right and top to bottom in the order of their increasing atomic numbers. Thus, Elements in the same group will have the same valence electron configuration and hence, similar chemical properties. Whereas, elements in the same period will have an increasing order of valence electrons. Therefore, as the energy level of the atom increases, the number of energy sub-levels per energy level increases. The first 94 elements of the periodic table are naturally occurring, while the rest from 95 to 118 have only been synthesized in laboratories or nuclear reactors. The basic law governing modern periodic table states that the properties of elements are periodic functions of their atomic number. These properties reappear at regular intervals or follow a particular trend at regular intervals. This phenomenon is known as the periodicity of elements. The periodic properties of elements occur due to the recurrence of similar electronic configuration that is having the same number of electrons in the outermost orbit. In a particular group, the number of valence electrons remains the same. On the other hand, the number of valence electrons increases, as we move from left to right across a period. The chemical property of an element depends on the number of electrons in the valence shell.

EXERCISE

MCQ

1. Find the successive elements of the periodic table with ionisation energies, 2372, 520 and 890 kJ per mol respectively

- | | |
|---------------|----------------|
| (a) Li, Be, B | (b) H, He, Li |
| (c) B, C, N | (d) He, Li, Be |

Answer: (d)

2. In the modern periodic table, the number of period of the element is the same as

- | | |
|------------------------------|-------------------|
| (a) principal quantum number | (b) atomic number |
| (c) azimuthal quantum number | (d) atomic mass |

Answer: (a)

3. The correct order for the size of I, I⁺, I⁻ is

- | | |
|-----------------------------------------|-----------------------------------------|
| (a) I > I ⁻ > I ⁺ | (b) I > I ⁺ > I ⁻ |
| (c) I ⁻ > I > I ⁺ | (d) I ⁺ > I ⁻ > I |

Answer: (c)

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4. For the same value of n , the penetration power of orbital follows the order
- (a) $s = p = d = f$ (b) $p > s > d > f$
(c) $f < d < p < s$ (d) $s < p < d < f$

Answer: (c)

5. Which of the reactions will need the maximum amount of energy?

- (a) $\text{Na} \rightarrow \text{Na}^+ + e^-$ (b) $\text{Ca}^+ \rightarrow \text{Ca}^{++} + e^-$
(c) $\text{K}^+ \rightarrow \text{K}^{++} + e^-$ (d) $\text{C}^{2+} \rightarrow \text{C}^{3+} + e^-$

Answer: (c)

6. Which of the following statements is incorrect?

- (a) I.E.1 of O is lower than that of N but I.E.2 O is higher than that of N
(b) The enthalpy of N to gain an electron is almost zero but of P is 74.3 kJ mol^{-1}
(c) iso electronic ions belong to the same period
(d) The covalent radius of iodine is less than its Van der Waal's radius

Answer: (c)

7. The correct order of electro negativity is

- (a) $\text{Cl} > \text{F} > \text{O} > \text{Br}$ (b) $\text{F} > \text{O} > \text{Cl} > \text{Br}$
(c) $\text{F} > \text{Cl} > \text{Br} > \text{O}$ (d) $\text{O} > \text{F} > \text{Cl} > \text{Br}$

Answer: (b)

8. Two different beakers contain $\text{M}_1\text{-O-H}$, and $\text{M}_2\text{-O-H}$ solutions separately. Find the nature of the two solutions if the electro negativity of $\text{M}_1 = 3.4$, $\text{M}_2 = 1.2$, $\text{O} = 3.5$, $\text{H} = 2.1$

- (a) acidic, acidic (b) basic, acidic
(c) basic, basic (d) acidic, basic

Answer: (d)

9. Which one is the most acidic among these?

- (a) MgO (b) CaO
(c) Al_2O_3 (d) Na_2O

Answer: (c)

10. Which one will have the highest 2nd ionisation energy?

- (a) $1s^2 2s^2 2p^6 3s^1$
(b) $1s^2 2s^2 2p^4$
(c) $1s^2 2s^2 2p^6$
(d) $1s^2 2s^2 2p^6 3s^2$

Answer: (a)

Review Questions

1. Define modern periodic law.
2. Describe the variation of electron affinity and ionization enthalpy in the periodic table.
3. Define the following:
 - (a) Electron gain enthalpy
 - (b) Ionization enthalpy
 - (c) Ionic radius
 - (d) Electro negativity.
4. What is electro negativity? How is it related to the type of bond formed?
5. Why is the electron gain enthalpy of Cl more in negative value as compared to that of F?

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Notes

4 CHEMICAL BONDING

- Understand the concept of chemical bonding.
- Understand the concept of chemical bond.
- Discuss the types of chemical bond.
- Understand the Lewis dot structure.
- Discuss the Octet rule.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of chemical bonding so that the applications of chemical bonding can be learned.

Introduction

We already know that atoms are the building blocks of matter. Under normal conditions no atom exists as an independent (single) entity in nature, except Noble gases. However, a group of atoms is found to exist together as one species. Such a group of atoms is called molecule. Obviously there should be a force to keep the constituent atoms together as the thread holds the owners together in a garland. This attractive force which holds the atoms together is called a bond.

A Chemical bond may be defined as the force of attraction between the two atoms that binds them together as a unit called molecule.

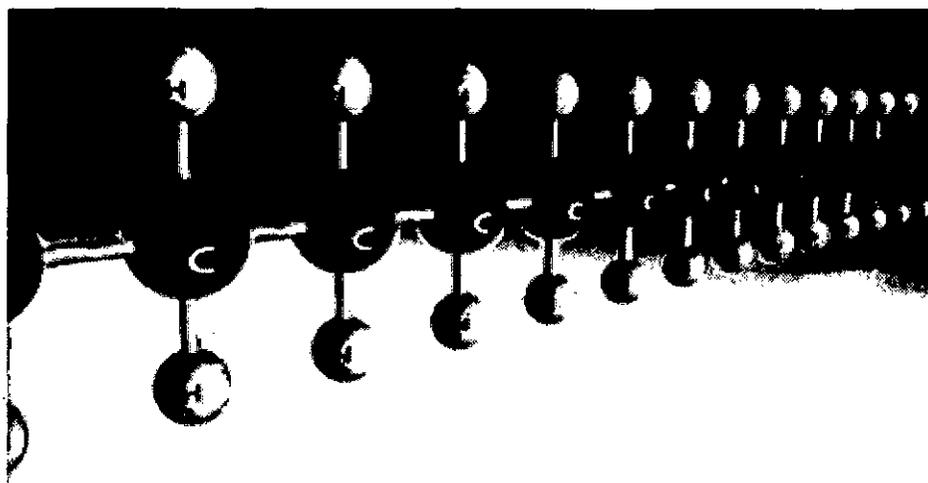
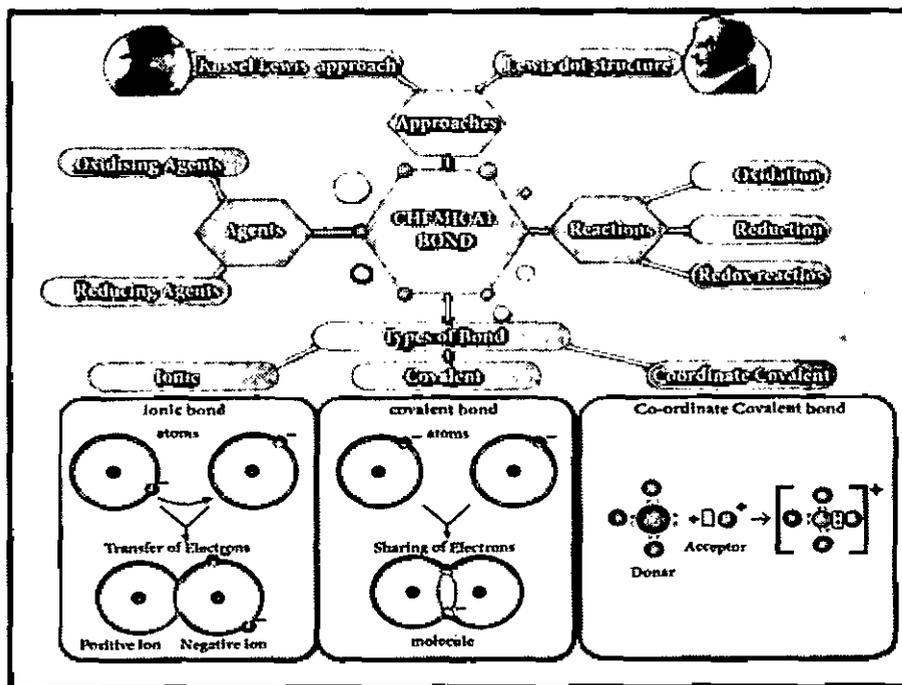


Figure. 5.2 Atoms held together by bond



Kossel - Lewis approach to chemical bonds

Octet rule

Atoms of various elements combine together in different ways to form chemical compounds. This phenomenon raised many questions.

- Why do atoms combine?
- How do atoms combine?
- Why do certain atoms combine while others do not?

To answer such questions different theories have been put forth from time to time and one of such theory which explained the formation of molecules is Kossel-Lewis theory.

Kossel and Lewis gave successful explanation based upon the concept of electronic configuration of noble gases about why atoms combine to form molecules. Atoms of noble gases have little or no tendency to combine with each other or with atoms of other elements. It means that these atoms must be having stable electronic configurations. The electronic configurations of noble gases are given in Table 5.1.

Table 5.1 The electronic configurations of noble gases

Name of the element	Atomic number	Shell electronic configuration
Helium (He)	2	2
Neon (Ne)	10	2,8
Argon (Ar)	18	2,8,8
Krypton (Kr)	36	2,8,18,8
Xenon (Xe)	54	2,8,18,18,8

Except Helium, all other noble gases have eight electrons in their valence shells. Even

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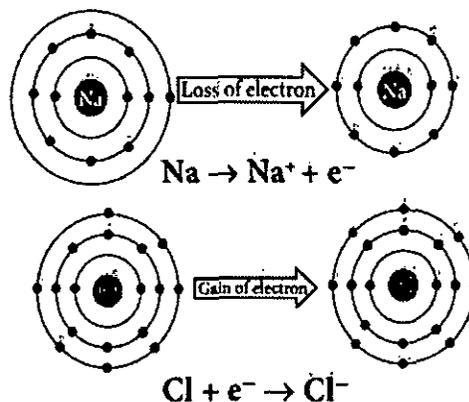
Notes

helium has its valence shell completely filled and hence no more electrons can be added. As by having stable valence electronic configuration, the noble gas atoms neither have any tendency to gain nor lose electrons and their valency is zero. They are so inert that they even do not form diatomic molecules and exist as mono atomic gaseous atoms.

Based on the noble gas electronic configuration, Kossel and Lewis proposed a theory in 1916 to explain chemical combination between atoms and this theory is known as 'Electronic theory of valence' or Octet rule. According to this, atoms of all elements, other than inert gases, combine to form molecules because they have incomplete valence shell and tend to attain a stable electronic configuration similar to noble gases. Atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to achieve the stable outer shell of eight electrons.

The tendency of atoms to have eight electrons in the valence shell is known as the 'Octet rule' or the 'Rule of eight'

For example, Sodium with atomic number 11 will readily lose one electron to attain Neon's stable electronic configuration. Similarly, chlorine has electronic configuration 2,8,7. To get the nearest noble gas (i.e., argon) configuration, it needs one more electron. So, chlorine readily gains one electron from another atom and obtains stable electronic configuration. All elements tend to have stable valence shell (eight electrons) either by losing or gaining electrons.



Which atoms tend to lose electrons?

Which atoms tend to gain electrons?

Atoms that have 1,2,3 electrons in their valence shell tend to lose whereas atoms having 5,6,7 valence electrons tend to gain.

Table 5.2 Unstable electronic configuration

Element	Atomic number	Electron distribution	Valence electrons
Boron	5	2, 3	3
Nitrogen	7	2, 5	5
Oxygen	8	2, 6	6
Sodium	11	2, 8, 1	1



Notes

Element	Atomic number	Electron distribution	Valence electrons	Stable	Unstable
Hydrogen	1	1	1		✓
Fluorine	9				
Krypton	36				
Xenon	54				



Walther Kossel
(1888-1956)



Gilbert N Lewis
(1875-1946)

Lewis dot structure

When atoms combine to form compounds, their valence electrons involve in bonding. Therefore, it is helpful to have a method to depict the valence electrons in the atoms. This can be done using Lewis dot symbol method. The Lewis dot structure or electron dot symbol for an atom consists of the symbol of the element surrounded by dots representing the electrons of the valence shell of the atom. The unpaired electron in the valence shell is represented by a single dot whereas the paired electrons are represented by a pair of dots. Symbols other than dots, like crosses or circles may be used to differentiate the electrons of the different atoms in the molecule.

Table 5.3 Lewis dot structure

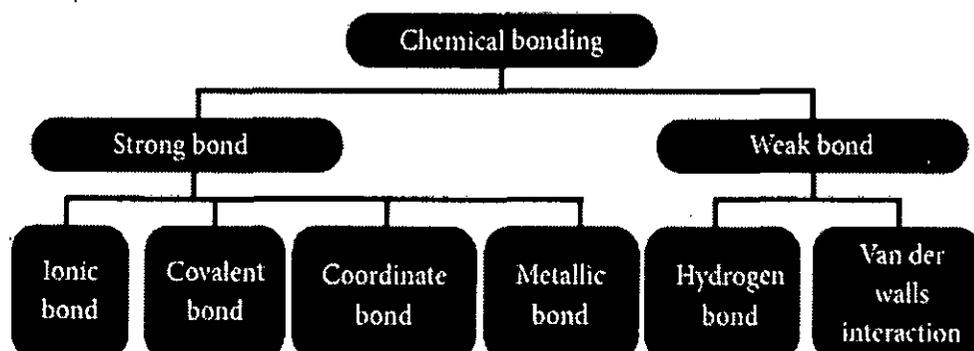
Element	Atomic number	Electron distribution	Valence electrons	Lewis dot structure
Hydrogen	1	1	1	H·
Helium	2	2	2	·He·
Beryllium	4	2, 2	2	·Be·
Carbon	6	2, 4	4	·C·
Nitrogen	7	2, 5	5	·N·
Oxygen	8	2, 6	6	·O·



Element	Atomic number	Electron distribution	Valence electrons	Stable	Lewis dot structure
Boron	5	2, 3	3	Yes	$\cdot\cdot\cdot$
Argon	18	2, 8, 8	8	Yes	$\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot$
Chlorine	17	2, 8, 7	7	Yes	$\cdot\cdot\cdot\cdot\cdot\cdot\cdot$
Sodium	11	2, 8, 1	1	Yes	\cdot
Fluorine	9	2, 7	7	Yes	$\cdot\cdot\cdot\cdot\cdot\cdot\cdot$

Types of chemical bond

All the elements differ with each other in their valence shell electronic configuration. So, the way in which they combine to form compounds also differs. Hence, there are different types of chemical bonding possible between atoms which make the molecules. Depending on the type of bond they show different characteristics or properties. Such types of bonding that are considered to exist in molecules are categorized as shown below. Among these, let us learn about the Ionic bond, Covalent bond and Coordinate bond in this chapter and other types of bond in the higher classes.



1. Ionic (or) Electrovalent bond

An ionic bond is a chemical bond formed by the electrostatic attraction between positive and negative ions. The bond is formed between two atoms when one or more electrons are transferred from the valence shell of one atom to the valence shell of the other atom. The atom that loses electrons will form a cation (positive ion) and the atom that gains electrons will form an anion (negative ion). These oppositely charged ions come closer to each other due to electrostatic force of attraction and thus form an ionic bond. As the bond is between the ions, it is called Ionic bond and the attractive forces being electrostatic, the bond is also called Electrostatic bond. Since the valence concept has been explained in terms of electrons, it is also called as Electrovalent bond.

Formation of ionic bond

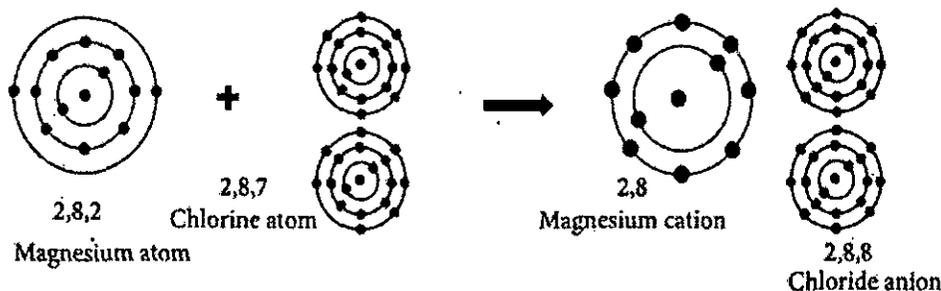
Let us consider two atoms A and B. Let atom A has one electron in excess and atom B has one electron lesser than the stable octet electronic configuration. If atom A transfer one electron to atom B, then both the atoms will acquire stable octet electronic configuration.



Notes

Illustration 2 – Formation of Magnesium Chloride (MgCl₂)

The atomic number of Magnesium is 12 and the electronic configuration is 2, 8, 2. It has two electron excess to the nearest stable electronic configuration of a noble gas - Neon. So, magnesium has a tendency to lose two electrons from its outermost shell and acquire a stable electronic configuration forming magnesium cation (Mg²⁺).



As explained earlier two chlorine atoms will gain two electrons lost by the magnesium atom forming magnesium chloride molecule (MgCl₂)

Characteristics of Ionic compounds

The nature of bonding between the atoms of a molecule is the primary factor that determine the properties of compounds. By this way, in ionic compounds the atoms are held together by a strong electrostatic force that makes the compounds to have its characteristic features as follows:

- a. Physical states compounds are formed because of the strong electrostatic force between cations and anions which are arranged in a well- de ned geometrical pattern. us Ionic compounds are crystalline solids at room temperature.
- b. Electrical conductivity – Ionic compounds are crystalline solids and so their ions are tightly held together. The ions, therefore, cannot move freely, so they do not conduct electricity in solid state. However, in molten state and their aqueous solutions conduct electricity.
- c. Melting point–the strong electrostatic force between the cations and anions holds the ions tightly together, so very high energy is required to separate them. Hence ionic compounds have high melting and boiling points.
- d. Solubility – Ionic compounds are soluble in polar solvents like water. They are insoluble in non-polar solvents like benzene (C₆H₆), carbon tetra chloride (CCl₄).
- e. Density, hardness and brittleness–Ionic compounds have high density and they are quite hard because of the strong electrostatic force between the ions. But they are highly brittle.
- f. Reactions – Ionic compounds undergo ionic reactions which are practically rapid and instantaneous.

2. Covalent bond

Atoms can combine with each other by sharing the,unpaired electrons in their outermost shell. Each of the two combining atoms contributes one electron to the electron pair which is needed for the bond formation and has equal claim on the shared electron pair. According to Lewis concept when two atoms form a covalent bond between them, each of the atoms attains the stable electronic configuration of the nearest noble gas. Since the covalent bond is formed because of the sharing of electrons which become common to both the atoms, it is also called as Atomic bond.



Formation of Covalent bond

Let us consider two atoms A and B. Let atom A has one valence electron and atom B has seven valence electrons. As these atoms approach nearer to each other, each atom contributes one electron and the resulting electron pair fills the outer shell of both the atoms. Thus, both the atoms acquire a completely filled valence shell electronic configuration which leads to stability.

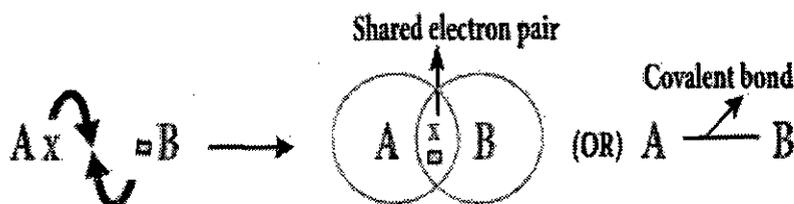


Illustration 1 – Formation of hydrogen molecule (H₂)

Hydrogen molecule is formed by two hydrogen atoms. Each having one valence electron (1s¹), it is contributed to the shared pair and both atoms acquire stable completely filled electronic configuration.

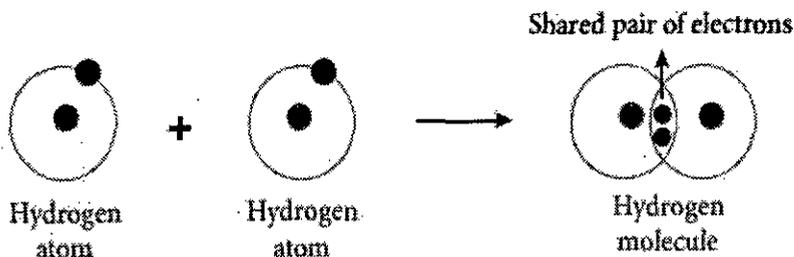
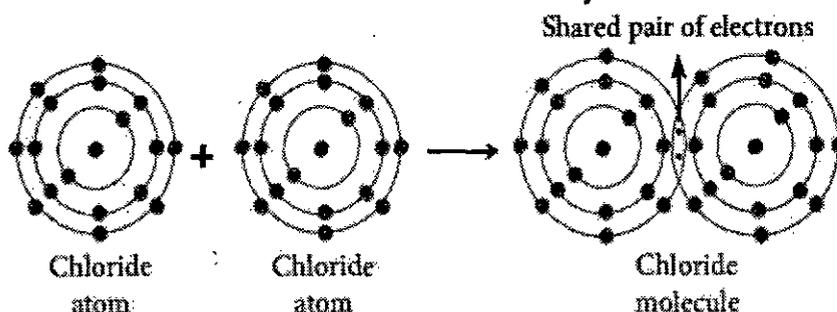


Illustration 2 – Formation of chlorine molecule (Cl₂)

Chlorine molecule is formed by two chlorine atoms. Each chlorine atom has seven valence electrons (2,8,7). These two atoms achieve a stable completely filled electronic configuration (octet) by sharing a pair of electrons.



Element	Atomic number	Electron distribution
Fluorine	9	2, 7



Notes

Illustration 3 – Formation of methane molecule (CH₄)

Methane molecule is formed by the combination of one carbon and four hydrogen atoms. The carbon atom has four valence electrons (2, 4). These four electrons are shared with four atoms of hydrogen to achieve a stable electronic configuration (octet) by sharing a pair of electrons.

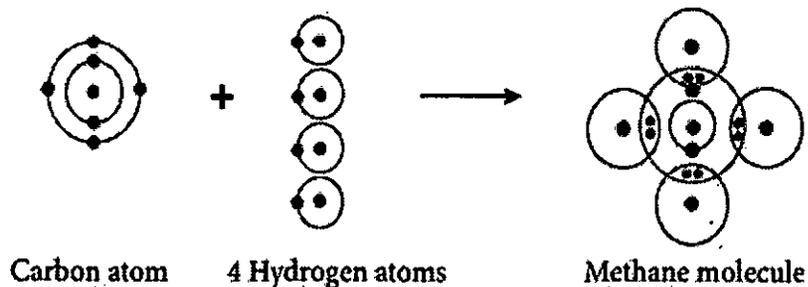


Illustration 4 – Formation of oxygen molecule (O₂)

Oxygen molecule is formed by two oxygen atoms. Each oxygen atom has six valence electrons (2, 6). These two atoms achieve a stable electronic configuration (octet) by sharing two pair of electrons. Hence a double bond is formed in between the two atoms.

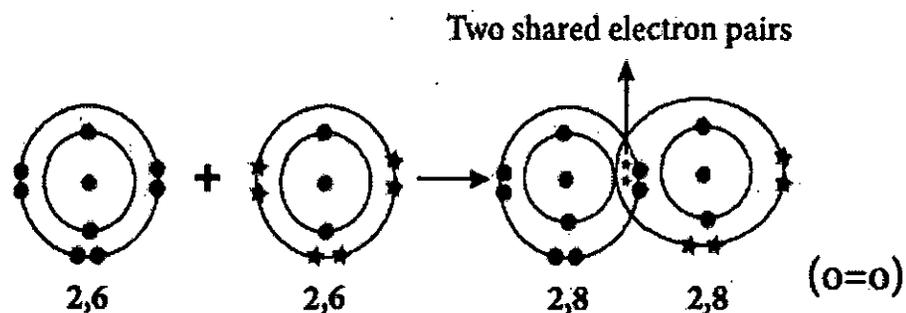
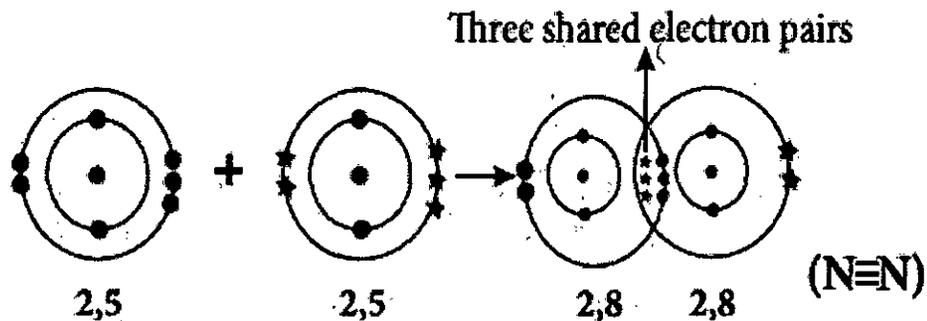


Illustration 5 – Formation of nitrogen molecule (N₂)

Nitrogen molecule is formed by two nitrogen atoms. Each nitrogen atom has five valence electrons (2, 5). These two atoms achieve a stable completely filled electronic configuration (octet) by sharing three pair of electrons. Hence a triple bond is formed in between the two atoms.





Characteristics of Covalent compounds

As said earlier, the properties of compounds depend on the nature of bonding between their constituent atoms. So, the compounds containing covalent bonds possess different characteristics when compared to ionic compounds.

- Physical state – Depending on force of attraction between covalent molecule the bond may be weaker or stronger. Thus, covalent compounds exist in gaseous, liquid and solid form. E.g., Oxygen-gas; Water-liquid; Diamond-solid.
- Electrical conductivity – Covalent compounds do not contain charged particles (ions), so they are bad conductors of electricity.
- Melting point – Except few covalent compounds (Diamond, Silicon carbide), they have relatively low melting points compared to Ionic compounds.
- Solubility – Covalent compounds are readily soluble in non-polar solvents like benzene (C₆H₆), carbon tetra chloride (CCl₄). They are insoluble in polar solvents like water.
- Hardness and brittleness – Covalent compounds are neither hard nor brittle. But they are soft and waxy.
- Reactions – Covalent compounds undergo molecular reactions in solutions and these reactions are slow.

Fajan's Rule:

As we know, a metal combines with a non-metal through ionic bond. The compounds so formed are called ionic compounds. A compound is said to be ionic when the charge of the cation and anion are completely separated. But in 1923, Kazimierz Fajans found, through his X-Ray Crystallographic studies, that some of the ionic compounds show covalent character. Based on this, he formulated a set rules to predict whether a chemical bond is ionic or covalent. Fajan's rules are formulated by considering the charge of the cation and the relative size of the cation and anion.

- When the size of the cation is small and that of anion is large, the bond is of more covalent character
- Greater the charge of the cation, greater will be the covalent character

This can be summarized as follows:

Ionic	Covalent
Low positive charge	High positive charge
Large cation	Small cation
Small anion	Large anion

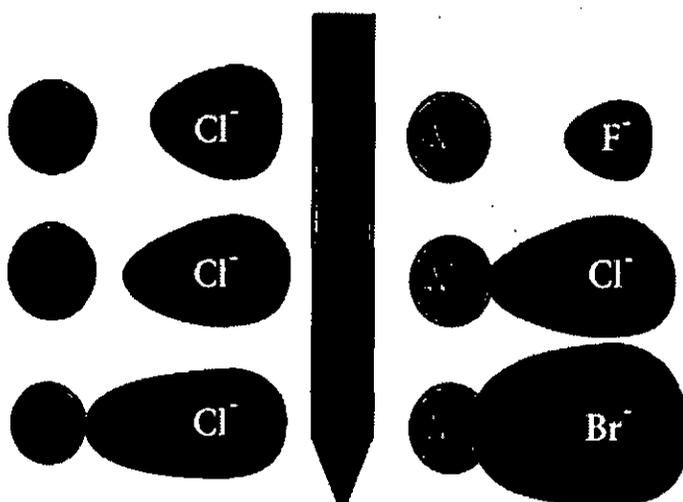
For example, in sodium chloride, low positive charge (+1), a fairly large cation and relatively small anion make the charges to separate completely. So, it is ionic. In aluminium triiodide, higher is the positive charge (+3), larger is the anion and thus no complete charge separation. So is covalent. The following picture depicts the relative charge separation of ionic compounds:



Notes

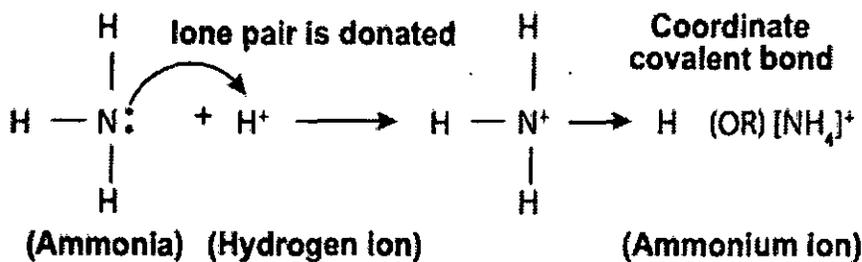
Table 5.4 Difference between Ionic and Covalent compounds

Ionic Compounds	Covalent Compounds
Formed by the transfer of electrons from a metal to a non-metal atom	Formed by sharing of electrons between non-metal atoms
Strong electrostatic force of attraction between cations and anions	Mutual sharing of electrons and so weak force of attraction between atoms
Solids at room temperature	Gases, liquids and soft solids
Conducts electricity in molten state or in solutions	Non-conductors of electricity
Have high melting and boiling points	Have low melting and boiling points
Soluble in polar solvents	Soluble in non-polar solvents
Hard and brittle	Soft and waxy
Undergo ionic reaction which are fast and instantaneous	Undergo molecular reactions which are slow



3. Coordinate covalent bond

In the formation of normal covalent bond each of the two bonded atoms contribute one electron to form the bond. However, in some compounds the formation of a covalent bond between two atoms takes place by the sharing of two electrons, both of which comes from only one of the combining atoms. This bond is called Coordinate covalent bond or Dative bond.



Mostly the lone pair of electrons from an atom in a molecule may be involved in the dative bonding. The atom which provides the electron pair is called donor atom while the other atom which accepts the electron pair is called acceptor atom. The Coordinate covalent bonds represented by an arrow (→) which points from the donor to the acceptor atom.

Formation of Coordinate covalent bond

Let us consider two atoms A and B. Let atom A has an unshared lone pair of electrons and atom B is in short of two electrons than the octet in its valence shell. Now atom A donates its lone pair while atom B accepts it. Thus, the lone pair of electrons originally belonged to atom A are now shared by both the atoms and the bond formed by this mutual sharing is called Coordinate covalent bond. ($A \rightarrow B$)

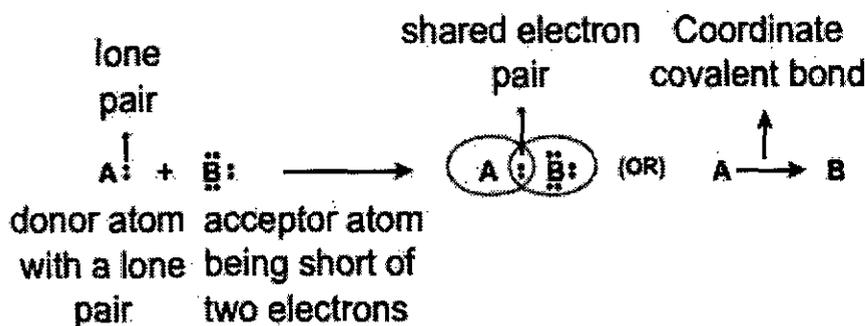
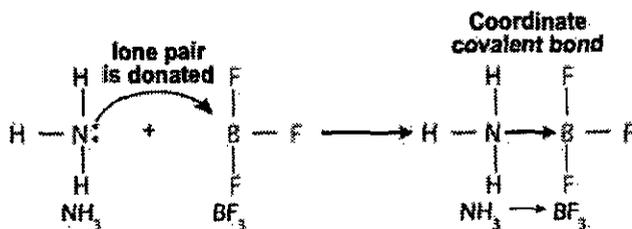


Illustration 1 – Formation of coordinate covalent bond in ammonium ion (NH_4^+)

Ammonium ion is formed by one ammonia (NH_3) molecule and one hydrogen (H^+) ion. In ammonia molecule the central nitrogen atom has five valence electrons (2,5) among which three electrons are shared with three hydrogen atoms and still it has an unshared lone pair of electrons. These lone pair electrons are donated to a Hydrogen ion and thus a $N \rightarrow H$ coordinate covalent bond is formed in ammonium ion molecule (NH_4^+)

Illustration 2 – Formation of coordinate covalent bond between $NH_3 \rightarrow BF_3$ molecules

In some cases, the donated pair of electrons comes from a molecule as a whole which is already formed to another acceptor molecule. Here the molecule ammonia (NH_3) gives a lone pair of electrons to Boron tri fluoride (BF_3) molecule which is electron deficient. Thus, a Coordinate covalent bond is formed between NH_3 (donor molecule) and BF_3 (acceptor molecule) and is represented by $NH_3 \rightarrow BF_3$.



Characteristics of coordinate covalent compounds

The compounds containing coordinate covalent bonds are called coordinate compounds.

- Physical state – These compounds exist as gases, liquids or solids.
- Electrical conductivity – Like covalent compounds, coordinate compounds also do not contain charged particles (ions), so they are bad conductors of electricity.
- Melting point – These compounds have melting and boiling points higher than those of purely covalent compounds but lower than those of purely Ionic compounds.
- Solubility – Insoluble in polar solvents like water but are soluble in non-polar solvents like benzene, CCl_4 , and toluene.
- Reactions – Coordinate covalent compounds undergo molecular reactions which are slow.



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Chemistry



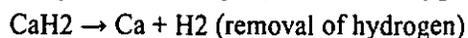
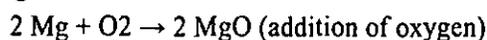
Notes

Oxidation, Reduction and Redox reactions

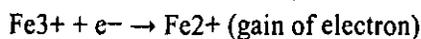
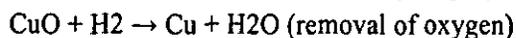
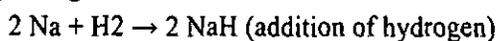
Look at the following pictures. When an apple is cut and left for sometimes, its surface turns brown. Similarly, iron bolts and nuts in metallic structures get rusted. Do you know why are these happening? It is because of a reaction called oxidation.



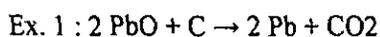
Oxidation: A chemical reaction which involves addition of oxygen or removal of hydrogen or loss of electrons is called oxidation.



Reduction: A chemical reaction which involves addition of hydrogen or removal of oxygen or gain of electrons is called reduction.



Redox reactions: Generally, the oxidation and reduction occur in the same reaction (simultaneously). If one reactant gets oxidised, the other gets reduced. Such reactions are called oxidation-reduction reactions or Redox reactions.



Oxidation (LEO)	addition of Oxygen
	removal of Hydrogen
	loss of electron
Reduction (GER)	removal of Oxygen
	addition of Hydrogen
	gain of electron



Notes

Oxidising agents and Reducing agents

Substances which have the ability to oxidise other substances are called Oxidising agents. These are also called as electron acceptors because they remove electrons from other substances.

Example: H_2O_2 , MnO_4^- , CrO_3 , $\text{Cr}_2\text{O}_7^{2-}$

Substances which have the ability to reduce other substances are called Reducing agents. These are also called as electron donors because they donate electrons to other substances.

Example: NaBH_4 , LiAlH_4 and metals like Palladium, Platinum.

Oxidation reactions in daily life:

In nature the oxygen present in atmospheric air oxidises many things, starting from metals to living tissues.

- The shining surface of metals tarnishes due to the formation of respective metal oxides on their surfaces. This is called corrosion.
- The freshly cut surfaces of vegetables and fruits turns brown or black in colour some time because of the oxidation of organic compounds present in them.
- The oxidation reaction in food materials that were left open for a long period is responsible for spoiling of food. is called Rancidity.

Oxidation number

Oxidation number of an element is defined as the formal charge which an atom of that element appears to have when electrons are counted.

Oxidation number also called Oxidation state, the total number of electrons that an atom either gains or losses in order to form a chemical bond with another atom. The sum of oxidation numbers of all the atoms in the formula for a neutral compound is ZERO. The sum of oxidation numbers of an ion is the same as the charge on that ion. Negative oxidation number in compounds of two unlike atoms is assigned to the more electronegative atom.

For example,

- Oxidation number of K and Br in KBr molecule is +1 and -1 respectively.
- Oxidation number of N in NH_3 molecule is -3
- Oxidation number of H is +1 (except hydrides)
- Oxidation number of oxygen in most cases is -2

(Oxidation Number = ON)

Problems on determination of Oxidation Number

ON of neutral molecule is always zero

Illustration 1 – Oxidation Number of H and O in H_2O

Let us take ON of H = +1 and ON of O = -2

$$2 \times (+1) + 1 \times (-2) = 0$$

$(+2) + (-2) = 0$ thus, ON of H is +1 and ON of O is -2

Illustration 2 – Oxidation Number of Na and Cl in NaCl

ON of Na = +1 and ON of Cl = -1

$(+1) + (-1) = 0$ thus, ON of Na is +1 and ON of Cl is -1



Illustration 3 – Oxidation Number of S in H₂SO₄

Let ON of S be (x) and we know ON of H = +1 and O = -2

$$2 \times (+1) + (x) + 4 \times (-2) = 0$$

$$(+2) + (x) + (-8) = 0$$

(x) = +6 therefore, ON of S is +6

Illustration 4 – Oxidation Number of Cr in K₂Cr₂O₇

Let ON of Cr be x and we know ON of K = +1 and O = -2

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

$$(+2) + (2x) + (-14) = 0$$

$$2x = +12$$

x = +6 therefore, ON of Cr in K₂Cr₂O₇ is +6

Illustration 5 – Oxidation Number of Fe in FeSO₄

Let ON of Fe be x and we know ON of S = +6 and O = -2

$$x + (+6) + 4 \times (-2) = 0$$

$$x + (+6) + (-8) = 0$$

x = +2 therefore, ON of Fe in FeSO₄ is +2

SUMMARY

We already know that atoms are the building blocks of matter. Under normal conditions no atom exists as an independent (single) entity in nature, except Noble gases. However, a group of atoms is found to exist together as one species. Such a group of atoms is called molecule. Obviously there should be a force to keep the constituent atoms together as the thread holds the owners together in a garland is attractive force which holds the atoms together is called a bond. A Chemical bond may be defined as the force of attraction between the two atoms that binds them together as a unit called molecule. All the elements differ with each other in their valence shell electronic configuration. So, the way in which they combine to form compounds also differs. Hence, there are different types of chemical bonding possible between atoms which make the molecules. Depending on the type of bond they show different characteristics or properties. Oxidation number also called Oxidation state, the total number of electrons that an atom either gains or losses in order to form a chemical bond with another atom. The sum of oxidation numbers of all the atoms in the formula for a neutral compound is ZERO. The sum of oxidation numbers of an ion is the same as the charge on that ion. Negative oxidation number in compounds of two unlike atoms is assigned to the more electronegative atom.

EXERCISE

MCQ

1. C-O bond length is minimum in

(a) CO₂

(b) CO₃²⁻

(c) HCOO⁻

(d) CO

Answer: (d)



2. Molecules are held together in a crystal by
 (a) hydrogen bond (b) electrostatic attraction
 (c) Van der Waal's attraction (d) dipole-dipole attraction
Answer: (c)
3. sp^3d^2 hybridization is present in $[Co(NH_3)_6]^{3+}$, find its geometry
 (a) octahedral geometry (b) square planar geometry
 (c) tetragonal geometry (d) tetrahedral geometry
Answer: (a)
4. Find the molecule with the maximum dipole moment
 (a) CH_4 (b) NH_3
 (c) CO_2 (d) NF_3
Answer: (b)
5. MX_6 is a molecule with octahedral geometry. How many $X - M - X$ bonds are at 180° ?
 (a) four (b) two
 (c) three (d) six
Answer: (c)
6. Find the pair with sp^2 hybridisation of the central molecule
 (a) NH_3 and NO_2^- (b) BF_3 and NH_2^-
 (c) BF_3 and NO_2^- (d) NH_2^- and H_2O
Answer: (c)
7. The formal charge and P-O bond order in PO_4^{3-} respectively are
 (a) 0.6, -0.75 (b) -0.75, 1.25
 (c) 1.0, -0.75 (d) 1.25, -3
Answer: (b)
8. Which of the molecules does not have a permanent dipole moment?
 (a) SO_3 (b) SO_2
 (c) H_2S (d) CS_2
Answer: (d)
9. $p\pi - d\pi$ bonding is present in which molecule
 (a) SO_3^{2-} (b) CO_3^{2-}
 (c) NO_3^- (d) BO_3^{3-}
Answer: (a)
10. Which one has a pyramidal shape?
 (a) SO_3 (b) PCl_3
 (c) CO_3^{2-} (d) NO_3^-
Answer: (b)

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Chemistry



Notes

Review Questions

1. Find the oxidation number of Mn in KMnO_4
2. Find the oxidation number of Cr in $\text{Na}_2\text{Cr}_2\text{O}_7$
3. Find the oxidation number of Cu in CuSO_4
4. Find the oxidation number of Fe in FeO
5. What do you understand by a chemical bond?
6. Explain the process of bond formation as a decrease in energy.
7. What do you understand by the term, 'bond length'?
8. Describe the two possible ways in which the noble gas electronic configuration is achieved in the process of bond formation.
9. What are Lewis electron dot symbols? Show the formation of MgCl_2 in terms of Lewis symbols.
10. Define a coordinate bond and give some examples.
11. What is VSEPR theory? Predict the shape of SF_6 molecule using this theory.
12. Why do we need the concept of hybridisation? How does it help in explaining the shape of methane?
13. Give the salient features of molecular orbital theory



Notes

5

GASEOUS AND LIQUID STATES

- Understand the concept of matter.
- Discuss the state of matter.
- Understand the concept of gaseous state.
- Discuss the types of matter.
- Understand the liquid state.
- Discuss the solid state.
- Discuss the Boyle's Law.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of state of matter so that the types of matter can be learned.

Introduction**What is Matter?**

As discovered by scientists, matter is made up of very tiny particles and these particles are so small that we cannot see them with naked eyes.

It has been observed that matter exists in nature in different forms. Some substances are rigid and have a fixed shape like wood and stone; some substances can flow and take the shape of their container like water, while there are forms of matter that do not have definite shape or size such as air.

Thus, matter can be classified into different categories based on the physical properties exhibited by them and the states in which they exist; these are called states of matter.

Following are the basic three states of matter:

- Solid
- Liquid
- Gas

Apart from the above mentioned three, there are 2 more states of matter which we do not see in our everyday life. They are Plasma & Bose-Einstein condensate.

Matter Definition

Chemistry is the study of the composition of matter and its transformation. Another term often considered synonymous with matter is substance, but a substance has a more limited

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Chemistry



Notes

definition in chemistry. Chemistry deals with the study of behaviour of – matter Chemistry is concerned with the – Composition, structure and properties of matter and the phenomenon which occurs when different kinds of matter undergo changes.

Matter theory covers the changing ideas and systems that were used to describe and explain the material world. A large part of matter theory was based on a theory of the elements.

Solid Definition

- In solids, particles are tightly or closely packed.
- The gaps between the particles are tiny and hence it is tough to compress them.
- Solid has a fixed shape and volume.
- Due to its rigid nature, particles in solid can only vibrate about their mean position and cannot move.
- Force of attraction between particles is adamant.
- The rate of diffusion in solids is very low.
- An example of solids: solid ice, sugar, rock, wood, etc.

Liquid

- In a liquid state of matter, particles are less tightly packed as compared to solids.
- Liquids take the shape of the container in which they are kept.
- Liquids are difficult to compress as particles have less space between them to move.
- Liquids have fixed volume but no fixed shape.
- The rate of diffusion in liquids is higher than that of solids.
- Force of attraction between the particles is weaker than solids.
- Example of a liquid state of matter: water, milk, blood, coffee, etc.

Gas

- In gases, particles are far apart from each other.
- Force of attraction between the particles is negligible, and they can move freely.
- Gases have neither a fixed volume nor a fixed shape.
- The gaseous state has the highest compressibility as compared to solids and liquids.
- The rate of diffusion is higher than solids and liquids.
- The kinetic energy of particles is higher than in solids and liquids.
- An example of gases: air, helium, nitrogen, oxygen, carbon dioxide, etc.

Plasma

Plasma is a not so generally seen form of matter. Plasma consists of particles with extremely high kinetic energy. Electricity is used to ionize noble gases and make glowing signs, which is essentially plasma.

Superheated forms of plasma are what stars are.

Bose-Einstein Condensates

Discovered in 1995, Bose-Einstein condensates were made with the help of the advancements in technology.



Carl Weiman and Eric Cornell cooled a sample of rubidium with the help of magnets and lasers to within a few degrees of absolute zero.

At the said temperature, the motion of the molecules becomes negligible. As this brings down the kinetic energy, the atoms no longer stay separate, but they begin to clump together. As the atoms join together, they form a super-atom.

Light slows down as it passes through a BEC helping scientists to study more about the nature of light as a wave and particle.

BEC's also show properties of a super fluid which implies, it flows without friction.

Gaseous State

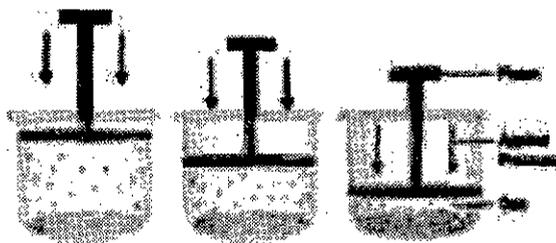
1. Why do gases not have fixed shape?

According to the kinetic theory of matter the particles in gases

1. Are not close to each other but are spread far apart from each other;
2. Are not held in any fixed positions;
3. Have very weak forces of attraction between each other, lesser than liquids;
4. Have a lot of kinetic energy and can move freely in all directions.

2. Why do gases not have fixed volume?

Since the particles in gases are far apart there is a lot of space between them. Therefore, they can be forced to get closer or in other words can easily be compressed.



Compression of a gas by applying pressure

By applying pressure, the particles in a gas can be brought closer. Gases are easily compressible.

Light, sound, heat etc. are not matter. They are different forms of Energy.

The Gas Laws

The gas laws have played a major role in the development of chemistry. The physical properties of all gases are governed by the gas laws that were formulated based on the studies of the properties like pressure, volume, etc., as a function of temperature. Before studying the gas laws in detail, let us understand an important parameter, namely, the pressure.



Notes

Pressure is defined as force divided by the area to which the force is applied. The SI unit of pressure is pascal which is defined as 1 Newton per square meter (Nm^{-2}). There are other units that are commonly used and their relation with the SI unit is as follows.

$$\text{Pressure} = \frac{\text{Force (N or kg m s}^{-2}\text{)}}{\text{Area (m}^2\text{)}}$$

Table 6.1 Units of pressure

Unit	Symbol	Value (Nm^{-2} or $\text{kgm}^{-1}\text{s}^{-2}$)
pascal	Pa	1 Pa = 1 Nm^{-2}
atmosphere	atm	1 atm = 101325 Pa
millimeter of mercury	mmHg	1 mmHg = 133.322 Pa
bar	bar	1 bar = 10^5 Pa
torr	Torr	1 Torr = 133.322 Pa
pound per square inch	psi	1 psi = 6894.76 pa

Boyle's Law: Pressure-Volume Relationship

Robert Boyle performed a series of experiments to study the relation between the pressure and volume of gases. The schematic of the apparatus used by him is shown in figure 6.1.

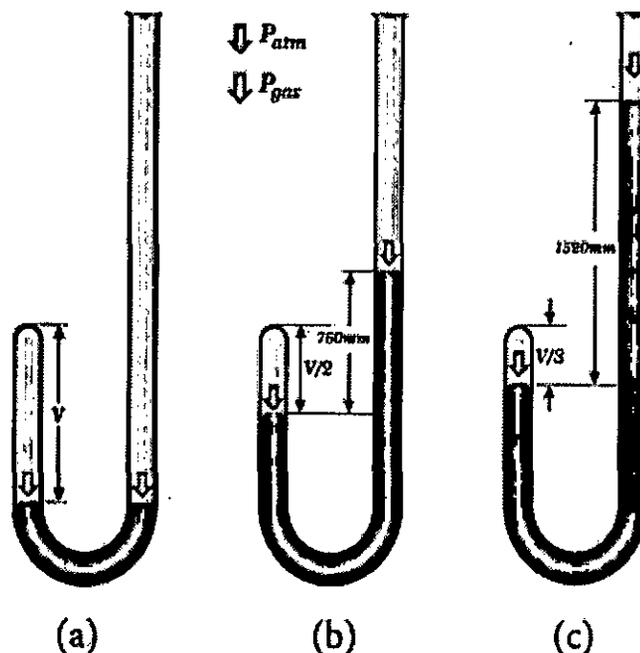


Figure. 6.1 Boyle's law experiment

Mercury was added through the open end of the apparatus such that the mercury level on both ends is equal as shown in the figure 6.1(a). Add more amount of mercury until the volume of the trapped air is reduced to half of its original volume as shown in figure 6.1(b). The pressure exerted on the gas by the addition of excess mercury is given by the difference



in mercury levels of the tube. Initially the pressure exerted by the gas is equal to 1 atm as the difference in height of the mercury levels is zero. When the volume is reduced to half, the difference in mercury levels increases to 760 mm. Now the pressure exerted by the gas is equal to 2 atm. It led him to conclude that at a given temperature the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

Mathematically, the Boyle's law can be written as

$$V \propto \frac{1}{P} \text{ ----- (6.1)}$$

(T and n are fixed, T-temperature, n- number of moles)

$$V = k \times \frac{1}{P} \text{ ----- (6.2)}$$

k – proportionality constant

When we rearrange equation 6.2.

$$PV = k \text{ at constant temperature and mass}$$

Boyle's law is applicable to all gases regardless of their chemical identity (provided the pressure is low). Therefore, for a given mass of a gas under two different sets of conditions at constant temperature we can write

$$P_1V_1 = P_2V_2 = k \text{ -----(6.3)}$$

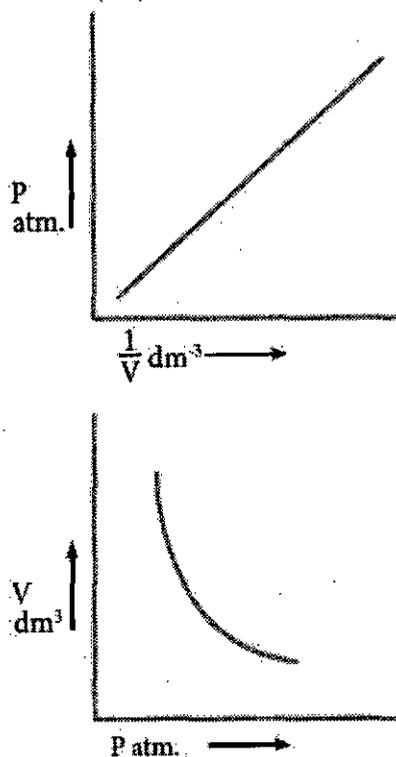


Figure. 6.2 Graphical representation of Boyle's law

The PV relationship can be understood as follows. The pressure is due to the force of the gas particles on the walls of the container. If a given amount of gas is compressed to half of its volume, the density is doubled and the number of particles hitting the unit area of the container will be doubled. Hence, the pressure would increase twofold.



Notes

Consequence of Boyle's law

The pressure-density relationship can be derived from the Boyle's law as shown below.

$$P_1V_1 = P_2V_2 \text{ (Boyle's law)}$$

$$P_1 \frac{m}{d_1} = P_2 \frac{m}{d_2}$$

where "m" is the mass, d₁ and d₂ are the densities of gases at pressure P₁ and P₂.

$$\frac{P_1}{d_1} = \frac{P_2}{d_2} \text{ (6.4)}$$

In other words, the density of a gas is directly proportional to pressure. All the passenger aeroplane cabins have to be artificially pressurised. do you know why?

Most commercial aeroplanes fly at about 30,000 feet altitude. The pressure decreases with the increase in altitude as there are fewer molecules per unit volume of air. Hence, while at air, the pressure around the aeroplane will be so low that one could pass out for lack of oxygen. For this reason, aeroplanes cabins are artificially pressurized.

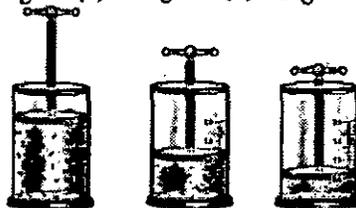


Similarly, the effect of drop in pressure is felt as a little pain in the ears by a person while ascending a mountain in a plain. Though the external pressure drops, the internal pressure within the ear cavities remains the same. This creates an imbalance. The greater internal pressure forces the eardrum to bulge outward causing pain. The excess air within the ear cavities escapes after some time and with the help of yawning and thereby equalizing the internal and external pressure to relieve the pain.

Underwater divers are advised not to hold the breath unnecessarily while diving. Do you know why?

In figure (6.3) let us find the missing parameters (volume in 6.3 (b) and pressure in 6.3(c))

Fig. 6.3(a) Fig. 6.3 (b) Fig. 6.3(c)



$P_1 = 1 \text{ atm.}$	$P_2 = 2 \text{ atm.}$	$P_3 = ? \text{ atm.}$
$V_1 = 1 \text{ dm}^3$	$V_2 = ? \text{ dm}^3$	$V_3 = 0.25 \text{ dm}^3$
$T = 298 \text{ K}$	$T = 298 \text{ K}$	$T = 298 \text{ K}$

Figure. 6.3 Effect of pressure on volume of the gas to verify Boyle's law



Notes

Solution:

According to Boyle's law, at constant temperature for a given mass of gas at constant temperature,

$$P_1V_1 = P_2V_2 = P_3V_3$$

$$1 \text{ atm} \times 1 \text{ dm}^3 = 2 \text{ atm} \times V_2 = P_3 \times 0.25 \text{ dm}^3$$

$$\square 2 \text{ atm} \times V_2 = 1 \text{ atm} \times 1 \text{ dm}^3$$

$$P_1V_1 = P_2V_2 = P_3V_3$$

$$1 \text{ atm} \times 1 \text{ dm}^3 = 2 \text{ atm} \times V_2 = P_3 \times 0.25 \text{ dm}^3$$

$$\therefore 2 \text{ atm} \times V_2 = 1 \text{ atm} \times 1 \text{ dm}^3$$

$$V_2 = \frac{1 \text{ atm} \times 1 \text{ dm}^3}{2 \text{ atm}}$$

$$\boxed{V_2 = 0.5 \text{ dm}^3}$$

$$\text{and } P_3 \times 0.25 \text{ dm}^3 = 1 \text{ atm} \times 1 \text{ dm}^3$$

$$P_3 = \frac{1 \text{ atm} \times 1 \text{ dm}^3}{0.25 \text{ dm}^3}$$

$$\boxed{P_3 = 4 \text{ atm}}$$

$$P_3 = 4 \text{ atm}$$

Charles Law (Volume-temperature relationship)

The relationship between volume of a gas and its temperature was examined by J. A. C. Charles. He observed that for a fixed mass of a gas at constant pressure, the volume is directly proportional to its temperature (K). Mathematically it can be represented as (at constant P and n)

$$\text{or } V = kT \text{ ----- (6.5)}$$

$$\text{or } V/T = \text{Constant}$$

If the temperature of the gas increases, the volume also increases in direct proportion, so that V/T is a constant.

For the same system at constant pressure, one can write

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{Constant} \text{ ----- (6.6)}$$

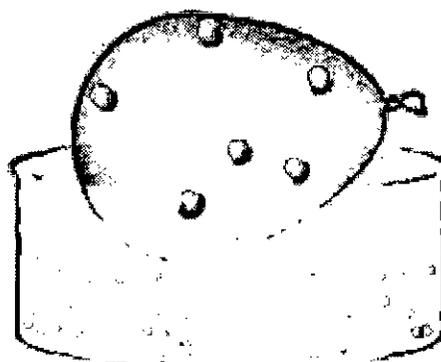
For example, if a balloon is moved from an ice-cold water bath to a boiling water bath, the temperature of the gas increases. As a result, the gas molecules inside the balloon move faster and gas expands. Hence, the volume increases.



Notes



Ice water



Boiling water

Figure. 6.4 Air filled balloon in ice cold and hot water

Variation of volume with temperature at constant pressure

The plot of the volume of the gas against its temperature at a given pressure is shown in the figure 6.5. From the graph it is clear that the volume of the gas linearly increases with temperature at a given pressure. Such lines are called isobars. It can be expressed by the following straight-line equation.

$V = mT + C$ where T is the temperature in degree Celsius and m & C are constants.

When $T = 0^\circ\text{C}$ the volume becomes V_0 . Hence, $V_0 = C$ and slope of the straight-line m is equal to $\Delta V / \Delta T$. Therefore, the above equation can be written in the following form.

$$V = \left(\frac{\Delta V}{\Delta T} \right) T + V_0 \text{ ----- (6.7)}$$

(n, P are constant)

Divide the equation 6.7 by V_0

$$\frac{V}{V_0} = \frac{1}{V_0} \left(\frac{\Delta V}{\Delta T} \right) T + 1 \text{ ----- (6.8)}$$

Charles and Gay Lussac found that under constant pressure, the relative increase in volume per degree increase in temperature is same for all gases. The relative increase in volume per $^\circ\text{C}$ (α) is equal to $1/V_0(\Delta V/\Delta T)$

Therefore

$$\begin{aligned} V &= \left(\frac{\Delta V}{\Delta T} \right) T + V_0 \\ V &= V_0 (\alpha T + 1) \text{ ----- (6.9)} \end{aligned}$$

Charles found that the coefficient of expansion is approximately equal to $1/273$. It means that at constant temperature for a given mass, for each degree rise in temperature, all gases expand by $1/273$ of their volume at 0°C

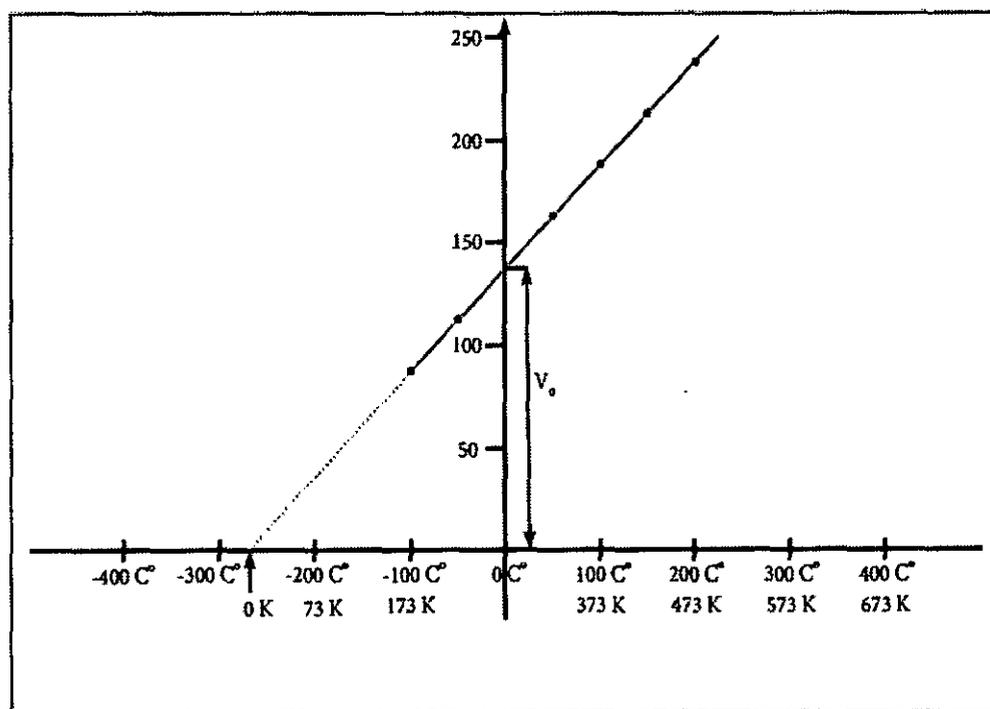
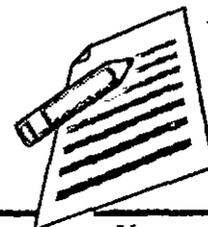


Figure. 6.5 Plot of volume vs temperature for an ideal gas

If we extrapolate the straight line in the figure 6.5 beyond the experimental measurements, the straight line intersects the temperature axis (x-axis) at -273.150°C . This shows that the volume of the gas becomes zero at -273.150°C , more precisely this temperature is -273.150°C . Beyond this temperature the gas would have a negative volume which is physically impossible. For this reason, this temperature was defined as absolute zero by Kelvin and he proposed a new temperature scale with absolute zero as starting point which is now called Kelvin scale. The only difference between the Kelvin scale of temperature and Celsius scale of temperature is that the zero position is shifted. The boiling and freezing point of water in both scales are given below.

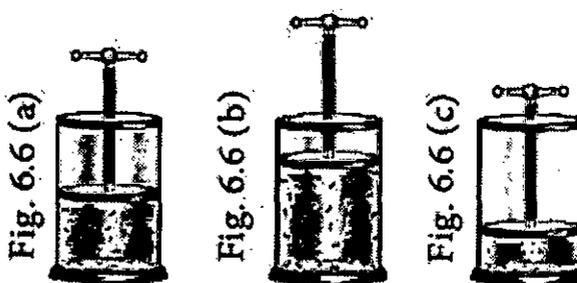
	Kelvin Scale	Celsius scale
Absolute Zero	0 K	-273.15°C
Freezing point of water	273.15 K	0°C
Boiling point of water	373.15 K	100°C

Example:

In figure 6.6 let us find the missing parameters (volume in 6.6 (b) and temperature in 6.6(c))



Notes



$P = 1 \text{ atm.}$ $P = 1 \text{ atm.}$ $P = 1 \text{ atm.}$
 $V_1 = 0.3 \text{ dm}^3$ $V_2 = ? \text{ dm}^3$ $V_3 = 0.15 \text{ dm}^3$
 $T_1 = 200 \text{ K}$ $T_2 = 300 \text{ K}$ $T_3 = ? \text{ K}$

Fig. 6.6. Effect of temperature on volume of the gas to verify Charles law

Solution:

According to Charles law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3}$$

$$\frac{0.3 \text{ dm}^3}{200 \text{ K}} = \frac{V_2}{300 \text{ K}} = \frac{0.15 \text{ dm}^3}{T_3}$$

$$\frac{V_2}{300 \text{ K}} = \frac{0.3 \text{ dm}^3}{200 \text{ K}}$$

$$V_2 = \frac{1.5}{200 \text{ K}} \times 0.3 \text{ dm}^3$$

$$V_2 = 0.45 \text{ dm}^3 \quad \text{and}$$

$$\frac{0.15 \text{ dm}^3}{T_3} = \frac{0.3 \text{ dm}^3}{200 \text{ K}}$$

$$T_3 = \frac{0.5}{0.15 \text{ dm}^3} \times 200 \text{ K}$$

$$T_3 = 100 \text{ K}$$

Gay-Lussac's Law (Pressure-temperature relationship)

Joseph Gay-Lussac stated that, at constant volume the pressure of a fixed mass of a gas is directly proportional to temperature.

$$P \propto T$$

$$\text{or } P/T = \text{Constant } k$$

If P_1 and P_2 are the pressures at temperatures T_1 and T_2 , respectively, then from Gay Lussac's law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Avogadro's Hypothesis

Avogadro hypothesised that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. The mathematical form of Avogadro's hypothesis may be expressed as

$$V \propto n$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{constant} \text{ ----- (6.10)}$$

where V_1 & n_1 are the volume and number of moles of a gas and V_2 & n_2 are a different set of values of volume and number of moles of the same gas at same temperature and pressure.

Ideal gas equation

The gaseous state is described completely using the following four variables T , P , V and n and their relationships were governed by the gas laws studied so far.

$$\text{Boyle's law } V \propto \frac{1}{P}$$

Charles law $V \propto T$

Avogadro's law $V \propto n$

We can combine these equations into the following general equation that describes the physical behaviour of all gases.

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

where, R is the proportionality constant called universal gas constant.

The above equation can be rearranged to give the ideal gas equation

$$PV = nRT. \text{ ----- (6.11)}$$

We already know that pressure is expressed in many different units (Table 6.1) hence it is important to know the values of gas constant R in different units as well.

We can calculate R using the equation,

$$R = \frac{PV}{nT}$$





Notes

For Conditions in which P is 1 atm., volume 22.414 dm³. for 1 mole at 273.15 K.

$$R = \frac{1 \text{ atm.} \times 22.414 \text{ dm}^3}{1 \text{ mol.} \times 273.15 \text{ K}}$$

$$= 0.0821 \text{ dm}^3 \text{ atm. mol}^{-1} \text{ K}^{-1}$$

Under standard conditions (STP) Where P = 1 bar (105 pascal), V = 22.71 × 10⁻³ m³ for 1 mole of a gas at 273.15 K

$$R = \frac{10^5 \text{ Pa} \times 22.71 \times 10^{-3} \text{ m}^3}{1 \text{ mol.} \times 273.15 \text{ K}}$$

$$= 8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^{-5} \text{ bar m}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^{-2} \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \times 10^{-2} \text{ bar L K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

The ideal gas equation is a relationship between four variables (P, V, T, n). Since it describes the state of any gas, it is referred to as the equation of state of gases.

Let us calculate the pressure exerted by 2 moles of sulphur hexafluoride in a steel vessel of volume 6 dm³ at 70 °C assuming it is an ideal gas.

We will use the ideal gas equation for this calculation as below:

$$P = \frac{nRT}{V} = \frac{2 \text{ mol} \times 0.0821 \text{ L atm. K}^{-1} \text{ mol}^{-1} \times (70 + 273 \text{ K})}{6 \text{ dm}^3}$$

$$= 9.39 \text{ atm.}$$

$$= 9.39 \text{ atm.}$$

Mixture of gases - Dalton's law of partial pressures

Studies of non-reacting gaseous mixtures showed that in a gaseous mixture each component behaves independently. For a gaseous mixture, it is important to know, how the pressure of individual component contributes to the total pressure of the mixture.

John Dalton stated that "the total pressure of a mixture of non-reacting gases is the sum of partial pressures of the gases present in the mixture" where the partial pressure of a component gas is the pressure that it would exert if it were present alone in the same volume and temperature. This is known as Dalton's law of partial pressures.

i.e., for a mixture containing three gases 1, 2 and 3 with partial pressures p₁, p₂ and p₃ in a container with volume V, the total pressure P total will be given by

$$P \text{ total} = p_1 + p_2 + p_3 \text{ ----- (6.12)}$$

Assuming that the gases behave ideally,



Notes

$$p_1 = n_1 \frac{RT}{V}; p_2 = n_2 \frac{RT}{V}; p_3 = n_3 \frac{RT}{V}$$

$$P_{\text{Total}} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V}$$

$$P_{\text{Total}} = n_{\text{Total}} \left(\frac{RT}{V} \right) \text{----- 6.13}$$

The partial pressure can also be expressed as

$$\left(\frac{RT}{V} \right) \text{ can be expressed as } \frac{P_1}{n_1} \text{ or } \frac{P_2}{n_2} \text{ or } \frac{P_3}{n_3}$$

$$\text{or in general } \frac{P_i}{n_i}$$

Therefore

$$P_{\text{Total}} = n_{\text{Total}} \frac{P_i}{n_i} = \frac{n_{\text{Total}}}{n_i} P_i$$

$$\Rightarrow P_i = \frac{n_i}{n_{\text{Total}}} P_{\text{Total}} = x_i P_{\text{Total}} \text{----- 6.14}$$

where x_i is the mole fraction of the i^{th} component.

Application of Dalton's law

In a reaction involving the collection of gas by downward displacement of water, the pressure of dry vapour collected can be calculated using Dalton's law.

P dry gas collected = ptotal - pwater vapour

pwater vapour is generally referred as aqueous tension and its values are available for air at various temperatures.

Let us understand Dalton's law by solving this problem. A mixture of gases contains 4.76 mole of Ne, 0.74 mole of Ar and 2.5 mole of Xe. Calculate the partial pressure of gases, if the total pressure is 2 atm. at a fixed temperature.

Solution:

$$P_{\text{Ne}} = x_{\text{Ne}} P_{\text{Total}}$$

$$x_{\text{Ne}} = \frac{n_{\text{Ne}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} \\ = \frac{4.76}{4.76 + 0.74 + 2.5} = 0.595$$

$$x_{\text{Ar}} = \frac{n_{\text{Ar}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} \\ = \frac{0.74}{4.76 + 0.74 + 2.5} = 0.093$$

$$x_{\text{Xe}} = \frac{n_{\text{Xe}}}{n_{\text{Ne}} + n_{\text{Ar}} + n_{\text{Xe}}} \\ = \frac{2.5}{4.76 + 0.74 + 2.5} = 0.312$$



$$\begin{aligned}
 P_{Ne} &= x_{Ne} P_{Total} = 0.595 \times 2 \\
 &= 1.19 \text{ atm.} \\
 P_{Ar} &= x_{Ar} P_{Total} = 0.093 \times 2 \\
 &= 0.186 \text{ atm.} \\
 P_{Xe} &= x_{Xe} P_{Total} = 0.312 \times 2 \\
 &= 0.624 \text{ atm.}
 \end{aligned}$$

Graham's Law of Diffusion

Gases have a tendency to occupy all the available space. When two non-reactive gases are allowed to mix, the gas molecules migrate from region of higher concentration to a region of lower concentration. This property of gas which involves the movement of the gas molecules through another gases is called diffusion. Effusion is another process in which a gas escapes from a container through a very small hole. The rate of diffusion or effusion is inversely proportional to the square root of molar mass. This statement is called Graham's law of diffusion/effusion.

$$\text{Mathematically, rate of diffusion} \propto \frac{1}{\sqrt{M}}$$

Otherwise

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \text{ ----- (6.15)}$$

When diffusing gases are at different pressures (P_A, P_B),

$$\frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} \text{ ----- (6.16)}$$

where r_A and r_B are the rates of diffusion of A and B and the M_A and M_B are their respective molar masses.

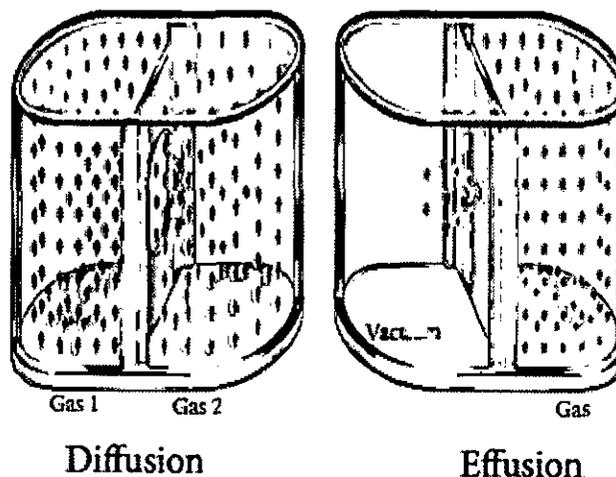


Figure. 6.7 Diffusion and effusion of gases



Notes

1. An unknown gas diffuses at a rate of 0.5 time that of nitrogen at the same temperature and pressure. Calculate the molar mass of the unknown gas

Solution:

$$\frac{\text{rate}_{\text{unknown}}}{\text{rate N}_2} = \sqrt{\frac{M_{\text{N}_2}}{M_{\text{unknown}}}}$$

$$0.5 = \sqrt{\frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}}$$

Squaring on both sides

$$(0.5)^2 = \frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}$$

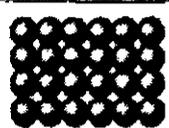
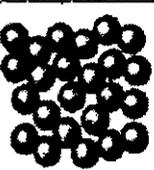
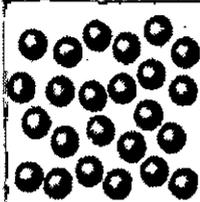
$$\Rightarrow M_{\text{unknown}} = \frac{28}{0.25} = 112 \text{ g mol}^{-1}$$

ted into liquid. You may learn more about this in higher classes.

Liquids State

1. Why do liquids not have shape?

According to the kinetic particle theory of matter the particles in liquids.

Physical States	Solid	Liquid	Gas
Arrangement of particles	Tightly packed Regular pattern	Loosely packed Low random arrangement	Far apart High random arrangement
Movement of particles	Vibrate on the spot	Move around each other	Move quickly in all directions
Diagram			

- Are not arranged in an orderly manner;
 - Are held together by weak forces of attraction;
 - Have more kinetic energy than the particles of solids;
 - Are free to move throughout the medium by colliding over each other.
2. Why do liquids have fixed volume?

The particles in liquids are slightly away from each other compared to solids. They are packed quite closer to each other. Moreover, the forces of attraction between them help to stay together. Thus, liquids cannot be compressed and they have fixed volume.



Liquid is one of the four primary states of matter, with the others being solid, gas and plasma. A liquid is a fluid. Unlike a solid, the molecules in a liquid have a much greater freedom to move. The forces that bind the molecules together in a solid are only temporary in a liquid, allowing a liquid to flow while a solid remains rigid.

A liquid, like a gas, displays the properties of a fluid. A liquid can flow, assume the shape of a container, and, if placed in a sealed container, will distribute applied pressure evenly to every surface in the container. If liquid is placed in a bag, it can be squeezed into any shape. Unlike a gas, a liquid is nearly incompressible, meaning that it occupies nearly a constant volume over a wide range of pressures; it does not generally expand to fill available space in a container but forms its own surface, and it may not always mix readily with another liquid. These properties make a liquid suitable for applications such as hydraulics.

Liquid particles are bound firmly but not rigidly. They are able to move around one another freely, resulting in a limited degree of particle mobility. As the temperature increases, the increased vibrations of the molecules cause distances between the molecules to increase. When a liquid reaches its boiling point, the cohesive forces that bind the molecules closely together break, and the liquid changes to its gaseous state (unless superheating occurs). If the temperature is decreased, the distances between the molecules become smaller. When the liquid reaches its freezing point, the molecules will usually lock into a very specific order, called crystallizing, and the bonds between them become more rigid, changing the liquid into its solid state (unless super cooling occurs).

Examples

Only two elements are liquid at standard conditions for temperature and pressure: mercury and bromine. Four more elements have melting points slightly above room temperature: francium, caesium, gallium and rubidium. Metal alloys that are liquid at room temperature include NaK, a sodium-potassium metal alloy, galinstan, a fusible alloy liquid, and some amalgams (alloys involving mercury).

Pure substances that are liquid under normal conditions include water, ethanol and many other organic solvents. Liquid water is of vital importance in chemistry and biology; it is believed to be a necessity for the existence of life.

Inorganic liquids include water, magma, inorganic nonaqueous solvents and many acids.

Important everyday liquids include aqueous solutions like household bleach, other mixtures of different substances such as mineral oil and gasoline, emulsions like vinaigrette or mayonnaise, suspensions like blood, and colloids like paint and milk.

Many gases can be liquefied by cooling, producing liquids such as liquid oxygen, liquid nitrogen, liquid hydrogen and liquid helium. Not all gases can be liquified at atmospheric pressure, however. Carbon dioxide, for example, can only be liquified at pressures above 5.1 atm.

Some materials cannot be classified within the classical three states of matter; they possess solid-like and liquid-like properties. Examples include liquid crystals, used in LCD displays, and biological membranes.

Applications

A lava lamp contains two immiscible liquids (a molten wax and a watery solution) which add movement due to convection. In addition to the top surface, surfaces also form between the liquids, requiring a tension breaker to recombine the wax droplets at the bottom.



Liquids have a variety of uses, as lubricants, solvents, and coolants. In hydraulic systems, liquid is used to transmit power.

In tribology, liquids are studied for their properties as lubricants. Lubricants such as oil are chosen for viscosity and flow characteristics that are suitable throughout the operating temperature range of the component. Oils are often used in engines, gear boxes, metalworking, and hydraulic systems for their good lubrication properties.

Many liquids are used as solvents, to dissolve other liquids or solids. Solutions are found in a wide variety of applications, including paints, sealants, and adhesives. Naphtha and acetone are used frequently in industry to clean oil, grease, and tar from parts and machinery. Body fluids are water-based solutions.

Surfactants are commonly found in soaps and detergents. Solvents like alcohol are often used as antimicrobials. They are found in cosmetics, inks, and liquid dye lasers. They are used in the food industry, in processes such as the extraction of vegetable oil.

Liquids tend to have better thermal conductivity than gases, and the ability to flow makes a liquid suitable for removing excess heat from mechanical components. The heat can be removed by channelling the liquid through a heat exchanger, such as a radiator, or the heat can be removed with the liquid during evaporation. Water or glycol coolants are used to keep engines from overheating. The coolants used in nuclear reactors include water or liquid metals, such as sodium or bismuth. Liquid propellant films are used to cool the thrust chambers of rockets. In machining, water and oils are used to remove the excess heat generated, which can quickly ruin both the work piece and the tooling. During perspiration, sweat removes heat from the human body by evaporating. In the heating, ventilation, and air-conditioning industry (HVAC), liquids such as water are used to transfer heat from one area to another.

Similarly, liquids are often used in cooking for their better heat-transfer properties. In addition to better conductivity, because warmer fluids expand and rise while cooler areas contract and sink, liquids with low kinematic viscosity tend to transfer heat through convection at a fairly constant temperature, making a liquid suitable for blanching, boiling, or frying. Even higher rates of heat transfer can be achieved by condensing a gas into a liquid. At the liquid's boiling point, all of the heat energy is used to cause the phase change from a liquid to a gas, without an accompanying increase in temperature, and is stored as chemical potential energy. When the gas condenses back into a liquid this excess heat-energy is released at a constant temperature. This phenomenon is used in processes such as steaming. Since liquids often have different boiling points, mixtures or solutions of liquids or gases can typically be separated by distillation, using heat, cold, vacuum, pressure, or other means. Distillation can be found in everything from the production of alcoholic beverages, to oil refineries, to the cryogenic distillation of gases such as argon, oxygen, nitrogen, neon, or xenon by liquefaction (cooling them below their individual boiling points).

Liquid is the primary component of hydraulic systems, which take advantage of Pascal's law to provide fluid power. Devices such as pumps and waterwheels have been used to change liquid motion into mechanical work since ancient times. Oils are forced through hydraulic pumps, which transmit this force to hydraulic cylinders. Hydraulics can be found in many applications, such as automotive brakes and transmissions, heavy equipment, and airplane control systems. Various hydraulic presses are used extensively in repair and manufacturing, for lifting, pressing, clamping and forming.

Liquids are sometimes used in measuring devices. A thermometer often uses the thermal expansion of liquids, such as mercury, combined with their ability to flow to indicate temperature. A manometer uses the weight of the liquid to indicate air pressure.



Physical Properties of Liquids

The most obvious physical properties of a liquid are its retention of volume and its conformation to the shape of its container. When a liquid substance is poured into a vessel, it takes the shape of the vessel, and, as long as the substance stays in the liquid state, it will remain inside the vessel. Furthermore, when a liquid is poured from one vessel to another, it retains its volume (as long as there is no vaporization or change in temperature) but not its shape. These properties serve as convenient criteria for distinguishing the liquid state from the solid and gaseous states. Gases, for example, expand to fill their container so that the volume they occupy is the same as that of the container. Solids retain both their shape and volume when moved from one container to another.

Liquids may be divided into two general categories: pure liquids and liquid mixtures. On Earth, water is the most abundant liquid, although much of the water with which organisms come into contact is not in pure form but is a mixture in which various substances are dissolved. Such mixtures include those fluids essential to life—blood, for example—beverages, and seawater. Seawater is a liquid mixture in which a variety of salts have been dissolved in water. Even though in pure form these salts are solids, in oceans they are part of the liquid phase. Thus, liquid mixtures contain substances that in their pure form may themselves be liquids, solids, or even gases.

The liquid state sometimes is described simply as the state that occurs between the solid and gaseous states, and for simple molecules this distinction is unambiguous. However, clear distinction between the liquid, gaseous, and solid states hold only for those substances whose molecules are composed of a small number of atoms. When the number exceeds about 20, the liquid may often be cooled below the true melting point to form a glass, which has many of the mechanical properties of a solid but lacks crystalline order. If the number of atoms in the molecule exceeds about 100–200, the classification into solid, liquid, and gas ceases to be useful. At low temperatures such substances are usually glasses or amorphous solids, and their rigidity falls with increasing temperature—i.e., they do not have fixed melting points; some may, however, form true liquids. With these large molecules, the gaseous state is not attainable, because they decompose chemically before the temperature is high enough for the liquid to evaporate. Synthetic and natural high polymers (e.g., nylon and rubber) behave in this way.

If the molecules are large, rigid, and either roughly planar or linear, as in cholesteryl acetate or *p*-azoxyanisole, the solid may melt to an anisotropic liquid (i.e., one that is not uniform in all directions) in which the molecules are free to move about but have great difficulty in rotating. Such a state is called a liquid crystal, and the anisotropy produces changes of the refractive index (a measure of the change in direction of light when it passes from one medium into another) with the direction of the incident light and hence leads to unusual optical effects. Liquid crystals have found widespread applications in temperature-sensing devices and in displays for watches and calculators. However, no inorganic compounds and only about 5 percent of the known organic compounds form liquid crystals. The theory of normal liquids is, therefore, predominantly the theory of the behaviour of substances consisting of simple molecules.

A liquid lacks both the strong spatial order of a solid, though it has the high density of solids, and the absence of order of a gas that results from the low density of gases—i.e., gas molecules are relatively free of each other's influence. The combination of high density and of partial order in liquids has led to difficulties in developing quantitatively acceptable



theories of liquids. Understanding of the liquid state, as of all states of matter, came with the kinetic molecular theory, which stated that matter consisted of particles in constant motion and that this motion was the manifestation of thermal energy. The greater the thermal energy of the particle, the faster it moved.

SUMMARY

As discovered by scientists, the matter is made up of very tiny particles and these particles are so small that we cannot see them with naked eyes. It has been observed that matter exists in nature in different forms. Some substances are rigid and have a fixed shape like wood and stone; some substances can flow and take the shape of their container like water, while there are forms of matter that do not have definite shape or size such as air. Thus, the matter can be classified into different categories based on the physical properties exhibited by them and the states in which they exist; these are called states of matter, Solid, Liquid, Gas. Apart from the above mentioned three, there are 2 more states of matter which we do not see in our everyday life. They are Plasma & Bose-Einstein condensate. Chemistry is the study of the composition of matter and its transformation. Another term often considered synonymous with matter is substance, but a substance has a more limited definition in chemistry. Chemistry deals with the study of behaviour of – matter Chemistry is concerned with the – Composition, structure and properties of matter and the phenomenon which occurs when different kinds of matter undergo changes. A liquid lack both the strong spatial order of a solid, though it has the high density of solids, and the absence of order of a gas that results from the low density of gases—i.e., gas molecules are relatively free of each other's influence. The combination of high density and of partial order in liquids has led to difficulties in developing quantitatively acceptable theories of liquids.

EXERCISE

MCQ

1. A container with a pin-hole contains equal moles of $H_2(g)$ and $O_2(g)$. Find the fraction of oxygen gas escaped at the same time when one-fourth of hydrogen gas escapes

- | | |
|------------|-----------|
| (a) $1/16$ | (b) $1/4$ |
| (c) $1/2$ | (d) $1/8$ |

Answer: (a)

2. What are the conditions for gas like Carbon monoxide to obey the ideal gas laws?

- (a) low temperature and low pressure
- (b) low temperature and high pressure
- (c) high temperature and low pressure
- (d) high temperature and high pressure

Answer: (c)

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3. If the temperature is doubled, the average velocity of a gaseous molecule increases by
- (a) 4 (b) 1.4
(c) 2 (d) 2.8
- Answer: (b)
4. Find the molecular mass of a gas that takes three times more time to effuse as compared to He with the same volume
- (a) 9 u (b) 64 u
(c) 27 u (d) 36 u
- Answer: (d)
5. At the same temperature, the average molar kinetic energy of N₂ and CO is
- (a) KE₁ > KE₂ (b) KE₁ < KE₂
(c) KE₁ = KE₂ (d) insufficient information given
- Answer: (c)
6. Find the temperature at which the rate of effusion of N₂ is 1.625 times to that of SO₂ at 500°
- (a) 620° (b) 173°
(c) 110° (d) 373°
- Answer: (a)
7. Find the change in the root mean square speed of the gas on raising the temperature from 27° to 927°
- (a) becomes times (b) gets doubled
(c) gets halved (d) remains same
- Answer: (b)
8. If 1.204×10^{21} molecules of H₂SO₄ are removed from 392 mg of H₂SO₄, find the moles of H₂SO₄ left.
- (a) 4×10^{-3} (b) 1.5×10^{-3}
(c) 1.2×10^{-3} (d) 2×10^{-3}
- Answer: (d)
9. Find the fraction of the total pressure exerted by hydrogen if it is mixed with ethane in an empty container at 25°
- (a) 15/16 (b) 1/16
(c) 1/2 (d) 1
- Answer: (a)

Review Questions

1. What is the volume occupied by one mole of a gas at STP (0°C , 1 bar pressure)?
2. The volume of a sample of a gas is 500 mL at a pressure of 1.5 atm. If the temperature is kept constant, what will be the volume of that gas at (i) 1 atm. (ii) 5.0 atm.
3. List the wrong assumptions of kinetic theory of gases which led to van der Waal's equation.
4. What is the standard temperature and pressure?
5. What is the lowest possible temperature?
6. CO_2 cannot be liquefied at 35°C , however large the pressure may be, Why?
7. A sample of nitrogen gas weighing 9.3 g at a pressure 0.99 atm occupies a volume of 12.4 litres when its temperature is 55K. What will be its volume when the temperature is 220 K? Assume pressure is kept constant.
8. Calculate the volume of one mole of oxygen at 27°C and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.
9. What is the Maxwell-Boltzmann Law?
10. Explain the following properties of liquids on the basis of their structure:
 - (i) Volume
 - (ii) Shape
 - (iii) Compressibility
 - (iv) Ability to flow
11. Why diffusion can occur in liquids. Explain.
12. Define
 - (i) vapour pressure and
 - (ii) boiling point.
13. Differentiate between evaporation and boiling

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Notes



Notes

6 SOLID STATES

- Understand the concept of solid.
- Discuss the properties of solid.
- Understand the classification of solid.
- Discuss the types of solids.

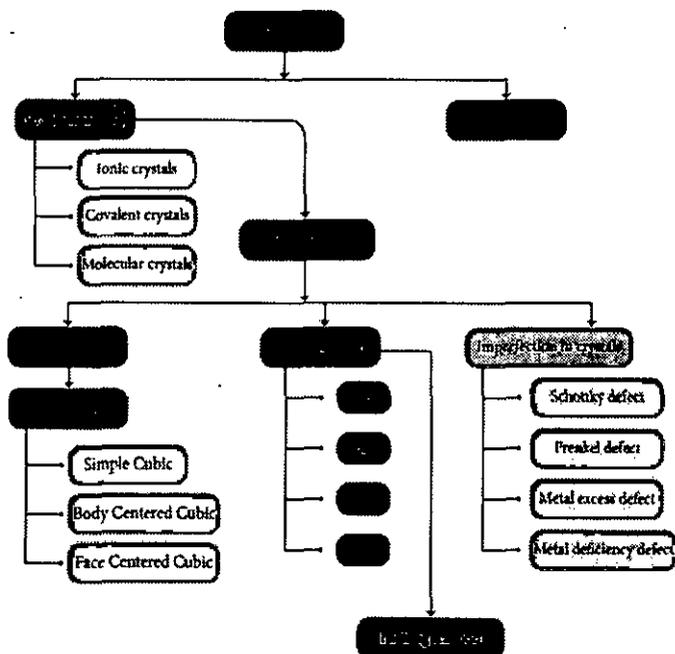
Objective of the Chapter:

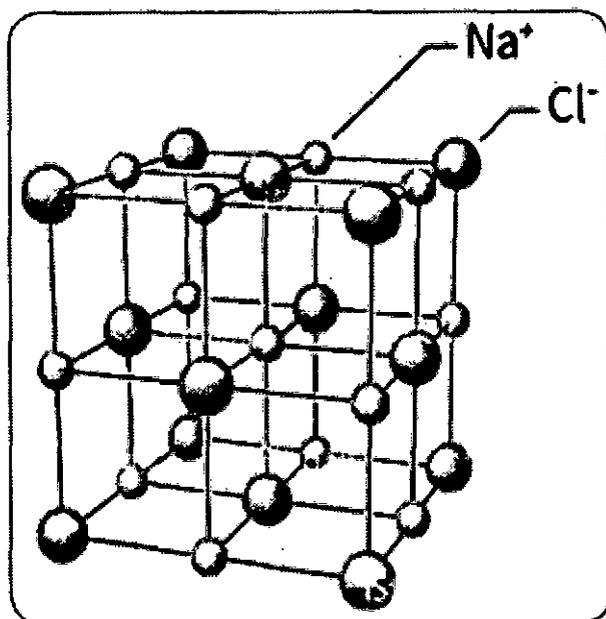
The basic objective of this chapter is to through some light on the initial concepts of solid state of matter so that the properties of solid state can be learned.

Introduction

Matter may exist in three different physical states namely solid, liquid and gas. If you look around, you may find mostly solids rather than liquids and gases. Solids differ from liquids and gases by possessing definite volume and definite shape. In the solids the atoms or molecules or ion are tightly held in an ordered arrangement and there are many types of solids such as diamond, metals, plastics etc., and most of the substances that we use in our daily life are in the solid state. We require solids with different properties for various applications. Understanding the relation between the structure of solids and their properties is very much useful in synthesizing new solid materials with different properties.

In this chapter, we study the characteristics of solids, classification, structure and their properties; we also discuss the crystal defects and their significance.



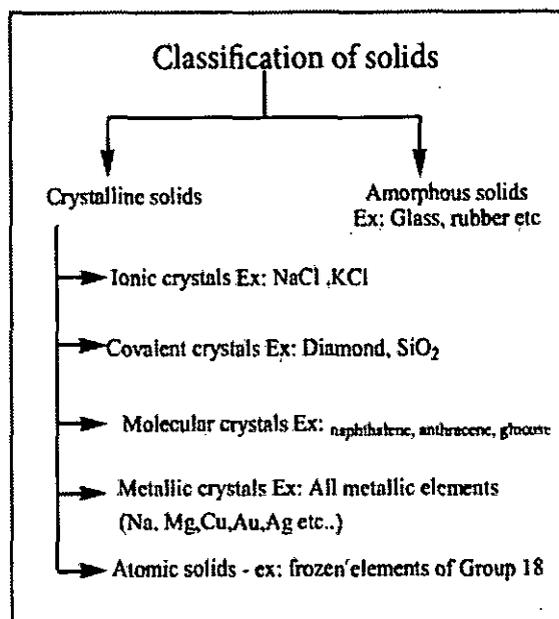


General characteristics of solids

We have already learnt that gas molecules move randomly without exerting reasonable forces on one another. Unlike gases, in solids the atoms, ions or molecules are held together by strong force of attraction. The general characteristics of solids are as follows,

- Solids have definite volume and shape.
- Solids are rigid and incompressible
- Solids have strong cohesive forces.
- Solids have short inter atomic, ionic or molecular distances.
- Their constituents (atoms , ions or molecules) have fixed positions and can only oscillate about their mean positions

Classification of solids:



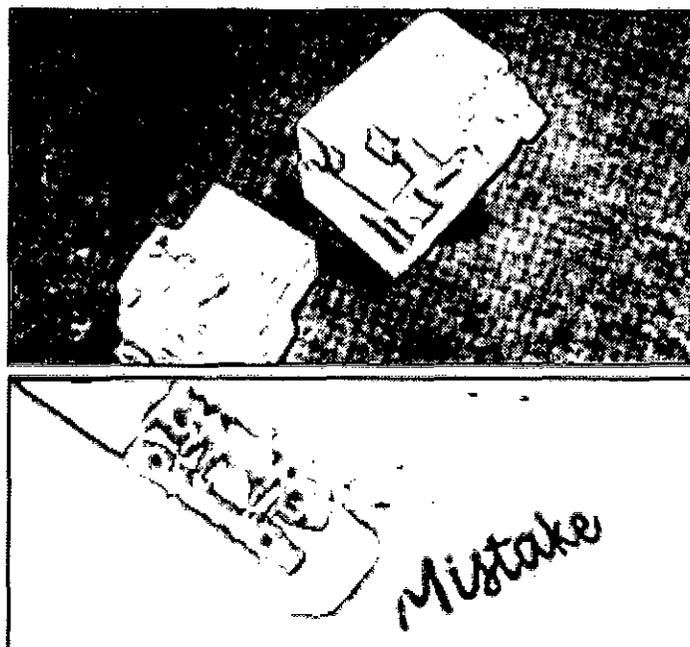


Notes

We can classify solids into the following two major types based on the arrangement of their constituents.

- (i) Crystalline solids
- (ii) Amorphous solids.

The term crystal comes from the Greek word "krystallos" which means clear ice. This term was first applied to the transparent quartz stones, and then the name is used for solids bounded by many flat, symmetrically arranged faces.



A crystalline solid is one in which its constituents (atoms, ions or molecules), have an orderly arrangement extending over a long range. The arrangement of such constituents in a crystalline solid is such that the potential energy of the system is at minimum. In contrast, in amorphous solids (In Greek, amorphous means no form) the constituents are randomly arranged.

The following table shows the differences between crystalline and amorphous solids.

S.no	Crystalline solids	Amorphous solids
1	Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
2	Definite shape	Irregular shape
3	Generally crystalline solids are anisotropic in nature	They are isotropic* like liquids
4	They are true solids	They are considered as pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded.
7	Examples: NaCl , diamond etc.,	Examples: Rubber , plastics, glass etc

Table 6.1 differences between crystalline and amorphous solids

Crystalline solids

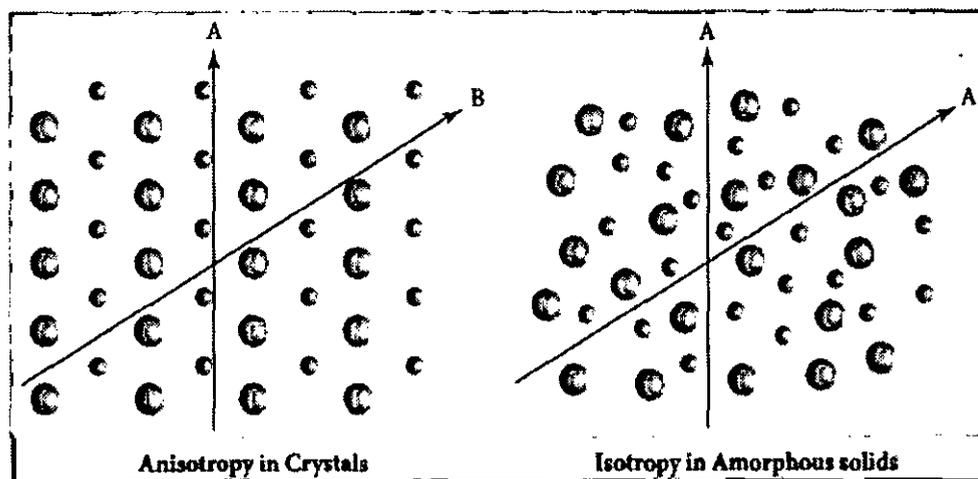
1. Long range orderly arrangement of constituents.
2. Definite shape
3. Generally crystalline solids are anisotropic in nature
4. They are true solids
5. Definite Heat of fusion
6. They have sharp melting points.
7. Examples: NaCl , diamond etc.,

Amorphous solids

1. Short range, random arrangement of constituents.
2. Irregular shape
3. They are isotropic* like liquids
4. They are considered as pseudo solids (or) super cooled liquids
5. Heat of fusion is not definite
6. Gradually soften over a range of temperature and so can be moulded.
7. Examples: Rubber , plastics, glass etc

*Isotropy

Isotropy means uniformity in all directions. In solid state isotropy means having identical values of physical properties such as refractive index, electrical conductance etc., in all directions, whereas anisotropy is the property which depends on the direction of measurement. Crystalline solids are anisotropic and they show different values of physical properties when measured along different directions. The following figure illustrates the anisotropy in crystals due to different arrangement of their constituents along different directions.



Classification of crystalline solids:

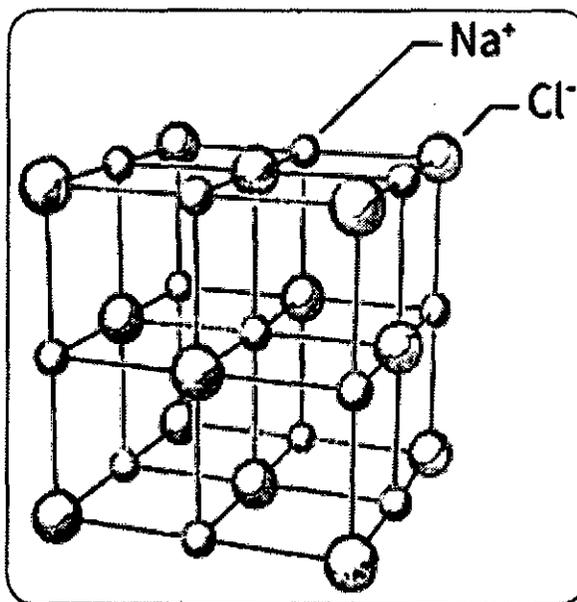
1. Ionic solids:

The structural units of an ionic crystal are cations and anions. They are bound together by strong electrostatic attractive forces. To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa. Ionic crystals possess definite





crystal structure; many solids are cubic close packed. Example: The arrangement of Na^+ and Cl^- ions in NaCl crystal.

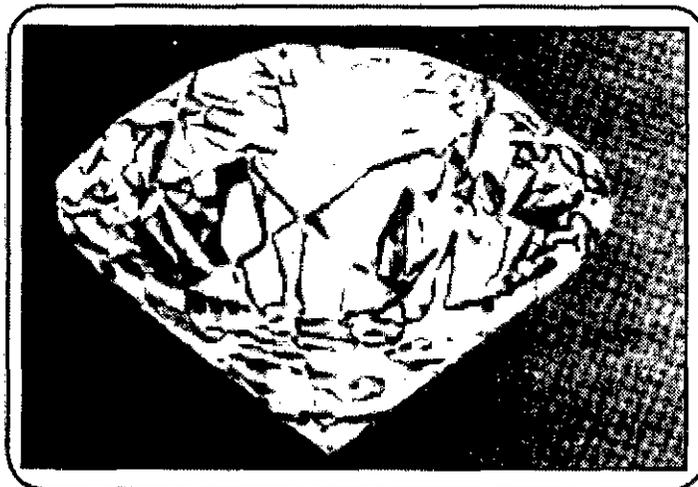


Characteristics:

- Ionic solids have high melting points.
- These solids do not conduct electricity, because the ions are fixed in their lattice positions.
- They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.
- They are hard as only strong external force can change the relative positions of ions.

2. Covalent solids:

In covalent solids, the constituents (atoms) are bound together in a three-dimensional network entirely by covalent bonds. Examples: Diamond, silicon carbide etc. Such covalent network crystals are very hard, and have high melting point. They are usually poor thermal and electrical conductors.





3. Molecular solids:

In molecular solids, the constituents are neutral molecules. They are held together by weak van der Waals forces. Generally molecular solids are soft and they do not conduct electricity. These molecular solids are further classified into three types.

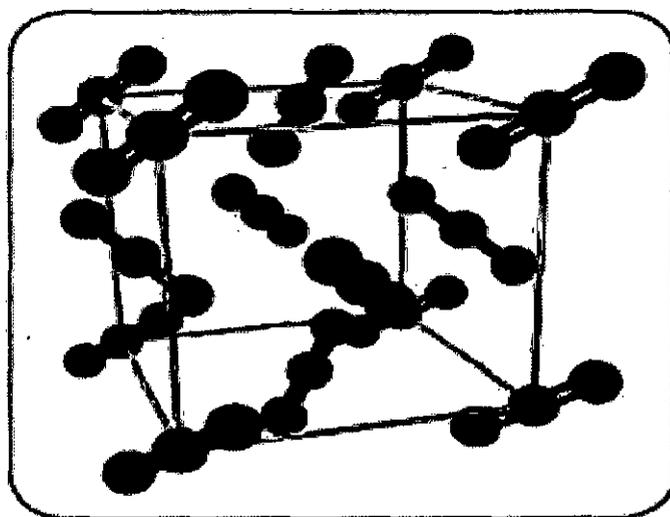
(i) Non-polar molecular solids:

In non-polar molecular solids constituent molecules are held together by weak dispersion forces or London forces.

They have low melting points and are usually in liquids or gaseous state at room temperature. Examples: naphthalene, anthracene etc.,

(ii) Polar molecular solids

The constituents are molecules formed by polar covalent bonds. They are held together by relatively strong dipole-dipole interactions. They have higher melting points than the non-polar molecular solids. Examples are solid CO_2 , solid NH_3 etc.



(iii) Hydrogen bonded molecular solids

The constituents are held together by hydrogen bonds. They are generally soft solids under room temperature. Examples: solid ice (H_2O), glucose, urea etc.,

3. Metallic solids:

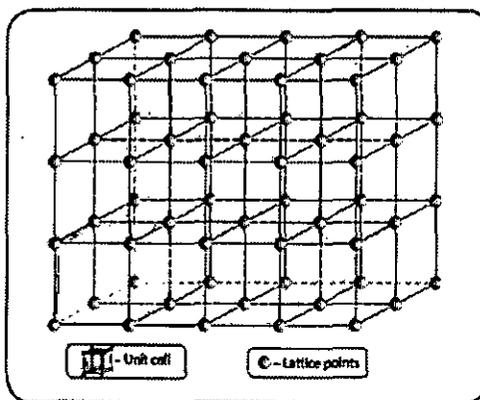
You have already studied in XI STD about the nature of metallic bonding. In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space. They are hard, and have high melting point. Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre. Examples: Metals and metal alloys belong to this type of solids, for example Cu, Fe, Zn, Ag, Au, Cu-Zn etc.

Crystal lattice and unit cell:

Crystalline solid is characterised by a definite orientation of atoms, ions or molecules, relative to one another in a three-dimensional pattern. The regular arrangement of these species throughout the crystal is called a crystal lattice. A basic repeating structural unit of a crystalline solid is called a unit cell. The following figure illustrates the lattice point and the unit cell.

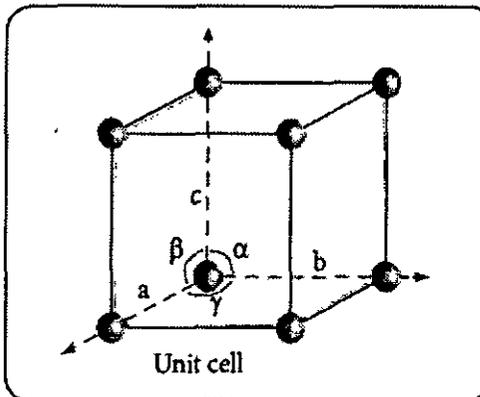


Notes



A crystal may be considered to consist of large number of unit cells, each one in direct contact with its nearer neighbour and all similarly oriented in space. The number of nearest neighbours that surrounding a particle in a crystal is called the coordination number of that particle.

A unit cell is characterised by the three edge lengths or lattice constants a , b and c and the angle between the edges α , and γ



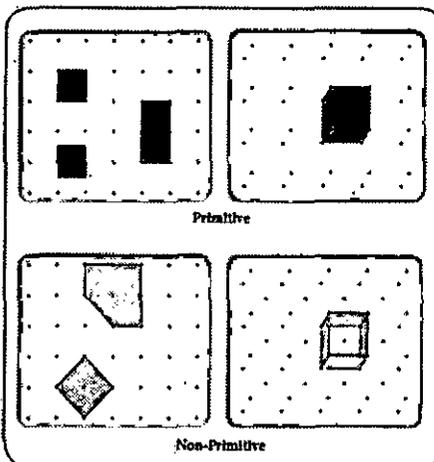
$$a \neq b \neq c$$

$$\alpha \neq \beta \neq \gamma$$

Primitive and non-primitive unit cell

There are two types of unit cells: primitive and non-primitive. A unit cell that contains only one lattice point is called a primitive unit cell, which is made up from the lattice points at each of the corners.

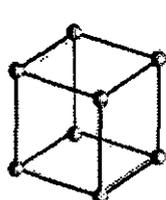
In case of non-primitive unit cells, there are additional lattice points, either on a face of the unit cell or with in the unit cell.



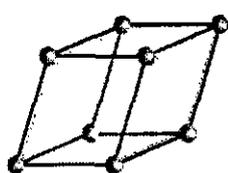


Notes

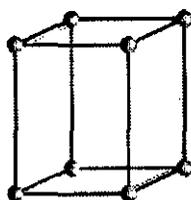
There are seven primitive crystal systems; cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral. They differ in the arrangement of their crystallographic axes and angles. Corresponding to the above seven, Bravais defined 14 possible crystal systems as shown in the figure.



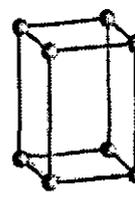
Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$



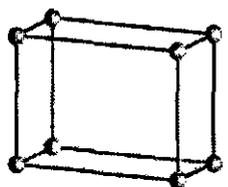
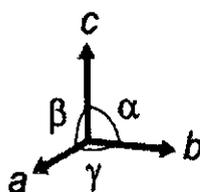
Rhombohedral
 $a = b = c$
 $\alpha = \beta = \gamma \neq 90^\circ$



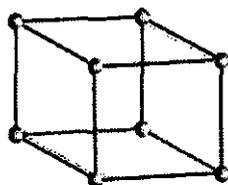
Hexagonal
 $a = b \neq c$
 $\alpha = \beta = 90^\circ, \gamma = 120^\circ$



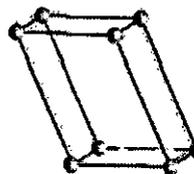
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



Monoclinic
 $a \neq b \neq c$
 $\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$



Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma \neq 90^\circ$

cubic	primitive	body centered	face centered
tetragonal	primitive	body centered	
hexagonal	primitive		
orthorhombic	primitive	body centered	face centered basis face centered
monoclinic	primitive		basis face centered
trigonal	primitive		
triclinic	primitive		

Table 6.2 14 Bravais Lattices



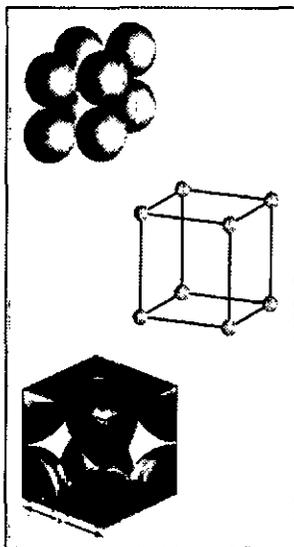
Notes

Number of atoms in a cubic unit cell:

1. Primitive (or) simple cubic unit cell.(SC)

In the simple cubic unit cell, each corner is occupied by an identical atoms or ions or molecules. And they touch along the edges of the cube, do not touch diagonally. The coordination number of each atom is 6.

Primitive (or) simple cubic unit cell.(SC)

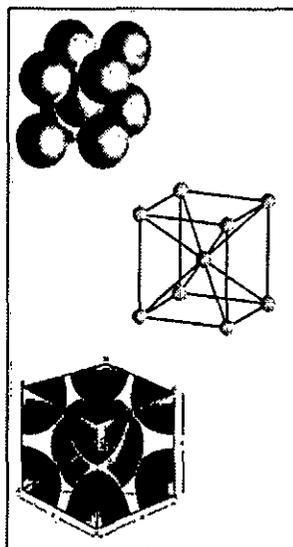


Each atom in the corner of the cubic unit cell is shared by 8 neighbouring unit cells and therefore atoms per unit cell is equal to $N_c/8$, where N_c is the number of atoms at the corners.

$$\begin{aligned} \therefore \text{no of atoms in a SC unit cell} &= \left(\frac{N_c}{8} \right) \\ &= \left(\frac{8}{8} \right) = 1 \end{aligned}$$

2. Body centered cubic unit cell. (BCC)

Body centered cubic unit cell. (BCC)



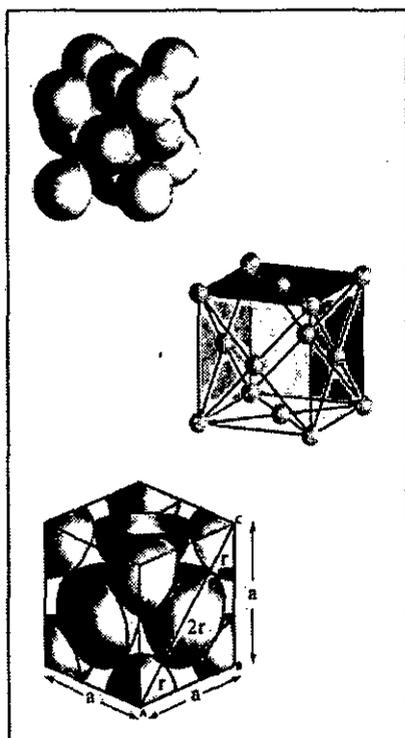


In a body centered cubic unit cell, each corner is occupied by an identical particle and in addition to that one atom occupies the body centre. Those atoms which occupy the corners do not touch each other, however they all touch the one that occupies the body centre. Hence, each atom is surrounded by eight nearest neighbours and coordination number is 8. An atom present at the body centre belongs to only to a particular unit cell i.e., unshared by another unit cell.

$$\begin{aligned} \therefore \text{Number of atoms in a bcc unit cell} &= \left(\frac{N_c}{8}\right) + \left(\frac{N_b}{1}\right) \\ &= \left(\frac{8}{8} + \frac{1}{1}\right) \\ &= (1+1) \\ &= 2 \end{aligned}$$

3. Face centered cubic unit cell.(FCC)

Face centered cubic unit cell.(FCC)



ni mots douna
not: 10/10

In a face centered cubic unit cell, identical atoms lie at each corner as well as in the centre of each face. Those atoms in the corners touch those in the faces but not each other. The atoms in the face centre are being shared by two-unit cells, each atom in the face centers makes (1/2) contribution to the unit cell.

$$\begin{aligned} \therefore \text{Number of atoms in a fcc unit cell} &= \left(\frac{N_c}{8}\right) + \left(\frac{N_f}{2}\right) \\ &= \left(\frac{8}{8} + \frac{6}{2}\right) \\ &= (1+3) \\ &= 4 \end{aligned}$$



Drawing the crystal lattice on paper is not an easy task. The constituents in a unit cell touch each other and form a three-dimensional network. This can be simplified by drawing crystal structure with the help of small circles (spheres) corresponding constituent particles and connecting neighbouring particles using a straight line as shown in the figure.

4. Calculations involving unit cell dimensions:

X-Ray diffraction analysis is the most powerful tool for the determination of crystal structure. The inter planar distance between two successive planes of atoms can be calculated using the following equation from the X-Ray diffraction data $2d\sin\theta = n\lambda$.

The above equation is known as Bragg's equation.

Where

λ is the wavelength of X-ray used for diffraction.

θ is the angle of diffraction

By knowing the values of θ , λ and n we can calculate the value of d .

$$d = n\lambda / 2\sin\theta$$

$$d = \frac{n\lambda}{2\sin\theta}$$

Using these values, the edge of the unit cell can be calculated.

5. Calculation of density:

Using the edge length of a unit cell, we can calculate the density (ρ) of the crystal by considering a cubic unit cell as follows.

$$\text{Density of the unit cell } \rho = \frac{\text{mass of the unit cell}}{\text{volume of the unit cell}} \quad \dots(1)$$

$$\text{mass of the unit cell} = \left\{ \begin{array}{l} \text{total number of} \\ \text{atoms belongs to} \\ \text{that unit cell} \end{array} \right\} \times \left\{ \begin{array}{l} \text{mass of} \\ \text{one atom} \end{array} \right\} \quad \dots(2)$$

$$\text{mass of one atom} = \frac{\text{molar mass (g mol}^{-1}\text{)}}{\text{Avagadro number (mol}^{-1}\text{)}}$$

$$m = \frac{M}{N_A} \quad \dots(3)$$

Substitute (3) in (2)

$$\text{mass of the unit cell} = n \times \frac{M}{N_A} \quad \dots(4)$$

For a cubic unit cell, all the edge lengths are equal i.e., $a=b=c$

$$\text{volume of the unit cell} = a \times a \times a = a^3 \quad \dots(5)$$

$$\therefore \text{Density of the unit cell } \rho = \frac{nM}{a^3 N_A} \quad \dots(6)$$

Equation (6) contains four variables namely ρ , n , M and a . If any three variables are known, the fourth one can be calculated.

Example 2

Barium has a body centered cubic unit cell with a length of 508pm along an edge. What is the density of barium in g cm^{-3} ?

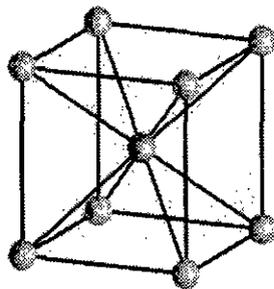


Solution:

In this case,

$n=2$; $M=137.3 \text{ gmol}^{-1}$; $a = 508\text{pm} = 5.08 \times 10^{-8}\text{cm}$

$$\rho = \frac{nM}{a^3 N_A}$$



In this case,

$n=2$; $M=137.3 \text{ gmol}^{-1}$; $a = 508\text{pm} = 5.08 \times 10^{-8}\text{cm}$

$$\rho = \frac{2 \text{ atoms} \times 137.3 \text{ g mol}^{-1}}{(5.08 \times 10^{-8} \text{ cm})^3 (6.023 \times 10^{23} \text{ atoms mol}^{-1})}$$

$$\rho = \frac{2 \times 137.3}{(5.08)^3 \times 10^{-24} \times 6.023 \times 10^{23}} \text{ g cm}^{-3}$$

$$\rho = 3.5 \text{ g cm}^{-3}$$

for unit a
to a g cm⁻³

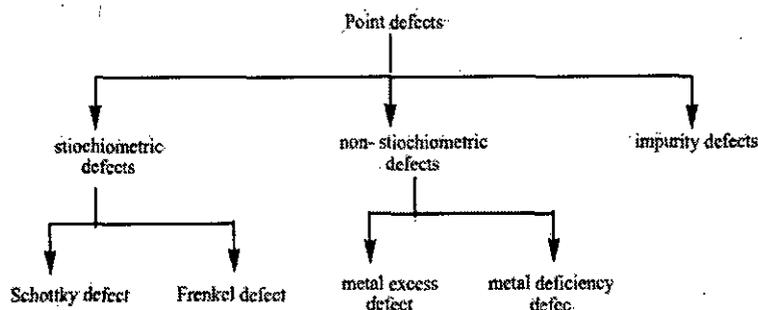
Imperfection in solids:

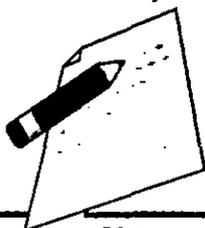
According to the law of nature nothing is perfect, and so crystals need not be perfect. They always found to have some defects in the arrangement of their constituent particles. These defects affect the physical and chemical properties of the solid and also play an important role in various processes. For example, a process called doping leads to a crystal imperfection and it increases the electrical conductivity of a semiconductor material such as silicon. The ability of ferromagnetic material such as iron, nickel etc., to be magnetized and demagnetized depends on the presence of imperfections. Crystal defects are classified as follows

- 1) Point defects
- 2) Line defects
- 3) Interstitial defects
- 4) Volume defects

In this portion, we concentrate on point defects, more specifically in ionic solids.

Point defects are further classified as follows



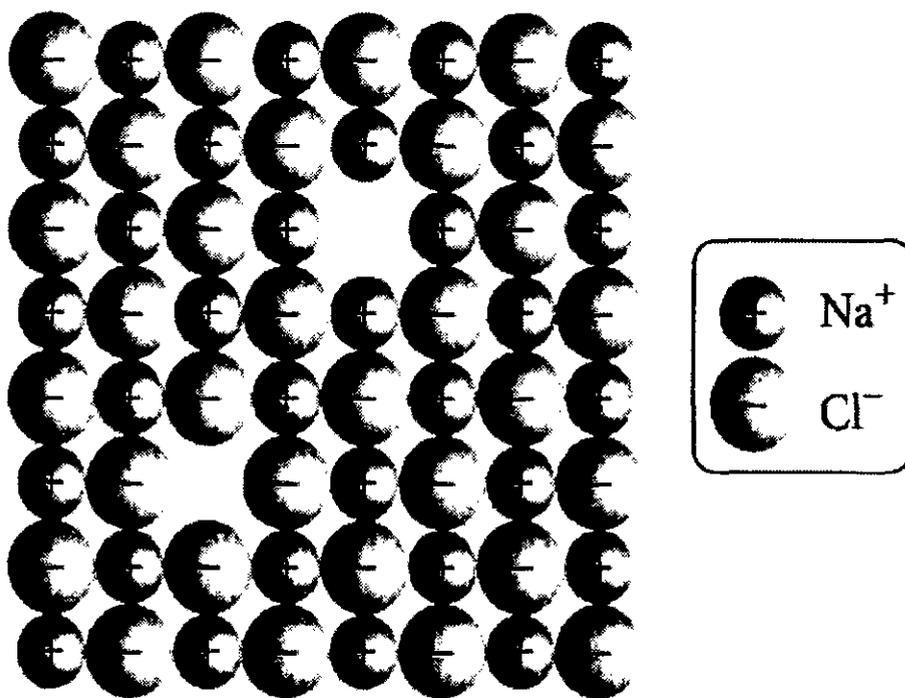


Stoichiometric defects in ionic solid:

This defect is also called intrinsic (or) thermodynamic defect. In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

1. Schottky defect:

Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice. This effect does not change the stoichiometry of the crystal. Ionic solids in which the cation and anion are of almost of similar size show Schottky defect. Example: NaCl.

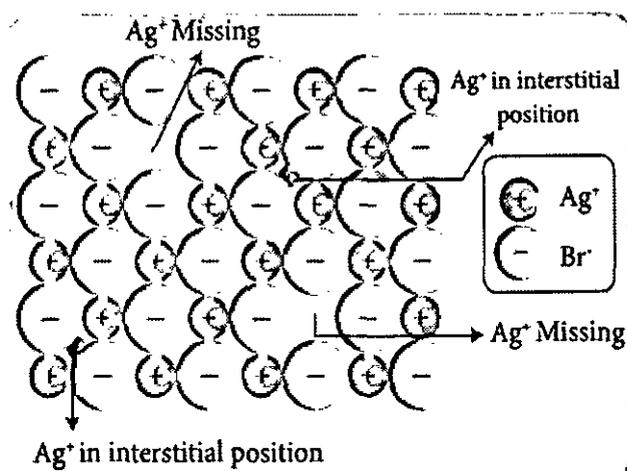


Schottky Defect

Presence of large number of Schottky defects in a crystal, lowers its density. For example, the theoretical density of vanadium monoxide (VO) calculated using the edge length of the unit cell is 6.5 g cm⁻³, but the actual experimental density is 5.6 g cm⁻³. It indicates that there is approximately 14% Schottky defect in VO crystal. Presence of Schottky defect in the crystal provides a simple way by which atoms or ions can move within the crystal lattice.

2. Frenkel defect:

Frenkel defect arises due to the dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position. This defect is shown by ionic solids in which cation and anion differ in size. Unlike Schottky defect, this defect does not affect the density of the crystal. For example, AgBr, in this case, small Ag⁺ ion leaves its normal site and occupies an interstitial position as shown in the figure.

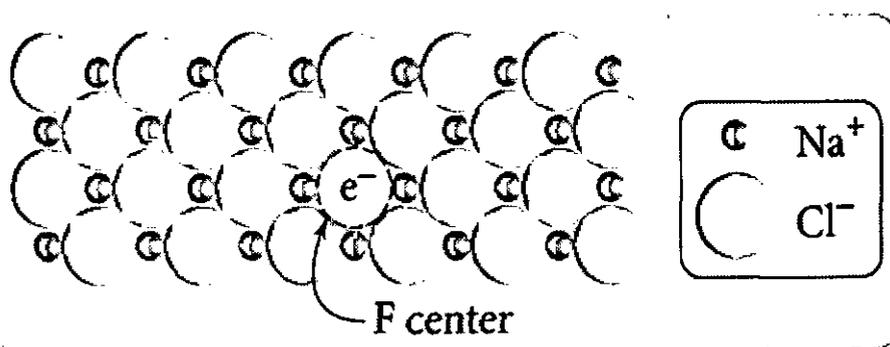


Frenkel Defect

3. Metal excess defect:

Metal excess defect arises due to the presence of more number of metal ions as compared to anions. Alkali metal halides NaCl, KCl show this type of defect.

The electrical neutrality of the crystal can be maintained by the presence of anionic vacancies equal to the excess metal ions (or) by the presence of extra caution and electron present in interstitial position.



Metal Excess Defect

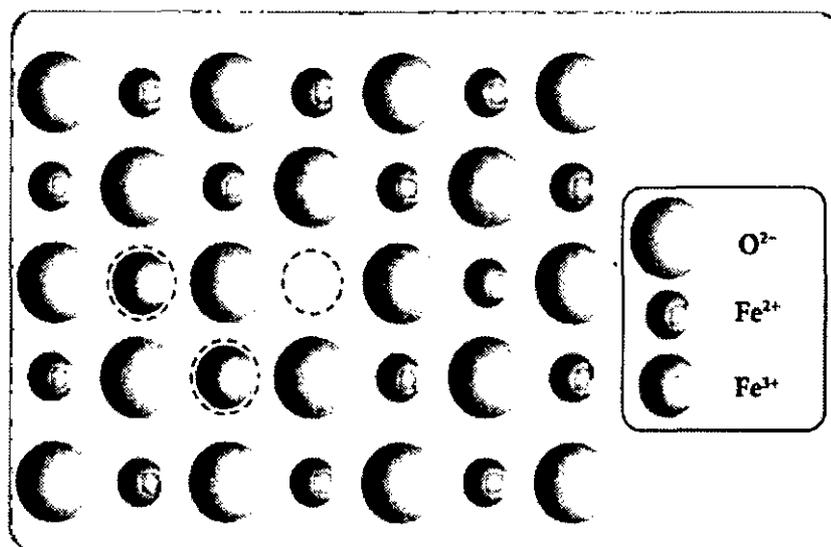
For example, when NaCl crystals are heated in the presence of sodium vapour, Na⁺ ions are formed and are deposited on the surface of the crystal. Chloride ions (Cl⁻) diffuse to the surface from the lattice point and combines with Na⁺ ion. The electron lost by the sodium vapour diffuse into the crystal lattice and occupies the vacancy created by the Cl⁻ ions. Such anionic vacancies which are occupied by unpaired electrons are called F centers. Hence, the formula of NaCl which contains excess Na⁺ ions can be written as Na_{1+x}Cl.

ZnO is colourless at room temperature. When it is heated, it becomes yellow in colour. On heating, it loses oxygen and thereby forming free Zn²⁺ ions. The excess Zn²⁺ ions move to interstitial sites and the electrons also occupy the interstitial positions.

4. Metal deficiency defect:

Metal deficiency defect arises due to the presence of less number of cations than the anions. This defect is observed in a crystal in which, the cations have variable oxidation states.

For example, in FeO crystal, some of the Fe²⁺ ions are missing from the crystal lattice.



Metal Deficiency Defect

To maintain the electrical neutrality, twice the number of other Fe^{2+} ions in the crystal is oxidized to Fe^{3+} ions. In such cases, overall number of Fe^{2+} and Fe^{3+} ions is less than the O^{2-} ions. It was experimentally found that the general formula of ferrous oxide is Fe_xO , where x ranges from 0.93 to 0.98.

5. Impurity defect:

A general method of introducing defects in ionic solids is by adding impurity ions. If the impurity ions are in different valance state from that of host, vacancies are created in the crystal lattice of the host. For example, addition of CdCl_2 to silver chloride yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag^+ . This will disturb the electrical neutrality of the crystal. In order to maintain the same, proportional number of Ag^+ ions leaves the lattice. This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

SUMMARY

Matter may exist in three different physical states namely solid, liquid and gas. If you look around, you may find mostly solids rather than liquids and gases. Solids differ from liquids and gases by possessing definite volume and definite shape. In the solids the atoms or molecules or ion are tightly held in an ordered arrangement and there are many types of solids such as diamond, metals, plastics etc., and most of the substances that we use in our daily life are in the solid state. We require solids with different properties for various applications. Understanding the relation between the structure of solids and their properties is very much useful in synthesizing new solid materials with different properties. According to the law of nature nothing is perfect, and so crystals need not be perfect. They always found to have some defects in the arrangement of their constituent particles. These defects affect the physical and chemical properties of the solid and also play an important role in various processes. For example, a process called doping leads to a crystal imperfection and it increases the electrical conductivity of a semiconductor material such as silicon. The ability of ferromagnetic material such as iron, nickel etc., to be magnetized and demagnetized depends on the presence of imperfections.

CLASS-12

Chemistry



Notes

7. Schottky defect in a crystal is observed when
- The ion leaves its normal position and occupies an interstitial location
 - the unequal number of cation and anions are missing from the lattice
 - the density of the crystal increases.
 - an equal number of cations and anions are missing from the lattice.

Answer: (d)

8. Copper crystalline in FCC with a unit cell length of 361pm. What is the radius of a copper atom?

- | | |
|----------|----------|
| a) 128pm | b) 157pm |
| c) 181pm | d) 108pm |

Answer: (a)

9. The total no of voids in 0.5 mol of a compound forming hexagonal close-packed structure are:

- | | |
|---------------------------|---------------------------|
| a) 6.022×10^{23} | b) 3.011×10^{23} |
| c) 9.033×10^{23} | d) 4.516×10^{23} |

Answer: (c)

10. For the orthorhombic system, axial ratios are $a \neq b \neq c$ and the axial angles are:

- | | |
|--------------------------------------------|--------------------------------------------------|
| a) $\alpha = \beta = \gamma \neq 90^\circ$ | b) $\alpha \neq \beta \neq \gamma \neq 90^\circ$ |
| c) $\alpha = \beta = \gamma = 90^\circ$ | d) $\alpha \neq \beta \neq \gamma = 90^\circ$ |

Answer: (c)

Review Questions

- Outline the differences between a crystalline and an amorphous solid.
- How can you classify solids on the basis of the nature of the forces between the constituent particles?
- What do you understand by the melting point of a solid? What information does it provide about the nature of interaction between the constituent particles of the solids?
- What do you understand by coordination number? What would be the coordination number of an ion occupying an octahedral void?
- Explain the following with the help of suitable examples.
 - Schottky defect
 - Frankel defect



Notes

7

SOLUTIONS

- Understand the concept of solutions.
- Discuss the properties of solutions.
- Understand the components of solutions.
- Discuss the types of solutions.

Objective of the Chapter:

The basic objective of this chapter is to through some light on the initial concepts of solutions so that the properties and types of solutions can be learned.

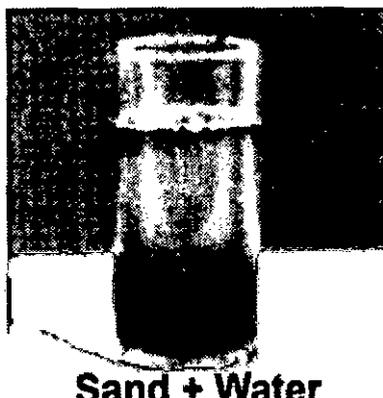
Introduction

You have learnt about mixtures in your lower classes. Most of the substances that we encounter in our daily life are mixtures of two or more substances. The substances present in a mixture may exist in one or more physical state. For example, when we burn wood, the smoke released is a mixture of solid carbon and gases like CO_2 , CO , etc.

In some cases of mixtures, their components can be separated easily whereas in some other cases they cannot be. Consider the two mixtures, one which contains salt and water, and another which contains sand and water. Water is the one of the components in both the mixtures. In the first case salt dissolves in water. In the second case the sand does not dissolve in water. Sand in water can be separated by filtration but salt cannot be separated as it dissolves in water to form a homogeneous mixture. These kinds of homogenous mixture are termed as "solutions".



Salt + water



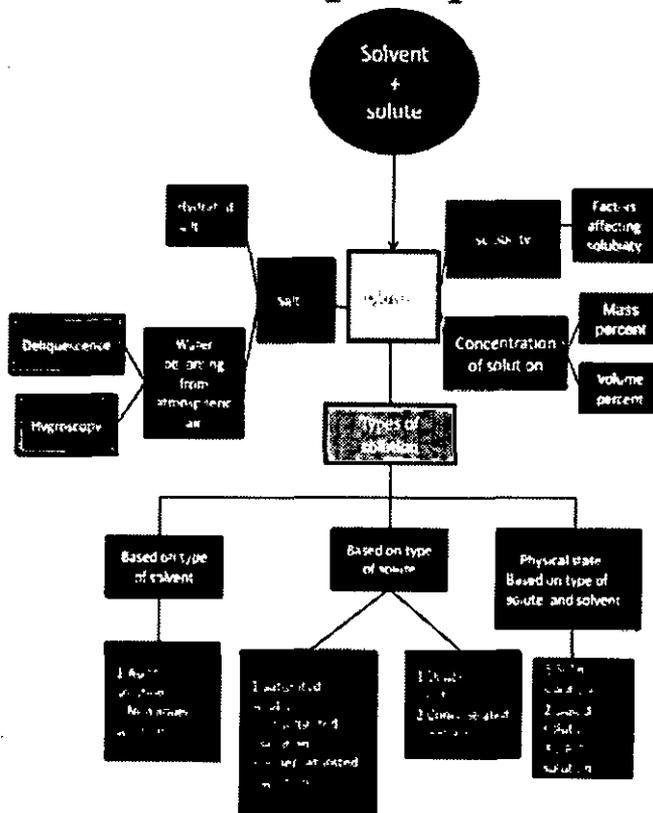
Sand + Water

Figure 9.1 Homogeneous and heterogeneous mixtures



Notes

Concept Map



Components of solutions

We know that, a solution is a homogeneous mixture of two or more substances. In a solution, the component which is present in lesser amount (by weight), is called solute and the component, which is present in a larger amount (by weight) is called solvent. The solute gets distributed uniformly throughout the solvent and thus forming the mixture homogeneous. So, the solvent acts as a dissolving medium in a solution. The process of uniform distribution of solute into solvent is called dissolution. Figure 9.2 shows the schematic representation of solution.

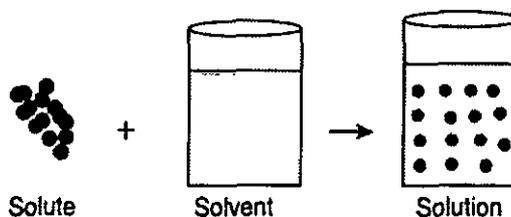
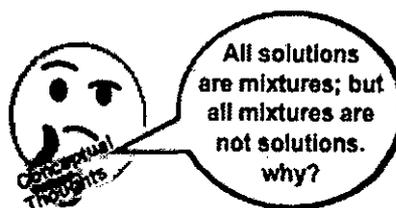


Figure 9.2 Formation of solution





A solution must at least be consisting of two components (a solute and a solvent). Such solutions which are made of one solute and one solvent (two components) are called binary solutions. e.g., On adding copper sulphate crystals to water, it dissolves in water forming a solution of copper sulphate as shown in Figure 9.3. It contains two components i.e., one solute- copper sulphate and one solvent-water. So, it is a binary solution. Similarly, a solution may contain more than two components. For example, if salt and sugar are added to water, both dissolve in water forming a solution. Here two solutes are dissolved in one solvent. Such kind of solutions which contain three components are called ternary solutions.

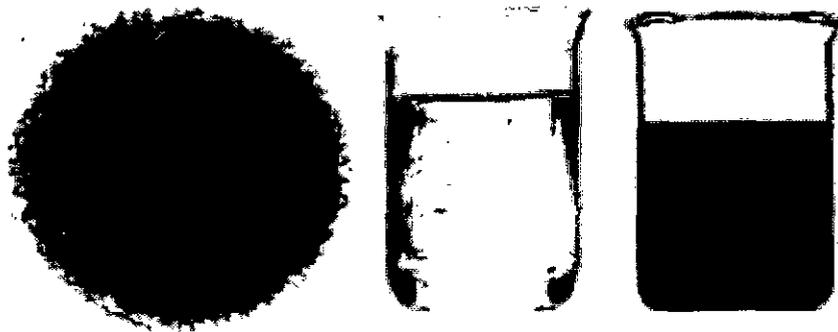


Figure 9.3 Formation of Copper sulphate solution

Types of Solutions

1. Based on the physical state of the solute and the solvent

We know that substances normally exist in three physical states (phases) i.e., solid, liquid and gas. In binary solutions, both the solvent and solute may exist in any of these physical states. But the solvent constitutes the major part of the solution. Its physical state is the primary factor which determine the characteristics of the solution. Therefore, there are different types of binary solutions as listed in Table 9.1.

Table 9.1 Types of binary solutions

Solute	Solvent	Example
Solid solution		
Solid	Solid	Copper dissolved in gold (Alloys)
Liquid	Solid	Mercury with sodium (amalgam)
Liquid solution		
Solid	Liquid	Sodium chloride dissolved in water
Liquid	Liquid	Ethyl alcohol dissolved in water
Gas	Liquid	carbon-di-oxide dissolved in water (Soda water)
Gaseous solution		
Liquid	Gas	Water vapour in air (cloud)
Gas	Gas	Mixture of Helium-Oxygen gases,



2. Based on the type of solvent

Most of the substances are soluble in water. That is why, water is called as 'Universal solvent'. However, some substances do not dissolve in water. Therefore, other solvents such as ethers, benzene, alcohols etc., are used to prepare a solution. On the basis of type of solvent, solutions are classified into two types. They are aqueous solutions and non-aqueous solutions.

a) Aqueous solution:

The solution in which water acts as a solvent is called aqueous solution. In general, ionic compounds are soluble in water and form aqueous solutions more readily than covalent compounds. E.g., Common salt in water, Sugar in water, Copper sulphate in water etc.

b) Non - Aqueous solution:

The solution in which any liquid, other than water, acts as a solvent is called non-aqueous solution. Solvent other than water is referred to as non-aqueous solvent. Generally, alcohols, benzene, ethers, carbon disulphide, acetone, etc., are used as non-aqueous solvents. Examples for non-aqueous solutions: Sulphur dissolved in carbon disulphide; Iodine dissolved in carbon tetrachloride.

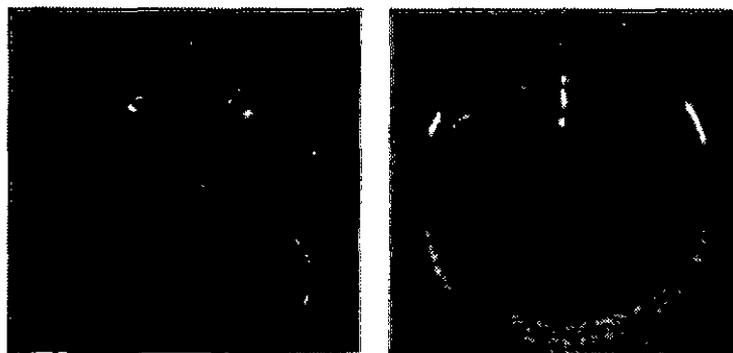


Figure 9.4 Sulphur in carbon-di-sulphide (Soluble), Sulphur in water (Insoluble)

3. Based on the amount of solute

The amount of the solute that can be dissolved in the given amount of solvent is limited under any given conditions. Based on the amount of solute, in the given amount of solvent, solutions are classified into the following types:

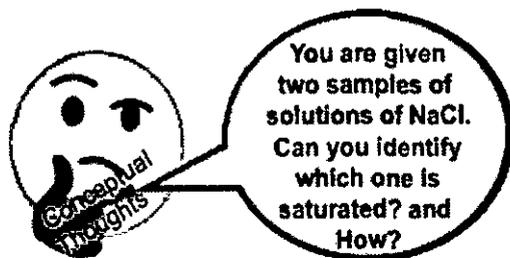
1. Saturated solution
2. Unsaturated solution
3. Super saturated solution

1. Saturated solution: A solution in which no more solute can be dissolved in a definite amount of the solvent at a given temperature is called saturated solution. e.g., 36 g of sodium chloride in 100 g of water at 25°C forms saturated solution.

Further addition of sodium chloride, leave it undissolved.

2. Unsaturated solution: Unsaturated solution is one that contains less solute than that of the saturated solution at a given temperature. e.g., 10 g or 20 g or 30 g of Sodium chloride in 100 g of water at 25°C forms an unsaturated solution.

3. Super saturated solution: Supersaturated solution is one that contains more solute than the saturated solution at a given temperature. e.g., 40 g of sodium chloride in 100 g of water at 25°C forms super saturated solution. This state can be achieved by altering any other conditions like temperature, pressure. Super saturated solutions are unstable, and the solute is reappearing as crystals when the solution is disturbed.



4. Concentrated and dilute solutions

It is another kind of classification of unsaturated solutions. It expresses the relative concentration of two solutions with respect to their solutes present in the given amount of the solvent. For example, you are given two cups of tea. When you taste them, you feel that one is sweeter than the other. What do you infer from it? The tea which is sweeter contains a higher amount of sugar than the other. How can you express your observation? You can say that the tea is stronger. But a chemist would say that it is 'concentrated'.

When we compare two having same solute and solvent in a solution, the one which contains a higher amount of solute per the given amount of solvent is said to be 'concentrated solution' and the other is said to be 'dilute solution'. They are schematically represented by Figure 9.5.

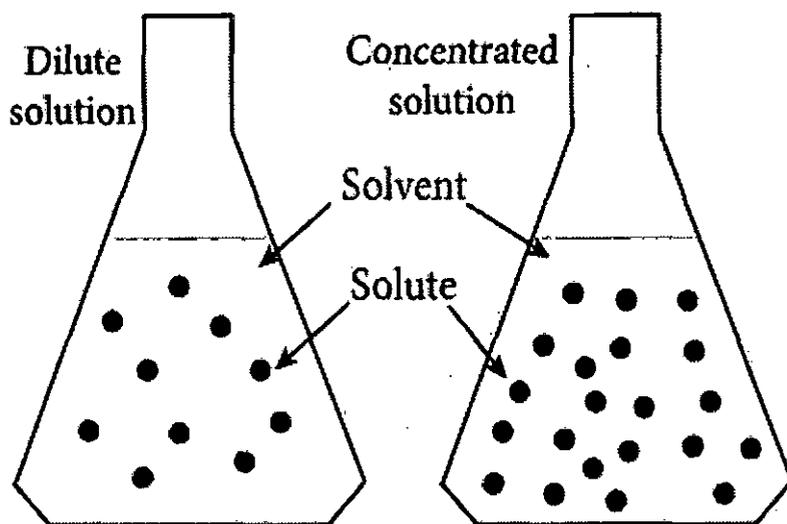


Figure 9.5 Dilute and Concentrated Solution

Differentiating solutions as dilute and concentrated is a qualitative representation. It does not imply the quantity of the solute. This difference is observed by means of some physical characteristics such as colour, density, etc.



Factors affecting solubility

There are three main factors which govern the solubility of a solute. They are: (i) Nature of the solute and solvent (ii) Temperature (iii) Pressure

Solubility

Usually, there is a limit to the amount of solute that can be dissolved in a given amount of solvent at a given temperature. When this limit is reached, we have a saturated solution and any excess solute that is added, simply resides at the bottom of the solution. The extent of dissolution of a solute in a solvent can be better explained by its solubility. Solubility is measure of how much of a solute can be dissolved in a specified amount of a solvent.

Solubility is defined as the number of grams of a solute that can be dissolved in 100 g of a solvent to form its saturated solution at a given temperature and pressure. For example, 36 g of sodium chloride need to be dissolved in 100 g of water to form its saturated solution at 25°C. Thus the solubility of NaCl in water is 36 g at 25°C. The solubility is mathematically expressed as

$$\text{Solubility} = \frac{\text{Mass of the solute}}{\text{Mass of the solvent}} \times 100$$

Table 9.2 Solubility's of some common substances in water at 25°C

Name of the solute	Formula of the solute	Solubility g/100 g water
Calcium carbonate	CaCO ₃ (s)	0.0013
Sodium chloride	NaCl (s)	36
Ammonia	NH ₃ (g)	48
Sodium hydroxide	NaOH(s)	80
Glucose	C ₆ H ₁₂ O ₆ (s)	91
Sodium bromide	NaBr(s)	95
Sodium iodide	NaI(s)	184

(i) Nature of the solute and solvent

The nature of the solute and solvent plays an important role in solubility. Although water dissolves an enormous variety of substances, both ionic and covalent, it does not dissolve everything. The phrase that scientists often use when predicting solubility is "like dissolves like." This expression means that dissolving occurs when similarities exist between the solvent and the solute. For example: Common salt is a polar compound and dissolves readily in polar solvent like water.



Non-polar compounds are soluble in non-polar solvents. For example, Fat dissolved in ether. But non-polar compounds, do not dissolve in polar solvents; polar compounds do not dissolve in non-polar solvents.

(ii) Effect of Temperature

Solubility of Solids in Liquid:

Generally, solubility of a solid solute in a liquid solvent increases with increase in temperature. For example, a greater amount of sugar will dissolve in warm water than in cold water.

In endothermic process, solubility increases with increase in temperature.

Solubility of Gases in liquid

Do you know why is it bubbling when water is boiled? Solubility of gases in liquid decrease with increase in temperature. Generally, water contains dissolved oxygen. When water is boiled, the solubility of oxygen in water decreases, so oxygen escapes in the form of bubbles.

Aquatic animals live more in cold regions because, more amount of dissolved oxygen is present in the water of cold regions. This shows that the solubility of oxygen in water is more at low temperatures.

(iii) Effect of Pressure

Effect of pressure is observed only in the case of solubility of a gas in a liquid. When the pressure is increased, the solubility of a gas in liquid increases.

The common examples for solubility of gases in liquids are carbonated beverages, i.e. soft drinks, household cleaners containing aqueous solution of ammonia, formalin- aqueous solution of formaldehyde, etc.

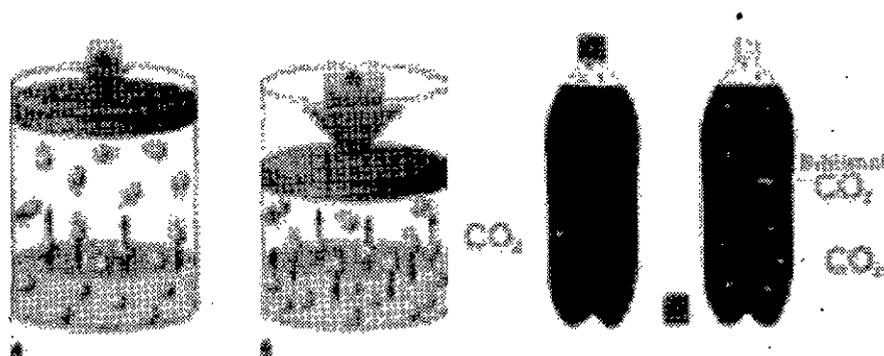


Figure 9.6 Effect of pressure on solubility

Concentration of a Solution

So far, we discussed what is a solution? what does it consist of and its types. Most of the chemical reactions take place in solutions form. So it is essential to quantify the solute in solvent to study the reactions. To quantify the solute in a solution, we can use the term "concentration".

Concentration of a solution may be defined as the amount of solute present in a given amount of solution or solvent.



Notes

Quantitatively, concentration of a solution may be expressed in different methods. But here, we shall discuss percentage by mass (% mass) and percentage by volume (% volume).

1. Mass percentage

Mass percentage of a solution is defined as the percentage by mass of the solute present in the solution. It is mostly used when solute is solid and solvent is liquid.

$$\text{Mass Percentage} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

$$\text{Mass Percentage} = \frac{\text{Mass of the solute}}{\text{Mass of the solute} + \text{Mass of the solvent}} \times 100$$

For example: 5% sugar solution (by mass) means 5 g of sugar in 95 g of water. Hence it is made 100g of solution.

Usually, mass percentage is expressed as w/w (weight / weight); mass percentage is independent of temperature.

2. Volume percentage

Volume percentage is defined as the percentage by volume of solute (in ml) present in the given volume of the solution.

$$\text{Volume Percentage} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$

$$\text{Volume Percentage} = \frac{\text{Volume of the solute}}{\text{Volume of the solute} + \text{volume of the solvent}} \times 100$$

For example, 10% by volume of the solution of ethanol in water, means 10 ml of ethanol in 100 ml of solution (or 90 ml of water)

Usually volume percentage is expressed as v/v (volume / volume). It is used when both the solute and solvent are liquids. Volume percentage decreases with increases in temperature, because of expansion of liquid.

You can notice that in the commercial products that we come across in our daily life such as a solution of syrups, mouth wash, antiseptic solution, household disinfectants etc., the concentration of the ingredients is expressed as v/v. Similarly, in ointments, antacid, soaps, etc., the concentration of solutions are expressed as w/w.

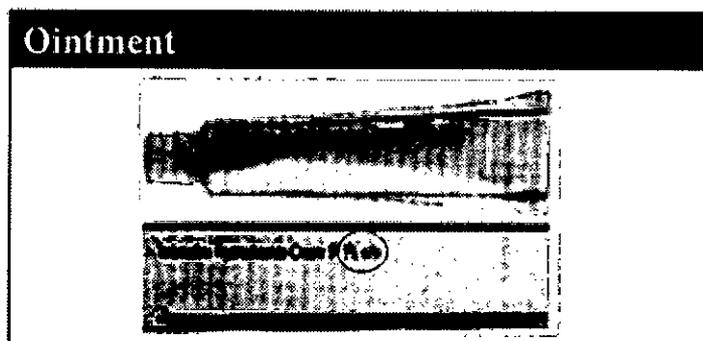


Figure 9.7 Ointment (w/w percent)



Hydrated salts and Water of Crystallization

When ionic substances are dissolved in water to make their saturated aqueous solution, their ions attract water molecules which then attached chemically in certain ratio. This process is called hydration. These ionic substances crystallize out from their saturated aqueous solution with a definite number of molecules of water. The number of water molecules found in the crystalline substance is called water of crystallization. Such salts are called hydrated salts.

On heating these hydrated crystalline salts, they lose their water of crystallization and become amorphous or lose their colour (if they are coloured). Table 9.3 shows some common hydrated salts:

Table 9.3 Hydrated salts

Common Name	IUPAC Name	Molecular Formula
Blue Vitriol	Copper (II) sulphate pentahydrate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Epsom Salt	Magnesium sulphate heptahydrate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Gypsum	Calcium sulphate dihydrate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Green Vitriol	Iron (II) sulphate heptahydrate	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
White Vitriol	Zinc sulphate heptahydrate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

1. Copper sulphate pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Blue vitriol)

The number of water molecules in blue vitriol is five. So its water of crystallization is 5. When blue coloured copper sulphate crystals are gently heated, it loses its five water molecules and becomes colourless anhydrous copper sulphate.

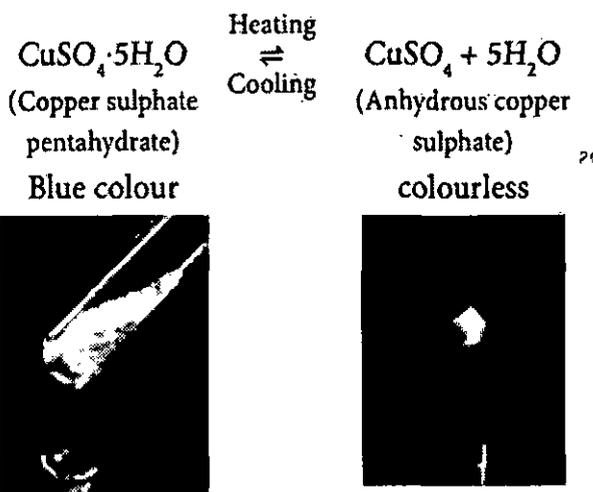


Figure 9.8 Copper sulphate heating before and after



Notes

If you add few drops of water or allow it to cool, the colourless anhydrous salt again turns back into blue coloured hydrated salt.

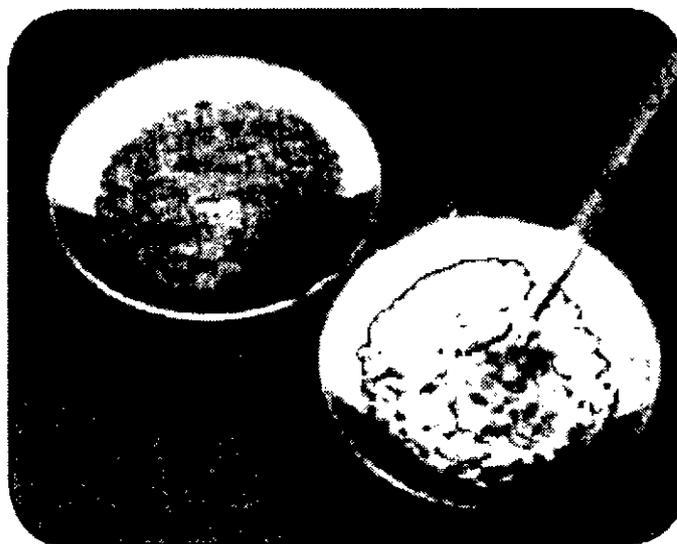
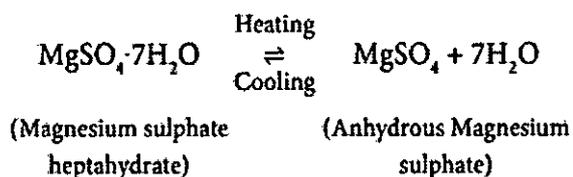


Figure 9.9 Hydrated copper sulphate and anhydrous copper sulphate

2. Magnesium sulphate heptahydrate $MgSO_4 \cdot 7H_2O$ (Epsom salt)

Its water of crystallization is 7. When magnesium sulphate heptahydrate crystals are gently heated, it loses seven water molecules, and becomes anhydrous magnesium sulphate.



If you add few drops of water or allow it to cool, the colourless anhydrous salt again turns back into hydrated salt.

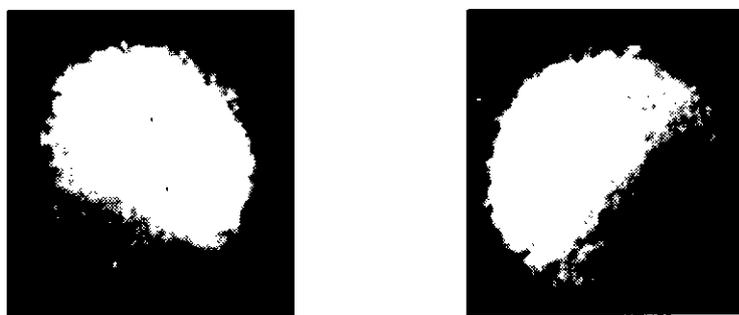


Figure 9.10 Crystalline hydrated salt, Amorphous anhydrous salt



Hygroscopy

Certain substances, when exposed to the atmospheric air at ordinary temperature, absorb moisture without changing their physical state. Such substances are called hygroscopic substances and this property is called hygroscopy.

Hygroscopic substances are used as drying agents.

Example:

1. Conc. Sulphuric acid (H_2SO_4).
2. Phosphorus Pentoxide (P_2O_5).
3. Quick lime (CaO).
4. Silica gel (SiO_2).
5. Anhydrous calcium chloride ($CaCl_2$).

Deliquescence

Certain substances which are so hygroscopic, when exposed to the atmospheric air at ordinary temperatures, absorb enough water and get completely dissolved. Such substances are called deliquescent substances and this property is called deliquescence.

Deliquescent substances lose their crystalline shape and ultimately dissolve in the absorbed water forming a saturated solution.

Deliquescence is maximum when:

- 1) The temperature is low
- 2) The atmosphere is humid

Examples: Calcium chloride ($CaCl_2$), Caustic soda ($NaOH$), Caustic potash (KOH) and Ferric chloride ($FeCl_3$).

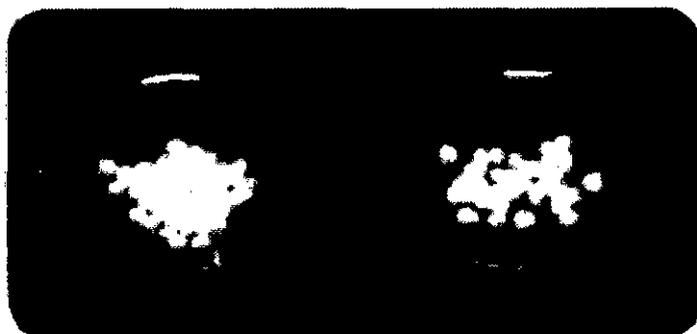


Figure 9.7 Deliquescence in Sodium hydroxide

Table 9.3 Difference between hygroscopic substances and deliquescence.

Hygroscopic substances	Deliquescence substances
When exposed to the atmosphere at ordinary temperature, they absorb moisture and do not dissolve.	When exposed to the atmospheric air at ordinary temperature, they absorb moisture and dissolve.
Hygroscopic substances do not change its physical state on exposure to air.	Deliquescent substances change its physical state on exposure to air.
Hygroscopic substances may be amorphous solids or liquids.	Deliquescent substances are crystalline solids.



Notes

SUMMARY

Most of the substances that we encounter in our daily life are mixtures of two or more substances. The substances present in a mixture may exist in one or more physical state. For example, when we burn wood, the smoke released is a mixture of solid carbon and gases like CO_2 , CO , etc. In some cases of mixtures, their components can be separated easily whereas in some other cases they cannot be. Consider the two mixtures, one which contains salt and water, and another which contains sand and water. Water is the one of the components in both the mixtures. In the first case salt dissolves in water. In the second case the sand does not dissolve in water. Sand in water can be separated by filtration but salt cannot be separated as it dissolves in water to form a homogeneous mixture. These kinds of homogenous mixture are termed as "solutions". When ionic substances are dissolved in water to make their saturated aqueous solution, their ions attract water molecules which then attached chemically in certain ratio. This process is called hydration. These ionic substances crystallize out from their saturated aqueous solution with a definite number of molecules of water. The number of water molecules found in the crystalline substance is called water of crystallization. Such salts are called hydrated salts. On heating these hydrated crystalline salts, they lose their water of crystallization and become amorphous or lose their colour (if they are coloured).

EXERCISE

MCQ

1. The mole fraction of the solute in one molal aqueous solution is

a) 0.009	b) 0.018
c) 0.027	d) 0.036
2. 5 cm^3 of acetone is added to 100 cm^3 of water, the vapour pressure of water over the solution will be
 - a) equal to the vapour pressure of pure water.
 - b) less than the vapour pressure of pure water.
 - c) greater than the vapour pressure of pure water.
 - d) very large.
3. The density of a solution prepared by dissolving 129 g of urea in 1000 g of water is 1.15 g/ml . The molarity of this solution is

a) 1.78M	b) 1.02M
c) 2.05M	d) 0.50M

Answer: (b)

Answer: (b)

Answer: (c)

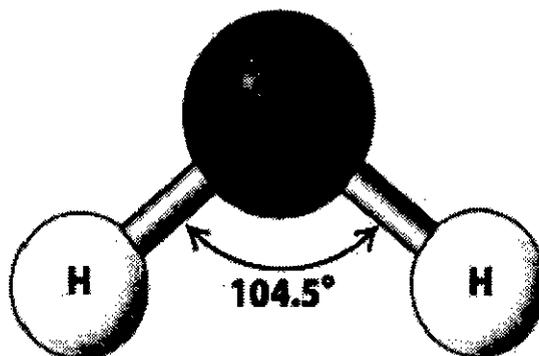


Notes

Compounds of Hydrogen

Water

Water is one of the most abundant compounds of hydrogen and our earth's surface contains approximately 70 % of ocean which is the major source of water. However, sea water contains many dissolved salts hence it cannot be used directly. Water is essential for all living things and our body contains about 65% water.



Ortho-H₂O and Para-H₂O

Water exists in the interstellar clouds, in proto-planetary disks, in the comets and icy satellites of the solar system. In particular, the ortho-to-para ratio (OPR) of water in space has recently received attention. Like hydrogen, water can also be classified into ortho-H₂O, in which the spin directions of the nuclei of the hydrogen atoms are parallel, and para-H₂O, in which the directions are antiparallel. At the temperature conditions of the earth (300 K), the OPR of H₂O is 3. However, at low temperatures (< 50 K) the amount of para-H₂O increases. It is known that the OPR of water in interstellar clouds and comets has more para-H₂O (OPR = 2.5) than on Earth.

Physical Properties:

Water is a colourless and volatile liquid. The peculiar properties of water in the condensed phases are due to the presence of inter molecular hydrogen bonding between water molecules. Hydrogen bonding is responsible for the high melting and boiling points of water. Some of the physical parameters of water are listed in Table 4.2.

Table 4.2 Properties of water, heavy water and super heavy water[†].

Property	H ₂ O	D ₂ O	T ₂ O
Molecular weight	18.015	22.028	22.0312
Melting point (K)	273.0	276.8	277.5
Boiling point (K)	373.0	374.4	374.5
Temperature of maximum density (K)	277.0	284.2	286.4
Maximum density (g/cm ³)	1.000	1.106	1.215
Density (g/cm ³)	0.997	1.104	1.214
Vapour pressure (mm Hg)	23.75	20.51	19.80
Viscosity (cP)	0.890	1.107	---
Dielectric constant	78.39	78.06	---
Enthalpy of formation (kJ/mol)	-285.9	-294.6	---
Enthalpy of vaporization (kJ/mol)	40.66	41.61	---

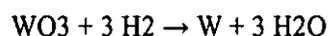
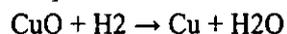
[†]Unless otherwise stated, all data are at 298 K.



2. It can be used to manufacture the industrial solvent, methanol from carbon monoxide using copper as catalyst.



3. Unsaturated fatty oils can be converted into saturated fats called Vanaspati (margarine) by the reduction reaction with Pt/H₂.
4. In metallurgy, hydrogen can be used to reduce many metal oxides to metals at high temperatures.



5. Atomic hydrogen and oxy-hydrogen torches are used for cutting and welding.
6. Liquid hydrogen is used as a rocket fuel.
7. Hydrogen is also used in fuel cells for generating electrical energy. The reversible uptake of hydrogen in metals is also attractive for rechargeable metal hydride battery.

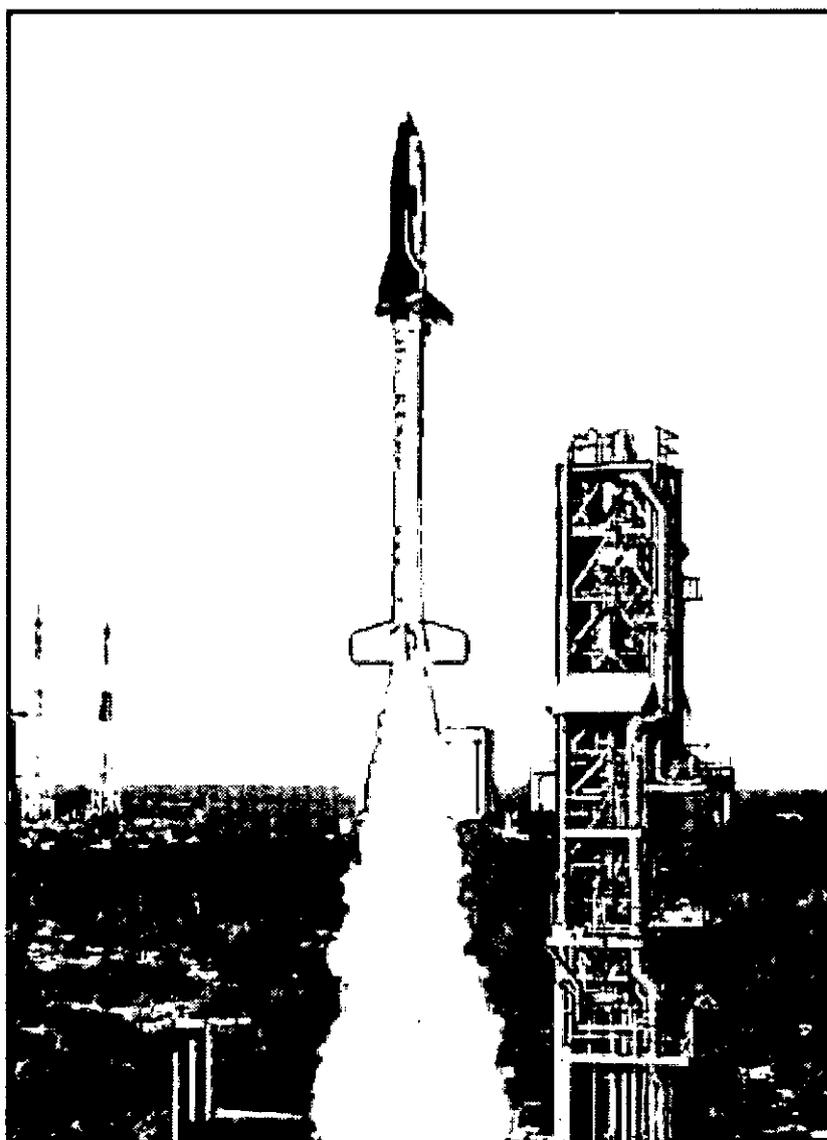
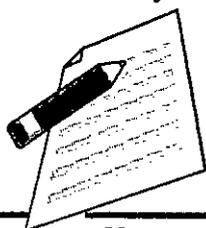


Figure 4.3: Application of rocket fuel

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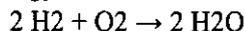
Chemistry



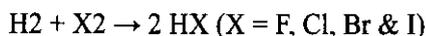
Notes

Chemical Properties:

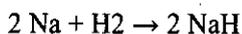
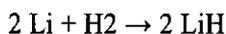
Hydrogen reacts with oxygen to give water. This is an explosive reaction and releases lot of energy. This is used in fuel cells to generate electricity.



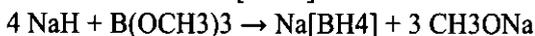
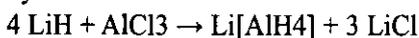
Similarly, hydrogen also reacts with halogens to give corresponding halides. Reaction with fluorine takes place even in dark with explosive violence while with chlorine at room temperature under light. It combines with bromine on heating and reaction with iodine is a photochemical reaction.



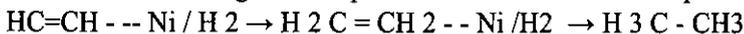
In the above reactions the hydrogen has an oxidation state of +1. It also has a tendency to react with reactive metals such as lithium, sodium and calcium to give corresponding hydrides in which the oxidation state of hydrogen is -1.



These hydrides are used as reducing agents in synthetic organic chemistry. It is used to prepare other important hydrides such as lithium aluminium hydride and sodium boro hydride.

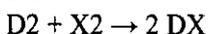
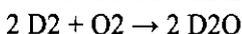


Hydrogen itself acts as a reducing agent. In the presence of finely divided nickel, it adds to the unsaturated organic compounds to form saturated compounds.



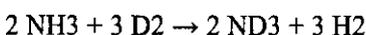
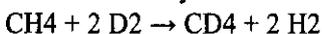
Chemical properties of Deuterium

Like hydrogen, deuterium also reacts with oxygen to form deuterium oxide called heavy water. It also reacts with halogen to give corresponding halides.



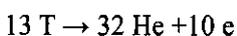
Deuterium exchange reactions:

Deuterium can replace reversibly hydrogen in compounds either partially or completely depending upon the reaction conditions. These reactions occur in the presence of deuterium or heavy water.



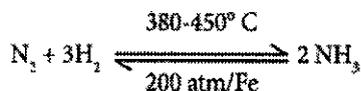
Properties of Tritium

It is a β -emitter with a half-life period of 12.3 years .



Uses of hydrogen

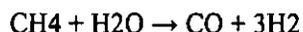
- Over 90 % hydrogen produced in industry is used for synthetic applications. One such process is Haber process which is used to synthesis ammonia in large scales. Ammonia is used for the manufacture of chemicals such as nitric acid, fertilizers and explosives.



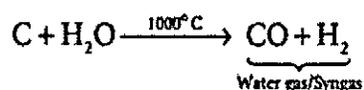


Industrial Production

In the large-scale, hydrogen is produced by steam-reforming of hydrocarbons. In this method hydrocarbon such as methane is mixed with steam and passed over nickel catalyst in the range 800-900 °C and 35 atm pressures.

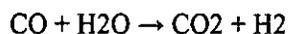


In an another process, steam is passed over a red-hot coke to produce carbon monoxide and hydrogen. The mixture of gases produced in this way is known as water gas (CO+H₂). This is also called syngas (Synthetic gas) as it is used in the synthesis of organic compounds such as methanol and simple hydrocarbons.

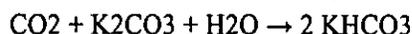


Conversion of Carbon monoxide in water gas to Carbon dioxide:

The carbon monoxide of the water gas can be converted to carbon dioxide by mixing the gas mixture with more steam at 400°C and passed over a shift converter containing iron/copper catalyst. This reaction is called as water-gas shift reaction.



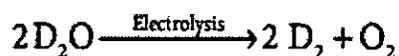
The CO₂ formed in the above process is absorbed in a solution of potassium carbonate.



Preparation of Deuterium:

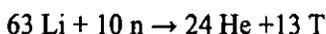
Electrolysis of heavy water:

Normal water contains 1.6 x 10⁻⁴ percentage of heavy water. The dissociation of protium water (H₂O) is more than heavy water (D₂O). Therefore, when water is electrolysed, hydrogen is liberated much faster than D₂. The electrolysis is continued until the resulting solution becomes enriched in heavy water. Further electrolysis of the heavy water gives deuterium.



Preparation of Tritium:

As explained earlier the tritium is present only in trace amounts. So it can be artificially prepared by bombarding lithium with slow neutrons in a nuclear fission reactor. The nuclear transmutation reaction for this process is as follows.



Properties of Hydrogen

Physical Properties:

Hydrogen is a colourless, odourless, tasteless, lightest and highly flammable gas. It is a non-polar diatomic molecule. It can be liquefied under low temperature and high pressure. Hydrogen is a good reducing agent. Various physical constants of hydrogen molecule are listed in Table 4.1.

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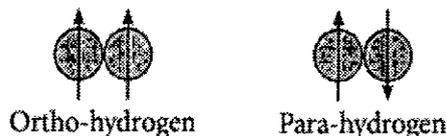
Chemistry



Notes

Ortho- and Para-Hydrogen:

In the hydrogen atom, the nucleus has a spin. When molecular hydrogen is formed, the spins of two hydrogen nuclei can be in the same direction or in the opposite direction as shown in the figure. These two forms of hydrogen molecules are called ortho and para hydrogens respectively.

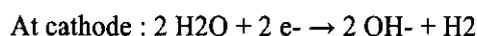
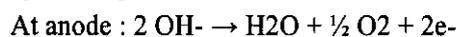


At room temperature, normal hydrogen consists of about 75% orthoform and 25% paraform. As the ortho-form is more stable than para-form, the conversion of one isomer into the other is a slow process. However, the equilibrium shifts in favour of para hydrogen when the temperature is lowered. The para-form can be catalytically transformed into ortho-form using platinum or iron. Alternatively, it can also be converted by passing an electric discharge, heating above 800°C and mixing with paramagnetic molecules such as O₂, NO, NO₂ or with nascent/atomic hydrogen.

Ortho and para hydrogen are similar in chemical properties but differ in some of the physical properties. For example, the melting point of para hydrogen is 13.83 K while that of ortho-H₂ 13.95 K; boiling point of para hydrogen is 20.26 K while that of ortho hydrogen 20.39 K. Since the nuclear spins are in opposite directions the magnetic moment of para hydrogen is zero and ortho hydrogen has magnetic moment twice that of a proton.

Preparation of Hydrogen

High purity hydrogen (>99.9 %) is obtained by the electrolysis of water containing traces of acid or alkali or the electrolysis of aqueous solution of sodium hydroxide or potassium hydroxide using a nickel anode and iron cathode. However, this process is not economical for large-scale production.



Laboratory Preparation

Hydrogen is conveniently prepared in laboratory by the reaction of metals, such as zinc, iron, tin with dilute acid.

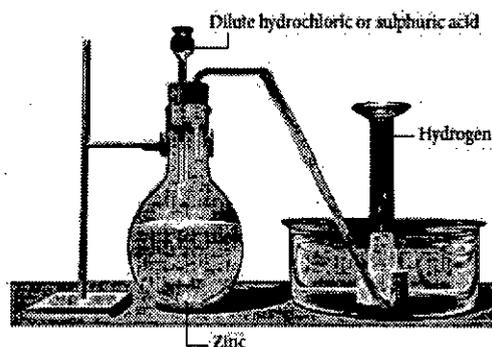
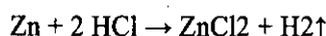


Figure 4.2 Laboratory preparation of hydrogen



Since, hydrogen has similarities with alkali metals as well as the halogens; it is difficult to find the right position in the periodic table. However, in most of its compounds hydrogen exists in +1 oxidation state. Therefore, it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

Isotopes of Hydrogen

Hydrogen has three naturally occurring isotopes, viz., protium (${}^1\text{H}$ or H), deuterium (${}^2\text{H}$ or D) and tritium (${}^3\text{H}$ or T). Protium (${}^1\text{H}$) is the predominant form (99.985 %) and it is the only isotope that does not contain a neutron.

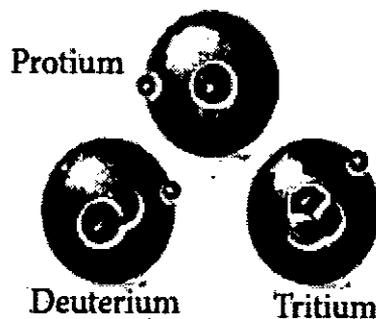


Figure 4.1 Isotopes of hydrogen

Deuterium, also known as heavy hydrogen, constitutes about 0.015 %. The third isotope, tritium is a radioactive isotope of hydrogen which occurs only in traces (~1 atom per 10¹⁸ hydrogen atoms). Due to the existence of these isotopes naturally occurring hydrogen exists as H₂, HD, D₂, HT, T₂, and DT. The properties of these isotopes are shown in Table 4.1.

Table 4.1 Properties of Hydrogen, Deuterium and Tritium molecules.

Table 4.1 Properties of Hydrogen, Deuterium and Tritium molecules.

Property	Protium	Deuterium	Tritium
Atomic Hydrogen			
	H	D	T
Atomic mass (<i>amu</i>)	1.008	2.014	3.016
No of electron / protons / neutrons	1 / 1 / 0	1 / 1 / 1	1 / 1 / 2
Nuclear stability	Stable	Stable	Radioactive ($t_{1/2}=12.3$ yrs)
Molecular Hydrogen	H ₂	D ₂	T ₂
Abundance (%)	99.985	0.015	$\sim 10^{-16}$
Molecular mass (<i>amu</i>)	2.016	4.028	6.032
Melting point (K)	13.96	18.73	20.62
Boiling point (K)	20.30	23.67	25.04
Internuclear distance (<i>pm</i>)	74.14	74.14	74.14
Critical Temperature (K)	33.19	38.35	40.60
Enthalpy of dissociation (kJ/mol) [†]	435.9	443.4	446.9

[†] Bond dissociation energy



Notes

13

HYDROGEN AND S-BLOCK ELEMENTS

- Understand the concept of hydrogen.
- Discuss the uses of hydrogen.
- Discuss the concept of s-block.
- Discuss the types of s-block elements.
- Discuss the characteristics of s-block elements.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of hydrogen and s-block elements so that the uses and characteristics of these concepts can be learned.

Introduction

Hydrogen, third most abundant on the surface of the Universe, is being visualised as the major feature source of energy. Hydrogen is the simplest atom which contains one electron and one proton. In contrast to other elements (except helium) its valence electron is directly in the sphere of action of the nucleus. It is invariably present in most of the compounds we come across in our daily life such as water, carbohydrate, proteins etc. As it has an unpaired electron, it is reactive and exists as a diatomic molecule (H₂). However, the abundance of hydrogen gas in the earth's atmosphere is very small.

Position in Periodic Table

The hydrogen has the electronic configuration of 1s¹ which resembles with ns¹ general valence shell configuration of alkali metals and shows similarity with them as follows:

1. It forms unipositive ion (H⁺) like alkali metals (Na⁺, K⁺, Cs⁺)
2. It forms halides (HX), oxides (H₂O), peroxides (H₂O₂) and sulphides (H₂S) like alkali metals (NaX, Na₂O, Na₂O₂, Na₂S)
3. It also acts as a reducing agent.

However, unlike alkali metals which have ionization energy ranging from 377 to 520 kJ mol⁻¹, the hydrogen has 1,314 kJ mol⁻¹ which is much higher than alkali metals.

Like the formation of halides (X⁻) from halogens, hydrogen also has a tendency to gain one electron to form hydride ion (H⁻) whose electronic configuration is similar to the noble gas, helium. However, the electron affinity of hydrogen is much less than that of halogen atoms. Hence, the tendency of hydrogen to form hydride ion is low compared to that of halogens to form the halide ions as evident from the following reactions:





9. Which one of the following is not feasible
- $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Zn}^{2+}(\text{aq})$
 - $\text{Cu(s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Zn(s)} + \text{Cu}^{2+}(\text{aq})$
 - $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow 2\text{Ag(s)} + \text{Cu}^{2+}(\text{aq})$
 - $\text{Fe(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Cu(s)} + \text{Fe}^{2+}(\text{aq})$
10. Electrochemical process is used to extract
- Iron
 - Lead
 - Sodium
 - silver

Review questions

- What are the differences between minerals and ores?
- What are the various steps involved in extraction of pure metals from their ores?
- What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3 ?
- Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.
- Out of coke and CO , which is better reducing agent for the reduction of ZnO ? Why?
- Describe a method for refining nickel.
- Explain zone refining process with an example using the Ellingham diagram given below.
- (A) Predict the conditions under which
 - Aluminium might be expected to reduce magnesia.
 - Magnesium could reduce alumina.(B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true –Explain.
(C) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K
- Give the uses of zinc.
- Explain the electrometallurgy of aluminium.

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Chemistry



Notes

- Roasting of sulphide ore gives the gas (A). (A) is a colourless gas. Aqueous solution of (A) is acidic. The gas (A) is
 - CO₂
 - SO₃
 - SO₂
 - H₂S
- Which one of the following reaction represents calcinations?
 - $2Zn + O_2 \rightarrow 2ZnO$
 - $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$
 - $MgCO_3 \rightarrow MgO + CO_2$
 - Both (a) and (c)
- The metal oxide which cannot be reduced to metal by carbon is
 - PbO
 - Al₂O₃
 - ZnO
 - FeO
- Which of the metal is extracted by Hall-Heroult process?
 - Al
 - Ni
 - Cu
 - Zn
- Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true?
 - ΔG_f° of sulphide is greater than those for CS₂ and H₂S.
 - ΔG_f° is negative for roasting of sulphide ore to oxide
 - Roasting of the sulphide to its oxide is thermodynamically feasible.
 - Carbon and hydrogen are suitable reducing agents for metal sulphides.
- Match items in column - I with the items of column - II and assign the correct code.

Column-I		Column-II	
A	Cyanide process	(i)	Ultrapure Ge
B	Froth floatation process	(ii)	Dressing of ZnS
C	Electrolytic reduction	(iii)	Extraction of Al
D	Zone refining	(iv)	Extraction of Au
		(v)	Purification of Ni

- A-i, B-ii, C-iii, D-iv
 - A-iii, B-iv, C-v, D-i
 - A-iv, B-ii, C-iii, D-i
 - A-ii, B-iii, C-i, D-v
- Wolframite ore is separated from tinstone by the process of
 - Smelting
 - Calcination
 - Roasting
 - Electromagnetic separation



Application of Cu

- Copper is the first metal used by the human and extended use of its alloy bronze resulted in a new era, 'Bronze age'
- Copper is used for making coins and ornaments along with gold and other metals.
- Copper and its alloys are used for making wires, water pipes and other electrical parts

Application of Au

- Gold, one of the expensive and precious metals. It is used for coinage, and has been used as standard for monetary systems in some countries.
- It is used extensively in jewellery in its alloy form with copper. It is also used in electroplating to cover other metals with a thin layer of gold which are used in watches, artificial limb joints, cheap jewellery, dental fillings and electrical connectors.
- Gold nano particles are also used for increasing the efficiency of solar cells and also used as catalysts.

SUMMARY

Metallurgy relates to the science and technology of metals. A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc... is called a **mineral**. Minerals that contain a high percentage of metal, from which it can be extracted conveniently and economically, are called **ores**. The extraction of a metal of interest from its ore consists of the following metallurgical processes. (i) concentration of the ore (ii) extraction of crude metal (iii) refining of crude metal. The extraction of crude metals from the concentrated ores is carried out in two steps namely, (i) conversion of the ore into oxides of the metal of interest and (ii) reduction of the metal oxides to elemental metals. The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram. Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction. Similar to thermodynamic principles, electrochemical principles also find applications in metallurgical process. If E_0 is positive then the ΔG is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive. When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution. Generally the metal extracted from its ore contains some impurities such as unreacted oxide ore, other metals, nonmetals etc... Removal of such impurities associated with the isolated crude metal is called refining process.

EXERCISE

MCQ

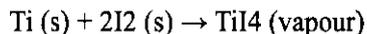
1. Bauxite has the composition

a) Al_2O_3	b) $Al_2O_3 \cdot nH_2O$
c) $Fe_2O_3 \cdot 2H_2O$	d) None of these

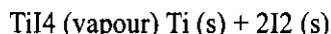


Van-Arkel method for refining zirconium/titanium:

This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals. Titanium and zirconium can be purified using this method. For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide (TiI_4). The impurities are left behind, as they do not react with iodine.



The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature around 1800 K. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.



Application of metals

Application of Al

Aluminium is the most abundant metal and is a good conductor of electricity and heat. It also resists corrosion. The following are some of its applications.

- Many heat exchangers/sinks and our day to day cooking vessels are made of aluminium.
- It is used as wraps (aluminium foils) and is used in packing materials for food items.
- Aluminium is not very strong. However, its alloys with copper, manganese, magnesium and silicon are light weight and strong and they are used in design of aeroplanes and other forms of transport.
- As Aluminium shows high resistance to corrosion, it is used in the design of chemical reactors, medical equipment's, refrigeration units and gas pipelines.
- Aluminium is a good electrical conductor and cheap, hence used in electrical overhead electric cables with steel core for strength.

Application of Zn

- Metallic zinc is used in **galvanising** metals such as iron and steel structures to protect them from rusting and corrosion.
- Zinc is also used to produce die-castings in the automobile, electrical and hardware industries.
- Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment. Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.
- Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.

Application of Fe

- Iron is one of the most useful metals and its alloys are used everywhere including bridges, electricity pylons, bicycle chains, cutting tools and rifle barrels.
- Cast iron is used to make pipes, valves and pumps stoves etc...
- Magnets can be made from iron and its alloys and compounds.
- An important alloy of iron is stainless steel, and it is very resistant to corrosion. It is used in architecture, bearings, cutlery, surgical instruments and jewellery. Nickel steel is used for making cables, automobiles and aeroplane parts. Chrome steels are used for manufacturing cutting tools and crushing machines



Electrolytic refining:

The crude metal is refined by electrolysis. It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal of interest. The rods of impure metal are used as anode and thin strips of pure metal are used as cathode. The metal of interest dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode. During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.

Let us understand this process by considering electrolytic refining of silver as an example.

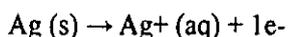
Cathode : Pure silver

Anode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

When a current is passed through the electrodes the following reactions will take place.

Reaction at anode



Reaction at cathode



During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode. Other metals such as copper, zinc etc., can also be refined by this process in a similar manner.

Zone Refining

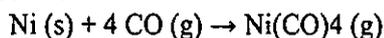
This method is based on the principles of fractional crystallisation. When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten region. i.e. impurities are more soluble in the melt than in the solid state metal. In this process the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater which results in melting of the metal on that portion of the rod. When the heater is slowly moved to the other end the pure metal crystallises while the impurities will move on to the adjacent molten zone formed due to the movement of the heater. As the heater moves further away, the molten zone containing impurities also moves along with it. The process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level. This process is carried out in an inert gas atmosphere to prevent the oxidation of metals. Elements such as germanium (Ge), silicon (Si) and gallium (Ga) that are used as semiconductor are refined using this process.

Vapour phase method

In this method, the metal is treated with a suitable reagent which can form a volatile compound with the metal. Then the volatile compound is decomposed to give the pure metal. We can understand this method by considering the following process.

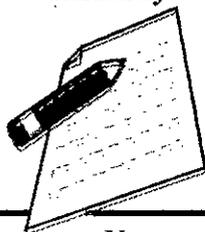
Mond process for refining nickel:

The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.



On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.



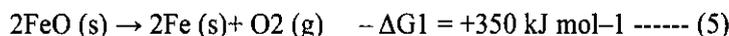


3. The carbon line cuts across the lines of many metal oxides and hence it can reduce all those metal oxides at sufficiently high temperature. Let us analyse the thermodynamically favourable conditions for the reduction of iron oxide by carbon. Ellingham diagram for the formation of FeO and CO intersects around 1000 K. Below this temperature the carbon line lies above the iron line which indicates that FeO is more stable than CO and hence at this temperature range, the reduction is not thermodynamically feasible. However, above 1000 K carbon line lies below the iron line and hence, we can use coke as reducing agent above this temperature. The following free energy calculation also confirm that the reduction is thermodynamically favoured.

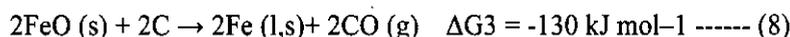
From the Ellingham Diagram at 1500 K,



Reverse the reaction (1)



Now couple the reactions (2) and (3)



The standard free energy change for the reduction of one mole of FeO is, $\Delta G_{3/2} = -65 \text{ kJ mol}^{-1}$

Limitations of Ellingham diagram

1. Ellingham diagram is constructed based only on thermodynamic considerations. It gives information about the thermodynamic feasibility of a reaction. It does not tell anything about the rate of the reaction. Moreover, it does not give any idea about the possibility of other reactions that might be taking place.
2. The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the products which is not always true.

Refining process

Generally the metal extracted from its ore contains some impurities such as unreacted oxide ore, other metals, nonmetals etc... Removal of such impurities associated with the isolated crude metal is called refining process. In this section, let us discuss some of the common refining methods.

Distillation

This method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K). In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

Liquation

This method, is employed to remove the impurities with high melting points from metals having relatively low melting points such as tin (Sb; mp= 904 K), lead (Pb; mp=600 K), mercury (Hg; mp=234 K), and bismuth (Bi; mp=545 K). In this process, the crude metal is heated to form fusible liquid and allowed to flow on a sloping surface. The impure metal is placed on sloping hearth of a reverberatory furnace and it is heated just above the melting point of the metal in the absence of air, the molten pure metal flows down and the impurities are left behind. The molten metal is collected and solidified.



The change in Gibbs free energy (ΔG) for a reaction is given by the expression.

$\Delta G = \Delta H - T\Delta S$ ----- (1) where, ΔH is the enthalpy change, T the temperature in kelvin and ΔS the entropy change. For an equilibrium process, ΔG^\ominus can be calculated using the equilibrium constant by the following expression

$$\Delta G^\ominus = -RT \ln K_p$$

Harold Ellingham used the above relationship to calculate the ΔG^\ominus values at various temperatures for the reduction of metal oxides by treating the reduction as an equilibrium process.

He has drawn a plot by considering the temperature in the x-axis and the standard free energy change for the formation of metal oxide in y-axis. The resultant plot is a straight line with ΔS as slope and ΔH as y-intercept. The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram

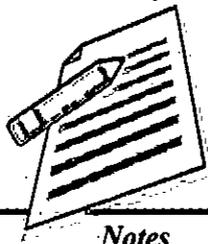
Observations from the Ellingham diagram.

1. For most of the metal oxide formation, the slope is positive. It can be explained as follows. Oxygen gas is consumed during the formation of metal oxides which results in the decrease in randomness. Hence, ΔS becomes negative and it makes the term, $T\Delta S$ positive in the straight line equation.
2. The graph for the formation of carbon monoxide is a straight line with negative slope. In this case ΔS is positive as 2 moles of CO gas is formed by the consumption of one mole of oxygen gas. It indicates that CO is more stable at higher temperature.
3. As the temperature increases, generally ΔG value for the formation of the metal oxide become less negative and becomes zero at a particular temperature. Below this temperature, ΔG is negative and the oxide is stable and above this temperature ΔG is positive. This general trend suggests that metal oxides become less stable at higher temperature and their decomposition becomes easier.
4. There is a sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO. This is due to the phase transition (melting or evaporation).

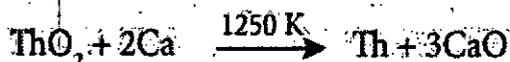
2. Applications of the Ellingham diagram:

Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction. The reduction of a metal oxide to its metal can be considered as a competition between the element used for reduction and the metal to combine with oxygen. If the metal oxide is more stable, then oxygen remains with the metal and if the oxide of element used for reduction is more stable, then the oxygen from the metal oxide combines with elements used for the reduction. From the Ellingham diagram, we can infer the relative stability of different metal oxides at a given temperature.

1. Ellingham diagram for the formation of Ag₂O and HgO is at upper part of the diagram and their decomposition temperatures are 600 and 700 K respectively. It indicates that these oxides are unstable at moderate temperatures and will decompose on heating even in the absence of a reducing agent.
2. Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal. Any metal can reduce the oxides of other metals that are located above it in the diagram. For example, in the Ellingham diagram, for the formation of chromium oxide lies above that of the aluminium, meaning that Al₂O₃ is more stable than Cr₂O₃. Hence aluminium can be used as a reducing agent for the reduction of chromic oxide. However, it cannot be used to reduce the oxides of magnesium and calcium which occupy lower position than aluminium oxide.

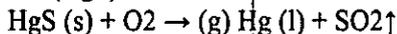


Notes



Auto-reduction:

Simple roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting of its ore cinnabar (HgS)



Thermodynamic principle of metallurgy

As we discussed, the extraction of metals from their oxides can be carried out by using different reducing agents. For example, consider the reduction of a metal oxide M_xO_y .



The above reduction may be carried out with carbon. In this case, the reducing agent carbon may be oxidised to either CO or CO_2 .



If carbon monoxide is used as a reducing agent, it is oxidised to CO_2 as follows,



A suitable reducing agent is selected based on the thermodynamic considerations. We know that for a spontaneous reaction, the change in free energy (ΔG) should be negative. Therefore, thermodynamically, the reduction of metal oxide [equation (1)] with a given reducing agent [Equation (2), (3) or (4)] can occur if the free energy change for the coupled reaction. [Equations (1) & (2), (1) & (3) or (1) & (4)] is negative. Hence, the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.

1. Ellingham diagram

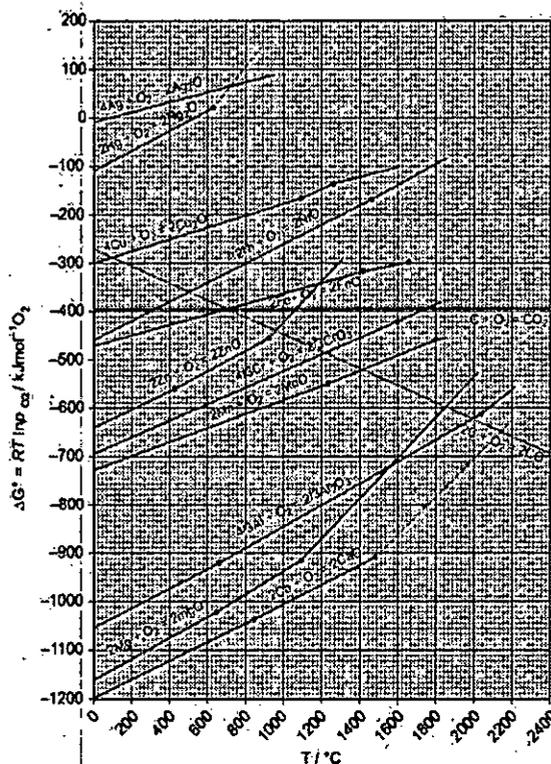
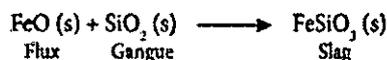
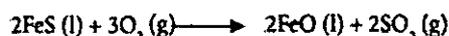
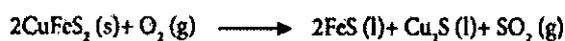
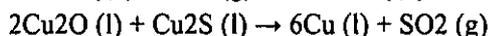
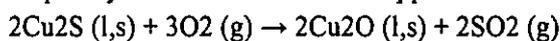


Figure 1.4 Ellingham diagram



The matte is separated from the slag and fed to the converting furnace. During conversion, the FeS present in the matte is first oxidised to FeO. This is removed by slag formation with silica. The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper as shown below.

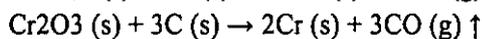
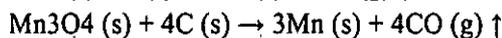
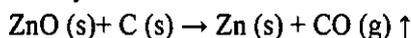


The metallic copper is solidified and it has blistered appearance due to evolution of SO_2 gas formed in this process. This copper is called blistered copper.

Reduction by carbon:

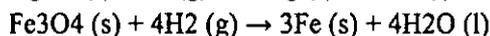
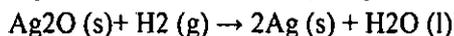
In this method the oxide ore of the metal is mixed with coal (coke) and heated strongly in a furnace (usually in a blast furnace). This process can be applied to the metals which do not form carbides with carbon at the reduction temperature.

Examples:

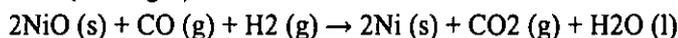


Reduction by hydrogen:

This method can be applied to the oxides of the metals (Fe, Pb, Cu) having less electro-positive character than hydrogen.



Nickel oxide can be reduced to nickel by using a mixture of hydrogen and carbon monoxide (water gas).



Reduction by metal:

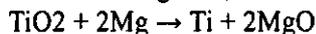
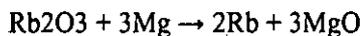
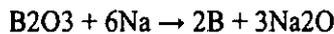
Metallic oxides such as Cr_2O_3 can be reduced by an aluminothermite process. In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible. To initiate the reduction process, an ignition mixture (usually magnesium and barium peroxide) is used.



During the above reaction a large amount of heat is evolved (temperature up to 2400°C , is generated and the reaction enthalpy is : 852 kJ mol^{-1}) which facilitates the reduction of Cr_2O_3 by aluminium powder.



Active metals such as sodium, potassium and calcium can also be used to reduce the metal oxide





Notes

Calcination

Calcination is the process in which the concentrated ore is strongly heated in the absence of air. During this process, the water of crystallisation present in the hydrated oxide escapes as moisture. Any organic matter (if present) also get expelled leaving behind a porous ore. This method can also be carried out with a limited supply of air.

For examples,

During calcination of carbonate ore, carbon dioxide is expelled



During calcination of hydrated ore, the water of hydration is expelled as vapour

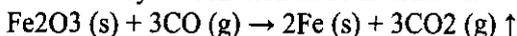


2. Reduction of metal oxides

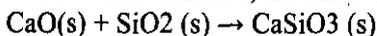
Metal oxide can be reduced to crude metal by using a suitable reducing agent like carbon, carbon monoxide, hydrogen, aluminium and other reactive metals such as sodium etc... The choice of reducing agent depends on the nature of the metal. For example, carbon cannot be used as a reducing agent for the reactive metals such as sodium, potassium, aluminium etc... Similarly CO cannot be used to reduce oxides such as ZnO, Al₂O₃. Later in this, we study selection of suitable reducing agents by applying Ellingham diagram.

Smelting

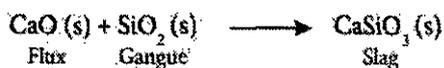
In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace. For example the oxide of iron can be reduced by carbon monoxide as follows.



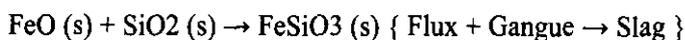
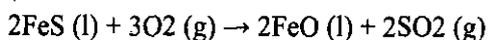
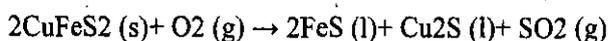
In this extraction, a basic flux, limestone (CaO) is used. Since the silica gangue present in the ore is acidic in nature, the limestone combines with it to form calcium silicate (slag).



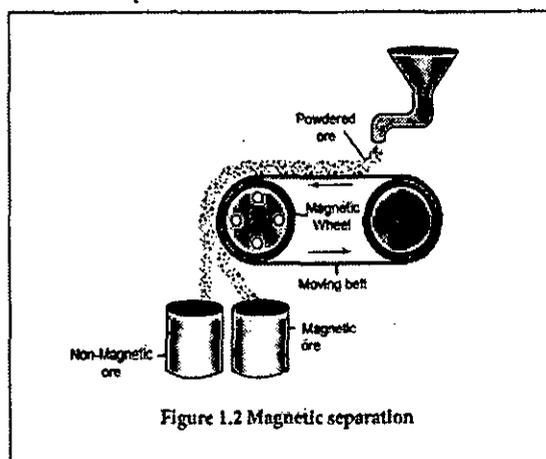
Flux + Gangue → Slag



In the extraction of copper from copper pyrites, the concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed due to melting is basic in nature and it combines with silica to form ferrous silicate (slag). The remaining metal sulphides Cu₂S and FeS are mutually soluble and form a copper matte.



a belt moving over two rollers of which one is magnetic. The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it as shown in the figure 1.2.



Extraction of crude metal

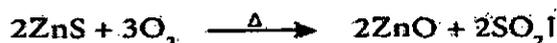
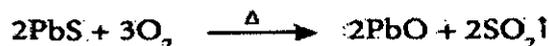
The extraction of crude metals from the concentrated ores is carried out in two steps namely, (i) conversion of the ore into oxides of the metal of interest and (ii) reduction of the metal oxides to elemental metals. In the concentrated ore, the metal exists in positive oxidation state and hence it is to be reduced to its elemental state. We can infer from the principles of thermodynamics, that the reduction of oxide is easier when compared to reduction of other compounds of metal and hence, before reduction, the ore is first converted into the oxide of metal of interest.

Let us discuss some of the common methods used to convert the concentrated ore into the oxides of the metal of interest.

1. Conversion of ores into oxides

Roasting

Roasting is the method, usually applied for the conversion of sulphide ores into their oxides. In this method, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.



Roasting also removes impurities such as arsenic, sulphur, phosphorous by converting them into their volatile oxides.

For example





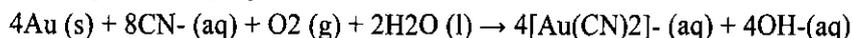
such as ZnS is present in galena (PbS), sodium cyanide (NaCN) is added to depresses the flotation property of ZnS by forming a layer of zinc complex $\text{Na}_2[\text{Zn}(\text{CN})_4]$ on the surface of zinc sulphide.

3. Leaching

This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution. In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble. The following examples illustrate the leaching processes.

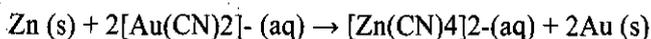
Cyanide leaching

Let us consider the concentration of gold ore as an example. The crushed ore of gold is leached with aerated dilute solution of sodium cyanide. Gold is converted into a soluble cyanide complex. The gangue, aluminosilicate remains insoluble.



Recovery of metal of interest from the complex by reduction:

Gold can be recovered by reacting the deoxygenated leached solution with zinc. In this process the gold is reduced to its elemental state (zero oxidation state) and the process is called **cementation**.

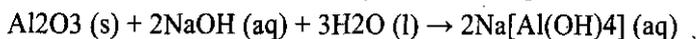


Ammonia leaching

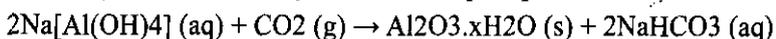
When a crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure, ammonia selectively leaches these metals by forming their soluble complexes viz. $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, and $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$ respectively from the ore leaving behind the gangue, iron(III) oxides/hydroxides and aluminosilicate.

Alkali leaching

In this method, the ore is treated with aqueous alkali to form a soluble complex. For example, bauxite, an important ore of aluminium is heated with a solution of sodium hydroxide or sodium carbonate in the temperature range 470 - 520 K at 35 atm to form soluble sodium meta-aluminate leaving behind the impurities, iron oxide and titanium oxide.



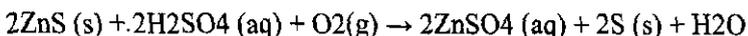
The hot solution is decanted, cooled, and diluted. This solution is neutralised by passing CO_2 gas, to the form hydrated Al_2O_3 precipitate.



The precipitate is filtered off and heated around 1670 K to get pure alumina Al_2O_3 .

Acid leaching

Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.



In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

4. Magnetic separation

This method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities. For example tin stone can be separated from the wolframite impurities which is magnetic. Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non-magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of

Concentration of ores

Generally, the ores are associated with non-metallic impurities, rocky materials and siliceous matter which are collectively known as gangue. The preliminary step in metallurgical process is removal of these impurities. This removal process is known as concentration of ore. It increases the concentration of the metal of interest or its compound in the ore. Several methods are available for this process and the choice of method will depend on the nature of the ore, type of impurity and environmental factors. Some of the common methods of ore concentration are discussed below.

1. Gravity separation or Hydraulic wash

In this method, the ore having high specific gravity is separated from the gangue that has low specific gravity by simply washing with running water. Ore is crushed to a finely powdered form and treated with rapidly flowing current of water. During this process the lighter gangue particles are washed away by the running water. This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe_2O_3), tin stone (SnO_2) etc.

2. Froth flotation

This method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS) etc... In this method, the metallic ore particles which are preferentially wetted by oil can be separated from gangue.

In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil etc.

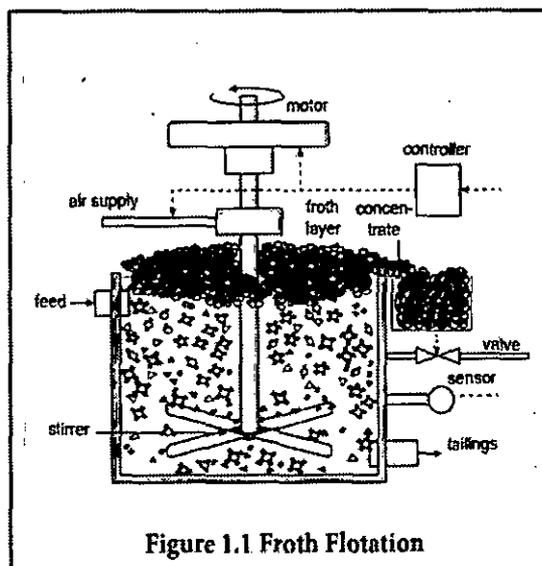


Figure 1.1 Froth Flotation

A small quantity of sodium ethyl xanthate which acts as a collector is also added. A froth is generated by blowing air through this mixture. The collector molecules attach to the ore particle and make them water repellent. As a result, ore particles, wetted by the oil, rise to the surface along with the froth. The froth is skimmed off and dried to recover the concentrated ore. The gangue particles that are preferentially wetted by water settle at the bottom.

When a sulphide ore of a metal of interest contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc are used to selectively prevent other metal sulphides from coming to the froth. For example, when impurities

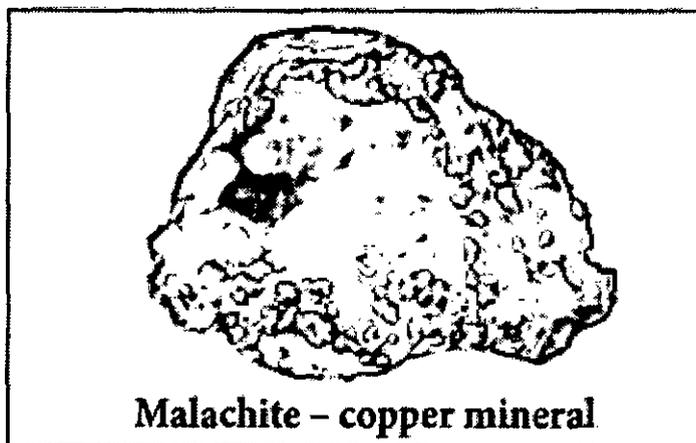




bauxite and china clay ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$). Both are minerals of aluminium. However, aluminium can be commercially extracted from bauxite while extraction from china clay is not a profitable one. Hence the mineral, bauxite is an ore of aluminium while china clay is not.

The extraction of a metal of interest from its ore consists of the following metallurgical processes.

- (i) concentration of the ore
- (ii) extraction of crude metal
- (ii) refining of crude metal



Malachite – copper mineral

Table 1.1 List of some metals and their common ores with their chemical formula

Table 1.1 List of some metals and their common ores with their chemical formula

Metal	Ore	Composition	Metal	Ore	Composition
Aluminium	Bauxite	$\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$	Zinc	Zinc blende or Sphalerite	ZnS
	Diaspore	$\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$		Calamine	ZnCO_3
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$		Zincite	ZnO
Iron	Haematite	Fe_2O_3	Lead	Galena	PbS
	Magnetite	Fe_3O_4		Anglesite	PbSO_4
	Siderite	FeCO_3		Cerrusite	PbCO_3
	Iron pyrite	FeS_2	Tin	Cassiterite (Tin stone)	SnO_2
	Limonite	$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Silver	Silver glance (Argentite)	Ag_2S
Copper	Copper pyrite	CuFeS_2		Pyrargyrite (Ruby silver)	Ag_3SbS_3
	Copper glance	Cu_2S		Chlorargyrite (Horn Silver)	AgCl
	Cuprite	Cu_2O		Stefinite	Ag_3SbS_4
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$		Proussite	Ag_3AsS_3
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$			

**Zinc:**Zinc blend/Sphalerite ZnS Calamine $ZnCO_3$ Zincite ZnO **Occurrence of Metals and Non-Metals****Native Metals**

A metal that exists in metallic form, either as pure metal or as an alloy. For example, cadmium, cobalt, bismuth, indium etc.

Two groups of metals are found in nature. They are classified on the basis of their nature of existence, that is, whether they exist single or in alloys-

The gold group consists of gold, copper, lead, aluminium, mercury, and silver.

The platinum group consists of platinum, iridium, osmium, palladium, rhodium, and ruthenium.

Aluminium is the most abundant element in nature. It is a major constituent of silica and clay. Iron is the second largest metal that exists in nature after aluminium. The process of extracting metals from ores is known as **Smelting** which was discovered around 6500 BC.

Alloys

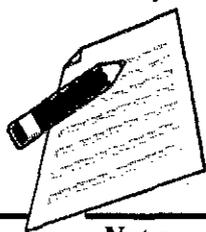
It is a mixture of two or more elements in which the major component is metal. Alloys are made to obtain desirable characteristics. The basic idea to make alloy is to make metal less brittle, hard and more resistant to corrosion. Alloys of iron are important in both quantity and commercial value. For example, stainless steel, cast iron, alloy steel etc. Iron alloyed with carbon gives low, mid and high carbon steels. Increase in carbon content reduces ductility and toughness. The addition of silicon to iron produces cast irons, whereas the addition of chromium, nickel and molybdenum to carbon steels results in stainless steels.

Occurrence of metals

In general, pure metals are shiny and malleable, however, most of them are found in nature as compounds with different properties. Metals having least chemical reactivity such as copper, silver, gold and platinum occur in significant amounts as native elements. Reactive metals such as alkali metals usually occur in their combined state and are extracted using suitable metallurgical process.

Mineral and ore

A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc... is called a **mineral**. In most of the minerals, the metal of interest is present only in small amounts and some of them contain a reasonable percentage of metal. For example iron is present in around 800 minerals. However, some of them such as hematite magnetite etc., containing high percentage of iron are commonly used for the extraction of iron. Such minerals that contain a high percentage of metal, from which it can be extracted conveniently and economically are called **ores**. Hence all ores are minerals but all minerals are not ores. Let us consider another example,



Notes

12 OCCURRENCE AND EXTRACTION OF METALS

- Understand the concept of metals.
- Discuss the concept of mining.
- Discuss the concept of extraction.
- Discuss the types of process of extraction of metals.
- Discuss the occurrence of metals and non-metals.

Objective of the Chapter:

The basic objective of this chapter is to through some light on the initial concepts of occurrence and extraction of metals so that the process of extraction of metals can be learned.

Introduction

The process of extracting metal ores buried deep underground is called Mining. The metal ores are found in the earth's crust in varying abundance. The extraction of metals from ores is what allows us to use the minerals in the ground! The ores are very different from the finished metals that we see in buildings and bridges. Ores consist of the desired metal compound and the impurities and earthly substances called Gangue. The extraction of metals and its isolation occurs over a few major steps:

Concentration of Ore

Isolation of metal from concentrated Ore

Purification of the metal

Aluminium:

Bauxite $\text{AlO}_x(\text{OH})_{3-2x}$ [where $0 < x < 1$]

Kaolinite (a form of clay) $[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]$

Iron:

Haematite Fe_2O_3

Magnetite Fe_3O_4

Siderite FeCO_3

Iron pyrites FeS_2

Copper:

Copper pyrites CuFeS_2

Malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$

Cuprite Cu_2O

Copper glance Cu_2S



8. A device that converts the energy of combustion of fields like hydrogen and methane directly into electrical energy is known as

- a) Electrolytic cell b) Dynamo
c) Ni-Cd cell d) Fuel cell

Answer: (d)

9. Which reaction is not feasible?

- a) $2\text{KO} + \text{Br}_2 \rightarrow 2\text{KBr} + \text{I}_2$ b) $2\text{KBr} + \text{I}_2 \rightarrow 2\text{KI} + \text{Br}_2$
c) $2\text{KBr} + \text{Cl}_2 \rightarrow 2\text{KCl} + \text{Br}_2$ d) $2\text{H}_2\text{O} + 2\text{F}_2 \rightarrow 4\text{HF} + \text{O}_2$

Answer: (b)

10. Without losing its concentration ZnCl_2 solution cannot be kept in contact with

- a) Au b) Al
c) Pb d) Ag

Answer: (b)

Review Questions

- Calculate the Oxidation number of the elements written in bold letters $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $\text{HC}-\text{O}_3$, Pb_3O_4 .
- Balance the following reactions by oxidation number method
(a) $\text{Fe}_2\text{O}_3 + \text{C} \rightarrow \text{Fe} + \text{CO}$. (b) $\text{C}_6\text{H}_6 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$.
- Balance the following reactions by ion-electron method:
(i) $\text{Zn} + \text{HNO}_3 \rightarrow \text{Zn}(\text{NO}_3)_2 + \text{NO}_2 + \text{H}_2\text{O}$
(ii) $\text{ClO}_3^- + \text{Mn}^{2+} \rightarrow \text{MnO}_2 + \text{Cl}^-$ in acidic medium
(iii) $\text{Fe}(\text{OH})_2 + \text{H}_2\text{O}_2 \rightarrow \text{Fe}(\text{OH})_3 + \text{H}_2\text{O}$ in basic medium
- Define the following and give its units:
(i) Conductivity (ii) Molar conductivity
- Draw a graph showing the variation in molar conductivity in a weak and a strong electrolytes with concentration.
- Explain why the molar conductivity of an electrolyte increases with dilution while conductivity decreases on dilution.
- The measured resistance of a conductance cell containing $7.5 \times 10^{-3}\text{M}$ solution of KCl at 25°C was 1005 ohms. Calculate (a) Conductivity (b) Molar conductivity of the solution. Given the cell constant 1.25 cm^{-1} .
- The conductivity of 0.05M solution of an electrolyte at 298 K is 0.0025 cm^{-1} . Calculate the molar conductivity.
- How much aluminium will be deposited on passing a current of 25 A for 10 hr by electrolysis of molten Al_2O_3 ?
- Equivalent mass of an element is 94 g. What is its electrochemical equivalent?



Notes

Example 1 : Predict whether the reaction



is feasible or not.

Solution : The cell half reactions are.



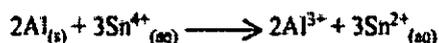
$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E^{\circ}_{\text{cell}} = -0.763 \text{ V} - 0.80 \text{ V}$$

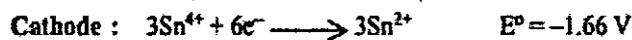
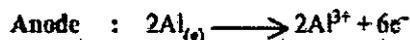
$$= -1.563 \text{ V}$$

Since E°_{cell} is negative, the given reaction is not feasible.

Example 2 : Determine the feasibility of the reaction



Solution : The given reaction consists of the following half reactions



$$E^{\circ}_{\text{cell}} = 0.15 - (-1.66) \quad E^{\circ} = +0.15 \text{ V}$$

$$= 1.81 \text{ V}$$

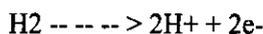
Since E°_{cell} is positive, the reaction is feasible.

SUMMARY

In electrochemistry, the inter conversion of chemical energy and electrical energy is an important aspect that possesses numerous applications. For example, batteries supply electrical energy stored in the form of chemical energy for the operation of torch, radio, calculators etc. Conversely, electrical energy is used to bring about certain chemical reactions which are industrially important such as purification of metals like copper, aluminium, generation of gaseous chlorine, oxygen, hydrogen, electroplating, metal coatings etc. The electrochemical or electrolytic processes are carried out in a device known as a cell. An electrolytic (or) electrochemical cell consists of two conducting metal electrodes in contact with an electrolyte solution which separates them (or) placed separately in compartments containing suitable electrolytes. The electrolyte may be an aqueous solution containing mostly the salt of the metal with which the electrode is made of (or) it may be an ionically conducting solid. There are two types of cells known as electrolytic cell and electrochemical cell. Each of them possesses different characteristics and used in different application. Generally at the anode oxidation reaction occurs and at the cathode reduction reaction occurs. When the electrodes are connected externally through a wire and electrons flow through them, the electrical circuit is said to be an open circuit. If the electrodes are not connected externally and the electrons do not flow from one electrode into the other, the electrical circuit is said to be a closed circuit.



The electrons flow to the SHE and it acts as the cathode. When the SHE is placed on the left hand side, the electrode reaction is



The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, the SHE can act both as anode and cathode and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25°C (298 K) for some common Reduction Half-reactions are listed in Table below.

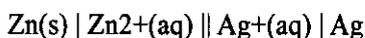
Standard Reduction Potentials at 25°C (298K)

Predicting Cell EMF

The standard emf E_o , of a cell is the standard reduction potential of right-hand electrode (cathode) minus the standard reduction potential of the left-hand electrode (anode). That is,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\ &= \text{Cathode potential} - \text{Anode potential} \end{aligned}$$

Let us predict the emf of the cell



by using the E_o values from the table.

$$E_{\text{cell}} = E_{\text{OR}} - E_{\text{OL}}$$

$$0.80 - (-0.763)$$

$$0.80 + 0.763 = 1.563 \text{ V}$$

Standard Reduction Potentials at 25°C (298K)

Reduction Half - reaction	$E^\circ \text{V}$
$\text{F}_2 + 2\text{e}^- \longrightarrow 2\text{F}^-$	2.87
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	1.78
$\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69
$\text{Au}^{3+} + 3\text{e}^- \longrightarrow \text{Au}$	1.50
$\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Cl}^-$	1.36
$\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag(s)}$	0.80
$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu(s)}$	0.34
$2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb(s)}$	-0.13
$\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn(s)}$	-0.76

Predicting Feasibility of Reaction

The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the cell reaction, E_{cell} , can be calculated from the expression

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

In general, if $E_{\text{cell}} = +ve$, the reaction is feasible

$E_{\text{cell}} = -ve$, the reaction is not feasible



them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. The emf of the newly constructed cell, E is determined with a voltmeter. The emf of the unknown half-cell E_0 can then be calculated from the expression

$$E_{\text{measured}} = E_R - E_L$$

If the standard half-cell acts as anode, the equation becomes

$$E_R = E_{\text{measured}} \quad (Q \text{ EL} = 0)$$

On the other hand, if standard half-cell is cathode, the equation takes the form

$$E_L = - E_{\text{measured}} \quad (Q \text{ ER} = 0)$$

The standard hydrogen half-cell or Standard Hydrogen Electrode (SHE), is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25 oC. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

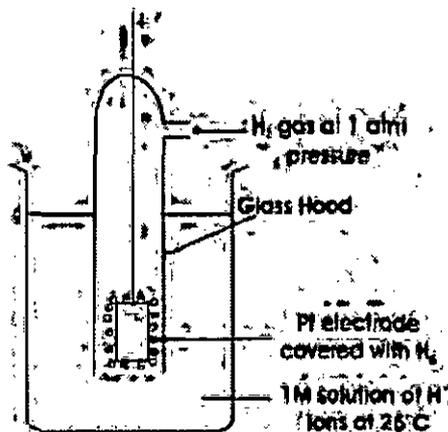
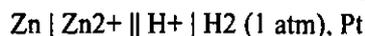


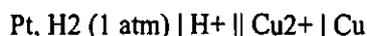
Fig. The standard hydrogen electrode

The half-cell whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

For example, it is desired to determine the emf of the zinc electrode, $Zn | Zn^{2+}$. It is connected with the SHE. The complete electrochemical cell may be represented as :



The emf of the cell has been found to be -0.76 V which is the emf the zinc half-cell. Similarly, the emf of the copper electrode, $Cu^{2+} | Cu$ can be determined by pairing it with the SHE when the electrochemical cell can be represented as :



The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

$$E_{\text{cell}} = E_{\text{Cu}/\text{Cu}^{2+}} - E_{\text{SHE}}$$

$$= 0.34 - \text{Zero}$$

$$= 0.34 \text{ V}$$

The two situations are explained as follows : When it is placed on the right-hand side of the zinc electrode, the hydrogen electrode reaction is





(5) The symbol for an inert electrode, like the platinum electrode is often enclosed in a bracket. For **example**,



(6) The value of emf of a cell is written on the right of the cell diagram. Thus a zinc-copper cell has emf 1.1 V and is represented as



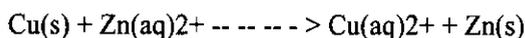
--- --> Direction of electron flow

If the emf acts in the opposite direction through the cell circuit it is denoted as a negative value.



< --- --- Direction of electron flow

The negative sign also indicates that the cell is not feasible in the given direction and the reaction will take place in the reverse direction only. The overall cell reaction for $E = -1.1 \text{ V}$ of the daniel cell is



The reversal of the cell current is accompanied by the reversal of direction of the cell reaction. Thus a reversible cell is defined as that operates by reversal of cell reactions when the direction of flow of current is reversed. The reversible behaviour operates only for infinitesimal changes in e.m.f. of the cell on the positive and negative sides from the balance point which corresponds to the actual emf of the cell.

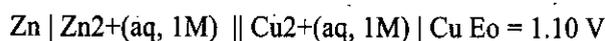
Single electrode potential

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the Single electrode potential. Thus in Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+} , a positive charge. The amount of the charge produced on an individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (a) concentration of ions in solution ; (b) tendency to form ions ; and (c) temperature.

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E . It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called the standard emf. The standard conditions are : (a) 1 M solutions of reactants and products ; and (b) temperature of 25o C. Thus standard emf may be defined as the emf of a cell with 1 M solutions of reactants and products in solution measured at 25o C. Standard emf of a cell is represented by the symbol E_o . For gases 1 atm. pressure is a standard condition instead of concentration. For Zn-Cu voltaic cell, the standard emf, E_o is 1.10V.



Determination of emf of a half-cell

By a single electrode potential, we also mean the emf of an isolated half-cell or its half-reaction. The emf of a cell that is made of two half-cells can be determined by connecting



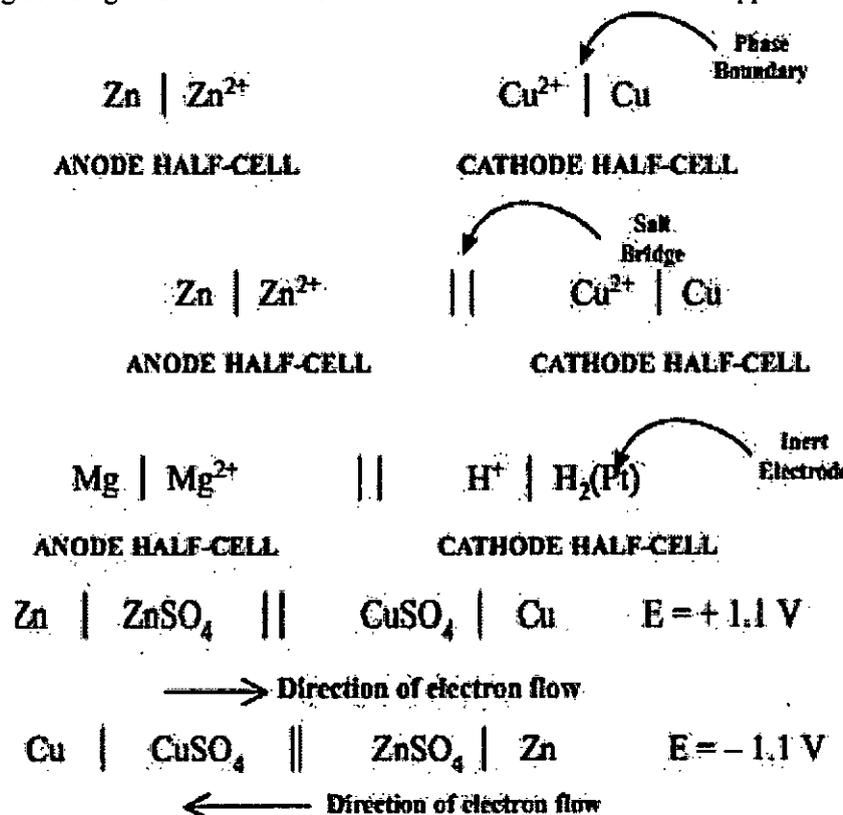
Cathode compartment is the compartment of the cell in which reduction half-reaction occurs. It contains the cathode.

Half-cell. Each half of an electrochemical cell, where oxidation occurs and the half where reduction occurs, is called the half cell.

Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode in contact with metal ion in solution.

IUPAC Conventions. In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.



(1) a single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as



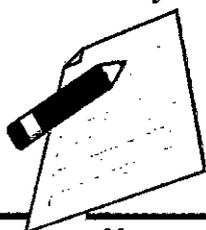
Anode half-cell cathode half-cell

It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.

A double vertical line represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing. Anode half-cell is written on the left and cathode half-cell on the right.

In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as





The reduction half reaction occurring at the copper electrode in contact with the aqueous electrolyte containing Cu^{2+} ions receives the electrons from the zinc electrode when connected externally, to produce metallic copper according to the reaction as,



The decrease in the energy which appears as the heat energy when a zinc rod is directly dipped into the zinc sulphate solution, is converted into electrical energy when the same reaction takes place indirectly in an electrochemical cell. The zinc sulphate is placed in the porous pot while copper sulphate is placed in a glass vessel.

The Daniel cell is also called as the voltaic cell. However for continuous supply of current for a long period, the two half cells each comprising the metal electrode and its aqueous electrolyte kept in separate containers and can be connected externally as below :

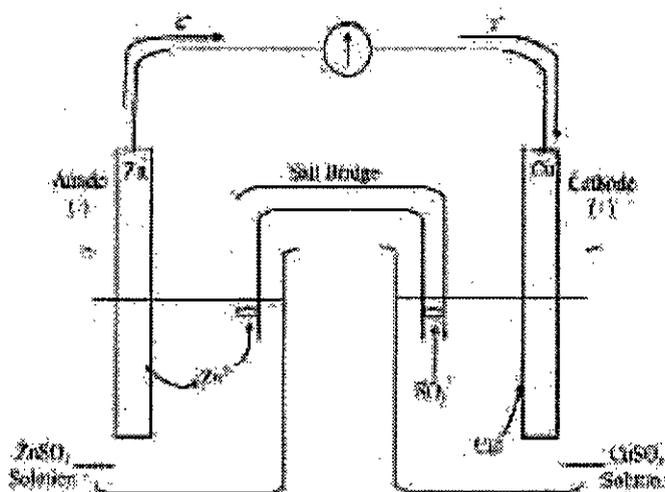


Fig. A simple voltaic (galvanic) cell

When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode. As a result, zinc dissolves in the anode solution to form Zn^{2+} ions. The Cu^{2+} ions in the cathode half-cell pick up electrons and are converted to Cu atoms on the cathode.

Electro Chemistry - Cell Terminology

Before taking up the study of the electrochemical cells, we should be familiar with a few common terms.

Current is the flow of electrons through a wire or any conductor.

Electrode is the material : a metallic rod/bar/strip which conducts electrons into and out of a solution.

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has negative charge and is shown as (-) in cell diagrams.

Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is known as (+) in the cell diagrams.

Electrolyte is the salt solution in a cell.

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

11

ELECTROCHEMISTRY



Notes

- Understand the concept of electrochemistry.
- Discuss the concept of cells.
- Discuss the types of cells.
- Understand the cell diagrams.

Objective of the Chapter:

The basic objective of this chapter is to through some light on the initial concepts of electrochemistry so that the types of cell and cell diagram can be learned.

Introduction

In electrochemistry, the inter conversion of chemical energy and electrical energy is an important aspect that possesses numerous applications. For example, batteries supply electrical energy stored in the form of chemical energy for the operation of torch, radio, calculators etc. Conversely, electrical energy is used to bring about certain chemical reactions which are industrially important such as purification of metals like copper, aluminium, generation of gaseous chlorine, oxygen, hydrogen, electroplating, metal coatings etc. The electrochemical or electrolytic processes are carried out in a device known as a cell. An electrolytic (or) electrochemical cell consists of two conducting metal electrodes in contact with an electrolyte solution which separates them (or) placed separately in compartments containing suitable electrolytes. The electrolyte may be an aqueous solution containing mostly the salt of the metal with which the electrode is made of (or) it may be an ionically conducting solid.

There are two types of cells known as electrolytic cell and electrochemical cell. Each of them possesses different characteristics and used in different application.

Generally at the anode oxidation reaction occurs and at the cathode reduction reaction occurs. When the electrodes are connected externally through a wire and electrons flow through them, the electrical circuit is said to be an open circuit. If the electrodes are not connected externally and the electrons do not flow from one electrode into the other, the electrical circuit is said to be a closed circuit.

Daniel cell : Daniel cell or a galvanic cell is an example of electrochemical cell. The overall reaction taking place in the cell is the redox reaction given as



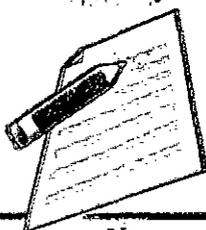
This overall reaction is made of the summation of two half reactions such as oxidation half reaction and reduction half reaction.

The oxidation half reaction occurring at the zinc electrode in contact with the aqueous electrolyte containing Zn^{2+} , accumulates the electrons at the zinc rod.



CLASS-12

Chemistry



Notes

3. Which of the following aqueous solutions will have highest pH?
(a) NaCl (b) CH₃COONa
(c) Na₂CO₃ (d) NH₄Cl
Answer: (c) Na₂CO₃
4. What is the pH of a 0.10 M solution of barium hydroxide, Ba(OH)₂?
(a) 11.31 (b) 11.7
(c) 13.30 (d) None of these
Answer: (c) 13.30
5. Which of the following oxides is not expected to react with sodium hydroxide?
(a) CaO (b) SiO₂
(c) BeO (d) B₂O₃
Answer: (a) CaO

Review Questions

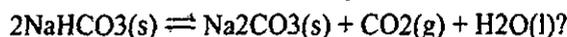
1. What is degree of dissociation? What are factors upon which it depends.
2. Write the equilibrium constant expression for the following reaction.
 $\text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq}) + \text{HCO}_2^-(\text{aq})$
3. Explain why does a strong Bronsted – Lowry acid has a weak conjugate base?
4. What do you understand by the term ‘amphoteric’? Show with the help of equations that water is amphoteric in nature.
5. Calculate the pH of 1×10^{-3} M solution of NH₄OH. The dissociation constant of NH₄OH is 1.85×10^{-5} mol dm⁻³.
6. The pH of an aqueous solution of HCl is 2.301. Find out the concentration of hydrogen ions in this solution.
7. What is a buffer solution? What are its main constituents?
8. Solubility of lead iodide PbI₂ is 1.20×10^{-3} mol dm⁻³ at 298K. Calculate its solubility product constant.
9. Calculate the solubility of Bi₂S₃ in water at 298K if its $K_{sp} = 1.0 \times 10^{-97}$ mol⁵ dm⁻¹⁵.
10. Calculate the solubility of AgI in 0.10M NaI at 298 K. K_{sp} for AgI is 8.5×10^{-7} at this temperature.



The equilibrium state is dynamic and not static in nature. A reaction is said to have attained equilibrium when the rate of forward reaction equals that of backward reaction

Homogeneous equilibrium? All the reactants and products of any reaction under equilibrium are in same physical state. Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Heterogeneous equilibrium? Physical state of one or more of the reacting species may differ i.e. all the reactants and products are not in same physical state. Example



Ionic Product:

- Product of ionic concentration due to ions already present in water or from a salt.
- I.P. may be and may not be equal to K_{sp} .
- If ionic Product (IP) $> K_{sp}$; precipitation takes place till I.P. equals K_{sp}
- If ionic Product $< K_{sp}$; a precipitate will not be formed and the solution will be unsaturated.
- If ionic Product = K_{sp} ; a precipitate will not form as the solution is saturated in that salt.

SUMMARY

In Ionic equilibrium, the ionic substance dissociates into their ions in polar solvents. The ions formed are always in equilibrium with its undissociated solute in the solution. Reactants and products coexist in equilibrium so that reactant conversion to product is always less than 100%. Equilibrium reactions may involve the decomposition of a covalent (non-polar) reactant or ionization of ionic compounds into their ions in polar solvents. Substances in Ionic Equilibrium can be classified into two categories on the basis of their ability to conduct electricity given as under. These are substances that consist of molecules that bear no electric charge, do not dissociate into their constituent ions and thus do not conduct electricity in their aqueous solution or molten state. For example sugar solution. These are substances that dissociate into their constituent ions in their aqueous solution and thus conduct electricity in their aqueous solutions or molten state. Example, salt solution, acid solution, base solution etc.

EXERCISE

MCQ

- The solubility of $Ca_3(PO_4)_2$ in water is y mol/L. Its solubility product is:
 - $6y^2$
 - $36y^4$
 - $64y^5$
 - $108y^5$

Answer: (d) $108y^5$
- A physician wishes to prepare a buffer solution at $pH = 3.85$ that efficiently resists changes in pH yet contains only small concentration of the buffering agents. Which of the following weak acids together with its sodium salt would be best to use?
 - 2, 5-Dihydroxy benzoic acid ($pK_a = 2.97$)
 - Acetoacetic acid ($pK_a = 3.58$)
 - m-Chlorobenzoic acid ($pK_a = 3.98$)
 - p-Chlorocinnamic acid ($pK_a = 4.41$)

Answer: (b) Acetoacetic acid ($pK_a = 3.58$)

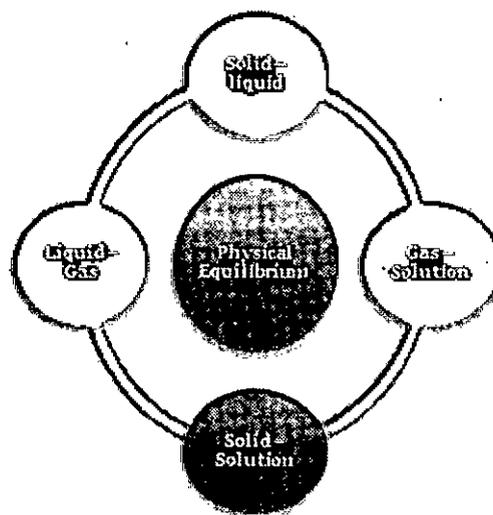


Notes

If the opposing processes involve only physical changes, the equilibrium is called **Physical Equilibrium**.

If the opposing processes are chemical reactions, the equilibrium is called **Chemical Equilibrium**.

Physical Equilibrium



Solid - liquid Equilibrium: $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$

Liquid - Gas Equilibrium: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$

Solid - Solution Equilibrium: $\text{Salt}(\text{Solid}) \rightleftharpoons \text{Salt}(\text{in solution})$

Gas - Solution equilibrium: $\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{in solution})$

Equilibrium in Chemical Process

Reversible reaction: A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions

Examples: $3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$

Irreversible reaction: A reaction cannot take place in the reverse direction, i.e. the products formed do not react to give back the reactants under the same condition.

Example: $\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{g})$

Generally, a chemical equilibrium is represented as $aA + bB \rightleftharpoons cC + dD$

Where A, B are reactants and C, D are products.

Note:

The double arrow between the left hand part and right hand part shows that changes are taking place in both the directions.

On the basis of extent of reaction, before equilibrium is attained chemical reactions may be classified into three categories.

Those reactions which proceed to almost completion.

Those reactions which proceed to almost only upto little extent.

Those reactions which proceed to such an extent, that the concentrations of reactants and products at equilibrium are comparable.



Dissociation of Ionic Compounds in Polar Solvents

Ionic compounds dissolve in polar solvents with ionization into cations and anions. The ionized ions are in equilibrium with the un-dissociated molecules.



Ionic Solids In Solutions

Strong electrolytes ($\alpha \approx 100\%$ ionization), Weak electrolytes ($\alpha \approx 10\%$ ionization), Sparingly soluble ($\alpha \approx 100\%$ ionization)

Example: HCl, NaOH, Salts NH_4OH , Organic acids $AgCl$, $BaSO_4$

Ionization of Weak Electrolytes

In infinite dilution, all electrolytes are fully ionized. In a concentrated solution, weak electrolytes exist in equilibrium with their unionized molecules. Concentrations of the ions are important in many practical situations like acid-base solubility, and conductance of the solution.

Common Ion Effect on Degree of Dissociation

Weak electrolytes are poorly ionized in aqueous solution. Their ionization may further be reduced if one of the ions are present from another source. This called a common ion effect.

- i) Ammonium hydroxide is a weak base. On addition of ammonium chloride (a salt) ammonium ion from it, will make the ammonium ions to combine with the hydroxide to form unionized ammonium hydroxide.



- ii) In the base hydrolysis of oil, the sodium salt of the fatty acid (soap) is in a dissolved state.

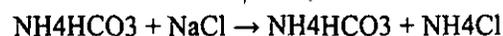
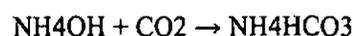
When sodium chloride salt is added, the concentration of Na^+ ions increases considerably.



Hence, the ionic product $[C_nH_{2n+1}COO^-][Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution. This is called salting out of soap.

- (iii) Manufacture of sodium bicarbonate (baking soda):

In Solvay's soda process. The CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.

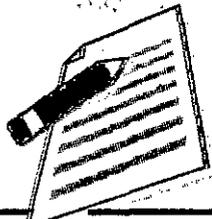


$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl , NH_3HCO_3 and $NaCl$.

Equilibrium

Equilibrium is the state of a process in which the properties like temperature, pressure, and concentration etc of the system do not show any change with passage of time. In all processes which attain equilibrium, two opposing processes are involved.

Equilibrium is attained when the rates of the two opposing processes become equal.



For example, NaCl undergoes complete ionization in its aqueous solution to render sodium ions (Na⁺) and chloride (Cl⁻) ions, whereas, acetic acid undergoes partial ionization to render some amount of acetate ions(CH₃COO⁻) and hydrogen(H⁺) ions.

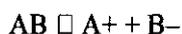
In case of a strong electrolyte, the dissociation reaction is said to be complete, thus moving in the forward direction only, whereas, in case of a weak electrolyte, the reaction is said to be reversible in nature.

In the case of the weak electrolyte, the equilibrium is established between the ions and the unionized molecules, which can be termed as ionic equilibrium. The same can be understood with the following example.

Ostwald's Dilution Law: Degree of Dissociation

Ostwald's dilution law is the application of the law of mass action to weak electrolytes in solution.

A binary electrolyte AB which dissociates into A⁺ and B⁻ ions.



(i) For very weak electrolytes, since $\alpha \ll 1$, $(1 - \alpha) = 1$

$$K = C\alpha^2 \quad \alpha = \sqrt{\frac{K}{C}} \quad \alpha = \sqrt{\frac{K}{V}}$$

(ii) Concentration of any ion = $C\alpha = \sqrt{CK} = \sqrt{K/V}$

Degree of ionization increases on dilution. Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

Limitations of Ostwald's Dilution law

The law holds good only for weak electrolytes and fails completely in the case of strong electrolytes.

Ionic Equilibrium Formulas

It becomes necessary to know what fraction of the initial amount of the reactants are converted into products at equilibrium.

The fraction of the initial molecules that are converted at equilibrium is called the degree of Dissociation/ionization.

Degree of dissociation or ionization = $\alpha = \frac{\text{(Number of reactant molecules dissociated/ionized at the start)}}{\text{(Number of reactant molecules at the start)}}$

Degree of dissociation in Ionic equilibrium can be expressed in percentage.

% Degree of dissociation or ionization = $\alpha = \frac{\text{(Number of reactant molecules dissociated or ionized at the start)}}{\text{(Number of reactant molecules at the start)}} \times 100$

Degree of Ionization

The degree of ionization depends on

Nature of the electrolyte: strong, weak, insoluble

Nature of the solvent: High dielectric solvents increase ionization

Dilution: larger the dilution higher the ionization

Temperature: higher the temperature, larger the ionization and

Presence of common ions decreases the ionization of the weak electrolyte.



Notes

10 IONIC EQUILIBRIUM

- Understand the concept of Ionic equilibrium.
- Discuss the types of ionic equilibrium.
- Understand the importance of ionic equilibrium.
- Discuss the laws of ionic equilibrium.
- Discuss the factors affecting ionic equilibrium.

Objective of the Chapter:

The basic objective of this chapter is to through some light on the initial concepts of ionic equilibrium so that the practical application of this concept can be learned.

Introduction

Ionic Equilibrium - Ostwald Dilution law

In Ionic equilibrium, the ionic substance dissociates into their ions in polar solvents. The ions formed are always in equilibrium with its undissociated solute in the solution.

□ Representation of Ionic Equilibrium: $X_a Y_b \rightleftharpoons aX^{b+} + bY^{a-}$

Introduction to Ionic Equilibrium

Reactants and products coexist in equilibrium so that reactant conversion to product is always less than 100%. Equilibrium reactions may involve the decomposition of a covalent (non-polar) reactant or ionization of ionic compounds into their ions in polar solvents.

In this section, we will learn about the ionic equilibrium in ionic solutions. Substances in Ionic Equilibrium can be classified into two categories on the basis of their ability to conduct electricity given as under,

Non-Electrolytes

These are substances that consist of molecules that bear no electric charge, do not dissociate into their constituent ions and thus do not conduct electricity in their aqueous solution or molten state. For example sugar solution.

Electrolytes

These are substances that dissociate into their constituent ions in their aqueous solution and thus conduct electricity in their aqueous solutions or molten state. Example, salt solution, acid solution, base solution etc.

Electrolytes in ionic equilibrium can be further classified into strong and weak electrolytes.

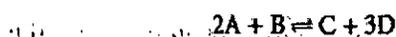
Strong electrolytes are substances that upon dissociation in their ionic solution ionize completely while in the case of weak electrolytes, the dissociation is partial in nature.



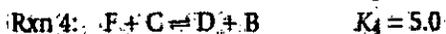
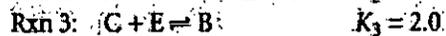
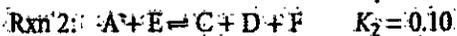
Notes

EXAMPLE 6.1

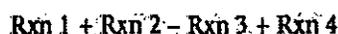
Calculate the equilibrium constant for the reaction



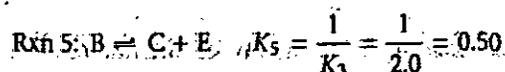
given the following information

**SOLUTION**

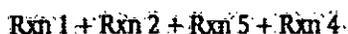
The overall reaction is given as



If Rxn 3 is reversed, giving



then the overall reaction is



and the overall equilibrium constant is

$$K_{\text{overall}} = K_1 \times K_2 \times K_5 \times K_4 = 0.40 \times 0.10 \times 0.50 \times 5.0 = 0.10$$

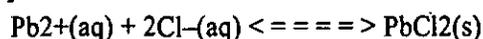
Equilibrium Constants for Chemical Reactions

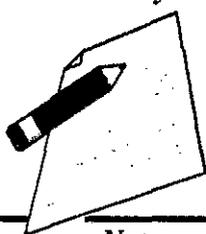
Several types of reactions are commonly used in analytical procedures, either in preparing samples for analysis or during the analysis itself. The most important of these are precipitation reactions, acid-base reactions, complexation reactions, and oxidation-reduction reactions. In this section we review these reactions and their equilibrium constant expressions.

1. Precipitation Reactions
2. Acid-Base Reactions
3. Complexation Reactions
4. Oxidation-Reduction Reactions

Precipitation Reactions

A precipitation reaction occurs when two or more soluble species combine to form an insoluble product that we call a **precipitate**. The most common precipitation reaction is a metathesis reaction, in which two soluble ionic compounds exchange parts. When a solution of lead nitrate is added to a solution of potassium chloride, for example, a precipitate of lead chloride forms. We usually write the balanced reaction as a net ionic equation, in which only the precipitate and those ions involved in the reaction are included. Thus, the precipitation of PbCl_2 is written as





Preparation of sulphuric acid by contacts process: In this process, the fundamental reaction is the oxidation of sulphur dioxide into sulphur trioxide. This involves chemical equilibrium.

Problems on Chemical Equilibrium

1. The equilibrium constant K_P for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is $1.6 \times 10^{-4} \text{ atm}^{-2}$ at 400°C . What will be the equilibrium constant of the Chemical equilibrium at 500°C if the heat of the reaction at this temperature range is -25.14 kcal ?

Solution:

Equilibrium constants at different temperature and heat of the reaction are related by the equation,

$$\log K_{P2} = -25140/2.303 \times 2 [773 - 673 / 773 \times 673] + \log 1.64 \times 10^{-4}$$

$$\log K_{P2} = -4.835$$

$$K_{P2} = 1.462 \times 10^{-5} \text{ atm}^{-2}$$

2. Given the equation, $N_2(g) + 3H_2(aq) \rightleftharpoons 2NH_3(g)$, Find Q and determine which direction the reaction will shift in order to reach the state of chemical equilibrium.

Solution:

$$\text{Given, } [N_2] = 0.04M, [H_2] = 0.09M, \text{ and } K = 0.040$$

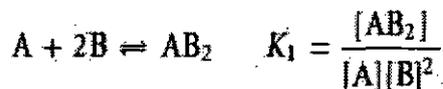
Since only nitrogen and hydrogen concentration is given, it can be assumed as the reactants and ammonia as the product. Since ammonia concentration is not given it can be assumed to be zero.

As q is the ratio of the relative concentration of products to reactants, here $Q = 0$.

Since $K = 0.04$ is larger than Q , nitrogen and hydrogen will combine to form product ammonia.

Manipulating Equilibrium Constants

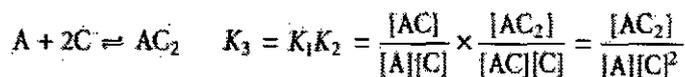
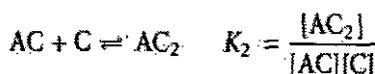
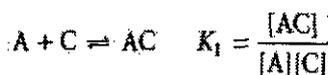
We will use two useful relationships when working with equilibrium constants. First, if we reverse a reaction's direction, the equilibrium constant for the new reaction is simply the inverse of that for the original reaction. For example, the equilibrium constant for the reaction



is the inverse of that for the reaction



Second, if we add together two reactions to obtain a new reaction, the equilibrium constant for the new reaction is the product of the equilibrium constants for the original reactions.



the change of pressure in both liquids and solids can be ignored because the volume is independent of pressure.

Change in Temperature:

The effect of temperature on chemical equilibrium depends upon the sign of ΔH of the reaction and follows Le-Chatelier's Principle.

As temperature increases the equilibrium constant of an exothermic reaction decreases.

In an endothermic reaction the equilibrium constant increases with increase in temperature.

Along with equilibrium constant, the rate of reaction is also affected by the change in temperature. As per Le Chatelier's principle, the equilibrium shifts towards the reactant side when the temperature increases in case of exothermic reactions, for endothermic reactions the equilibrium shifts towards the product side with an increase in temperature.

Effect of a Catalyst:

A catalyst does not affect the chemical equilibrium. It only speeds up a reaction. In fact, catalyst equally speeds up the forward as well as the reverse reaction. This results in the reaction reaching its equilibrium faster.

The same amount of reactants and products will be present at equilibrium in a catalysed or a non-catalysed reaction. The presence of a catalyst only facilitates the reaction to proceed through a lower-energy transition state of reactants to products.

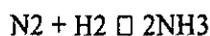
Effect of Addition of an Inert Gas:

When an inert gas like argon is added to a constant volume it does not take part in the reaction so the equilibrium remains undisturbed. If the gas added is a reactant or product involved in the reaction then the reaction quotient will change.

Examples of Chemical Equilibrium

In chemical reactions, reactants are converted into products by the forward reaction and the products may be converted into the reactants by the backward reaction. The two states, reactants and products are different in composition.

After some time of the start of the reaction, the rate of the forward and the backward reactions may become equal. After this, the number of reactants converted will be formed again by the reverse reaction such that the concentration of reactants and products do not change any more. Hence, the reactants and products are in chemical equilibrium.



Importance of Chemical Equilibrium

It is useful in many industrial processes like,

Preparation of ammonia by Haber's process: In this nitrogen combines with hydrogen to form ammonia, the yield of ammonia is more at low temperature, high pressure and in the presence of iron as catalyst.





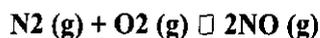
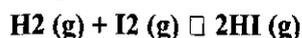
Notes

Homogeneous Equilibrium

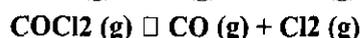
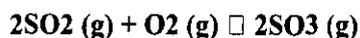
Heterogeneous Equilibrium

Homogenous Chemical Equilibrium

In this type, the reactants and the products of chemical equilibrium are all in the same phase. Homogenous equilibrium can be further divided into two types: Reactions in which the number of molecules of the products is equal to the number of molecules of the reactants. For example,

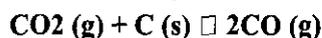


Reactions in which the number of molecules of the products is not equal to the total number of reactant molecules. For example,



Heterogeneous Chemical Equilibrium

In this type, the reactants and the products of chemical equilibrium are present in different phases. A few examples of heterogeneous equilibrium are listed below.



Thus, the different types of chemical equilibrium are based on the phase of the reactants and products.

Factors Affecting Chemical Equilibrium

Chemical Equilibrium – Factors Affecting Equilibrium

According to Le-Chatelier's principle, if there is any change in the factors affecting the equilibrium conditions, the system will counteract or reduce the effect of the overall transformation. This principle applies to both chemical and physical equilibrium.

There are several factors like temperature, pressure and concentration of the system which affect equilibrium. Some important factors affecting chemical equilibrium are discussed below.

Change in Concentration:

The concentration of the reactants or products added is relieved by the reaction which consumes the substance which is added.

The concentration of reactants or products removed is relieved by the reaction which is in the direction that replenishes the substance which is removed.

When the concentration of the reactant or product is changed, there is a change in the composition of the mixture in chemical equilibrium.

Change in Pressure:

Change in pressure happens due to the change in the volume. If there is a change in pressure it can affect the gaseous reaction as the total number of gaseous reactants and products are now different. According to Le Chatelier's principle, in heterogeneous chemical equilibrium,



Notes

9

CHEMICAL EQUILIBRIUM

- Understand the concept of chemical equilibrium.
- Discuss the types of chemical equilibrium.
- Understand the importance of chemical equilibrium.
- Discuss the factors affecting chemical equilibrium.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of chemical equilibrium so that the practical application of this concept can be learned.

Introduction**What is Chemical Equilibrium?**

Chemical equilibrium refers to the state of a system in which the concentration of the reactant and the concentration of the products do not change with time and the system does not display any further change in properties.

When the rate of the forward reaction is equal to the rate of the reverse reaction, the state of chemical equilibrium is achieved by the system. When there is no further change in the concentrations of the reactants and the products due to the equal rates of the forward and reverse reactions, the system is said to be in a state of dynamic equilibrium.

State of Chemical Equilibrium

A graph with the concentration on the y-axis and time on the x-axis can be plotted. Once the concentration of both the reactants and the products stops showing change, chemical equilibrium is achieved.

Why Chemical Equilibrium is called Dynamic Equilibrium?

The stage at which the rate of the forward reaction is equal to the rate of backward reaction is called an equilibrium stage. At this point, the number of reactant molecules converting into products and product molecules into reactants are the same. The same equilibrium can be carried out with the same reactants anywhere with similar conditions with continuous interchanging of molecules hence chemical equilibrium is dynamic.

Types of Chemical Equilibrium

There are two types of chemical equilibrium:

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Chemistry



2. Arrange the following systems in the order of increasing randomness,
(i) 1 mol of gas A (ii) 1 mol of solid A
(iii) 1 mol of liquid A
Answer:- 1 mol of solid, 1 mol of liquid, 1 mol of gas.
3. Indicate whether you would expect the entropy of the system to increase or decrease
(a) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
(b) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
(c) $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$.
Answer:- Decrease (b) Decrease (c) Increase

Review Questions

1. What do you call the measure of disorder or randomness in a system?
2. Predict the sign of ΔS for each of the following processes. (i) $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$ (ii) $\text{O}_2(\text{g}, 300\text{ K}) \rightarrow \text{O}_2(\text{g}, 500\text{ K})$
3. Define entropy.
4. Explain why entropy is not a good criteria for determining the spontaneity of a process?
5. What is the relationship between the enthalpy and the entropy change for a system at equilibrium?
6. For the reaction $\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$ $\Delta_r H = -391.9\text{ kJ mol}^{-1}$ and $\Delta_r S = 10.3\text{ J K}^{-1}\text{ mol}^{-1}$ at 298 K. Calculate $\Delta_r G$ at this temperature and state whether the reaction is spontaneous or not.
7. What happens to $\Delta_r G$ during (a) a spontaneous process (b) a non-spontaneous process (c) a process at equilibrium.
8. Calculate $\Delta_r G^\circ$ at 298 K for the reaction $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$ Given $\Delta_r H = -57.20\text{ kJ mol}^{-1}$ and $\Delta_r S = -175.8\text{ J K}^{-1}\text{ mol}^{-1}$ Is this reaction spontaneous?
9. The standard Gibbs energies of formation at 298 K are $-202.85\text{ kJ mol}^{-1}$ for $\text{NH}_4\text{Cl}(\text{s})$, $-16.45\text{ kJ mol}^{-1}$ for $\text{NH}_3(\text{g})$ and -95.3 kJ mol^{-1} for $\text{HCl}(\text{g})$ (a) What is $\Delta_r G^\circ$ for the reaction $\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$ (b) Calculate the equilibrium constant for this decomposition.
10. For the following reaction $\text{CCl}_4(\text{l}) + \text{H}_2(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{CHCl}_3(\text{l})$ $\Delta_r G^\circ = -103.7\text{ kJ mol}^{-1}$ at 298 K. Calculate the equilibrium constant for this reaction.



We now come back to the question: Why does heat always flows from a state of higher temperature to one of lower temperature and not in the opposite direction? Because entropy increases when heat flows from hot object to cold object. If heat were to flow from a cold to a hot object, entropy will decrease leading to violation of second law thermodynamics.

Entropy is also called 'measure of disorder'. All natural process occur such that the disorder should always increases.

Consider a bottle with a gas inside. When the gas molecules are inside the bottle it has less disorder. Once it spreads into the entire room it leads to more disorder. In other words when the gas is inside the bottle the entropy is less and once the gas spreads into entire room, the entropy increases. From the second law of thermodynamics, entropy always increases. If the air molecules go back in to the bottle, the entropy should decrease, which is not allowed by the second law of thermodynamics. The same explanation applies to a drop of ink diffusing into water. Once the drop of ink spreads, its entropy is increased. The diffused ink can never become a drop again. So the natural processes occur in such a way that entropy should increase for all irreversible process.

SUMMARY

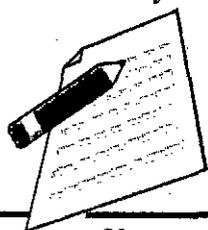
A spontaneous process is a process that occurs in a system by itself; once started, no action from outside the system (outside agency) is necessary to make the process continue. A non-spontaneous process will not take place unless some external action is continuously applied. Let us consider another example, we know that when iron objects are exposed to moist atmosphere, rusting of iron takes place. Although the rusting of iron is a slow process but it always takes place in the same direction. We say that the rusting of iron is a spontaneous process. During rusting of iron, iron is oxidised to iron (III) oxide. $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$ The reverse of the above reaction is also possible but it is non-spontaneous. An external agency has to be used to reduce iron (III) oxide to iron. From our discussion it can be concluded that if a process is spontaneous, the reverse process is non-spontaneous. All the spontaneous processes and most of the non-spontaneous processes are possible. spontaneous processes occur naturally whereas non-spontaneous processes require the help of an outside agency to occur. According to the First Law of Thermodynamics, the total energy of an isolated system always remains constant. The first law explains about the relationship between the work done by the system or by the system and the heat absorbed without putting any limitation on the direction of heat flow. However, all processes which occur naturally tend to proceed spontaneously in one direction only. A spontaneous process is an irreversible process and it could only be reversed by some external agents. The entropy of any system is defined as the degree of randomness in it.

EXERCISE

MCQ

1. Which of the following conditions would predict a process that is always spontaneous?
- | | |
|------------------------------------|-----------------------------------|
| (i) $\Delta H > 0, \Delta S > 0$ | (ii) $\Delta H > 0, \Delta S < 0$ |
| (iii) $\Delta H < 0, \Delta S > 0$ | (iv) $\Delta H < 0, \Delta S < 0$ |

Answer:- (iii)



Criteria for spontaneous change:

The second law of thermodynamics

So far we have studied about internal energy, enthalpy and entropy. Can we define the spontaneity of a process in terms of these properties? Let us see whether these changes in properties can be used as a criterion for determining the spontaneity of a process or not.

- (i) We know that most of the processes which occur spontaneously are exothermic. Water kept in a container at room temperature evaporates spontaneously. It is an endothermic process. Thus enthalpy change cannot be used as a criteria for spontaneous change.
- (ii) Can we use the increase of entropy as a criteria for the spontaneous change? Then how do we explain the spontaneous freezing of water at -10°C ? We know that crystalline ice is more ordered than the liquid water and therefore the entropy must decrease. The answer to this question is that we must consider simultaneously two entropy changes:
 - (a) the entropy change of the system itself, and
 - (b) the entropy change of the surroundings $\Delta S_{\text{total}} = \Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$ (10.2) The equation is one of the many forms of the second law of thermodynamics. According to the second law of thermodynamics all spontaneous or natural processes produce an increase in entropy of the universe. Thus, for a spontaneous process when a system is at equilibrium, the entropy is maximum, and the change in entropy is zero $\Delta S = 0$ (at equilibrium)

Third law of thermodynamics and absolute entropy

When temperature of a substance is increased, the translational, vibrational and rotational motions become more vigorous. It leads to greater disorder and as a result the entropy of the substance increases. Thus, on increasing the temperature of a substance the entropy of a substance increases. It decreases on decreasing the temperature of a substance. The entropy of a pure and perfectly crystalline solid at absolute zero temperature is zero. This is known as the Third law of thermodynamics. This third law of thermodynamics helps us to calculate the absolute value of molar entropies (S_m) of substances at different temperatures.

Entropy and second law of thermodynamics

We have seen in the equation (8.66) that the quantity Q_H/T_H is equal to Q_L/T_L . The quantity Q/T is called entropy. It is a very important thermodynamic property of a system. It is also a state variable. Q_H/T_H is the entropy received by the Carnot engine from hot reservoir and Q_L/T_L is entropy given out by the Carnot engine to the cold reservoir. For reversible engines (Carnot Engine) both entropies should be same, so that the change in entropy of the Carnot engine in one cycle is zero. This is proved in equation (8.66). But for all practical engines like diesel and petrol engines which are not reversible engines, they satisfy the relation $Q_L/T_L > Q_H/T_H$. In fact we can reformulate the second law of thermodynamics as follows

“For all the processes that occur in nature (irreversible process), the entropy always increases. For reversible process entropy will not change”. Entropy determines the direction in which natural process should occur.



Criteria for spontaneity of a process

- The spontaneity of any process depends on three different factors.
- If the enthalpy change of a process is negative, then the process is exothermic and may be spontaneous. (ΔH is negative)
- If the entropy change of a process is positive, then the process may occur spontaneously. (ΔS is positive)
- The Gibbs free energy which is the combination of the above two ($\Delta H - T\Delta S$) should be negative for a reaction to occur spontaneously, i.e., the necessary condition for a reaction to be spontaneous is $\Delta H - T\Delta S < 0$

Table 7.5 Effect of Temperature on Spontaneity of Reactions:

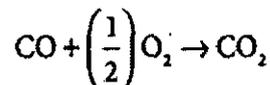
ΔH_r	ΔS_r	$\Delta G_r = \Delta H_r - T\Delta S_r$	Description	Example
-	+	-(at all T)	Spontaneous at all temperature	$2O_3(g) \rightarrow 3O_2(g)$
-	-	-(at low T)	spontaneous at low temperature	Adsorption of gases
		+(at high T)	non-spontaneous at high temperature	
+	+	+(at low T)	non-spontaneous at low temperature	Melting of a solid
		-(at high T)	spontaneous at high temperature	
+	-	+(at all T)	non spontaneous at all temperatures	$2H_2O(g) + O_2(g) \rightarrow 2H_2O_2(l)$

The Table assumes ΔH and ΔS will remain the way indicated for all temperatures. It may not be necessary that way. The Spontaneity of a chemical reaction is only the potential for the reaction to proceed as written. The rate of such processes is determined by kinetic factors, outside of thermo dynamical prediction.

Problem: 7. 8

Show that the reaction $CO + \left(\frac{1}{2}\right)O_2 \rightarrow CO_2$

at 300K is spontaneous. The standard Gibbs free energies of formation of CO_2 and CO are -394.4 and -137.2 kJ mole⁻¹ respectively.



$$\Delta G_{(reaction)}^0 = \sum G_{f(Products)}^0 - \sum G_{f(Reactants)}^0$$

$$\Delta G_{(reaction)}^0 = [G_{CO_2}^0] - \left[G_{CO}^0 + \frac{1}{2} G_{O_2}^0 \right]$$

$$\Delta G_{(reaction)}^0 = -394.4 + [137.2 + 0]$$

$$\Delta G_{(reaction)}^0 = -257.2 \text{ kJ mol}^{-1}$$

$\Delta G_{(reaction)}$ of a reaction at a given temperature is negative hence the reaction is spontaneous.



Notes

What is spontaneity?

Let us try to understand the meaning of spontaneity. A spontaneous process is an irreversible process and it could only be reversed by some external agents. The entropy of any system is defined as the degree of randomness in it.

Predicting the spontaneity of a reaction

Generally, total entropy change is the essential parameter which defines the spontaneity of any process. Since most of the chemical reactions fall under the category of a closed system and open system; we can say there is a change in enthalpy too along with the change in entropy. Since, change in enthalpy also increases or decreases the randomness by affecting the molecular motions, entropy change alone cannot account for the spontaneity of such a process. Therefore, for explaining the spontaneity of a process we use the Gibbs energy change. Gibbs' energy is a state function and an extensive property. The general expression for Gibbs energy change at constant temperature is expressed as:

Gibbs Equation \Rightarrow

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

Where,

ΔG_{sys} = Gibbs energy change of the system

ΔH_{sys} = enthalpy change of the system

ΔS_{sys} = entropy change of the system

T = Temperature of the system

This is known as the Gibbs equation.

For a spontaneous process, the total entropy change, ΔS_{total} is always greater than zero.

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

Where,

ΔS_{total} = total entropy change for the process

ΔS_{sys} = entropy change of the system

ΔS_{surr} = entropy change of the surrounding

The change in temperature between the system and the surrounding in the case of thermal equilibrium between system and surrounding is 0, i.e. $DT=0$. Thus, enthalpy lost by the system is gained by the surrounding. Hence, the entropy change of the surrounding is given as,

ΔH_{surr} = change in enthalpy of the surrounding

ΔH_{sys} = change in enthalpy of the system

Also, for a spontaneous process, the total change in entropy is 0, i.e. $\Delta S_{\text{total}} > 0$.

Therefore;

$$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$$

$$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

Using the Gibbs equation, it can be said that

$$\Delta G_{\text{sys}} < 0$$

Thus, it can be inferred that any process is spontaneous if the change in Gibbs energy of the system is less than zero or else the process is not spontaneous.

Therefore, with the help of the above relation, spontaneity of a reaction can be easily predicted.

In the case of exothermic reactions, enthalpy of the system is negative thereby making all exothermic reactions spontaneous.

In the case of endothermic reactions, Gibbs free energy becomes negative only when the temperature is very high or the entropy change is very high.



Notes

8

SPONTANEITY OF CHEMICAL REACTIONS

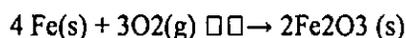
- Understand the concept of reaction.
- Discuss the concept of chemical reactions.
- Understand the concept of spontaneity.
- Discuss the criteria for spontaneity of process.
- Discuss the Gibbs equation.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of spontaneity of chemical reactions so that the practical application of this concept can be learned.

Introduction

A spontaneous process is a process that occurs in a system by itself; once started, no action from outside the system (outside agency) is necessary to make the process continue. A non-spontaneous process will not take place unless some external action is continuously applied. Let us consider another example, we know that when iron objects are exposed to moist atmosphere, rusting of iron takes place. Although the rusting of iron is a slow process but it always takes place in the same direction. We say that the rusting of iron is a spontaneous process. During rusting of iron, iron is oxidised to iron (III) oxide.



The reverse of the above reaction is also possible but it is non-spontaneous. An external agency has to be used to reduce iron (III) oxide to iron. From our discussion it can be concluded that if a process is spontaneous, the reverse process is non-spontaneous. All the spontaneous processes and most of the non-spontaneous processes are possible. Spontaneous processes occur naturally whereas non-spontaneous processes require the help of an outside agency to occur.

Spontaneity in Thermodynamics

According to the First Law of Thermodynamics, the total energy of an isolated system always remains constant. The first law explains about the relationship between the work done by the system or by the system and the heat absorbed without putting any limitation on the direction of heat flow. However, all processes which occur naturally tend to proceed spontaneously in one direction only. What does spontaneity mean here? What factors determine the direction in a spontaneous change?

CLASS-12

Chemistry



Notes

- 8) A solution is made from 35 ml of Methanol and 65 ml of water. Calculate the volume percentage.

Volume of the ethanol = 35 ml

Volume of the water = 65 ml

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

$$\text{Volume percentage} = \frac{\text{Volume of the solute}}{\text{Volume of the solute} + \text{Volume of the solvent}} \times 100$$

$$\text{Volume percentage} = \frac{35}{35+65} \times 100$$

$$\begin{aligned} \text{Volume percentage} &= \frac{35}{100} \times 100 \\ &= 35\% \end{aligned}$$

$$\text{Volume percentage} = [35 / 35+65] \times 100$$

$$\text{Volume percentage} = [35/100] \times 100$$

$$= 35\%$$

- 9) Calculate the volume of ethanol in 200 ml solution of 20% v/v aqueous solution of ethanol.

Volume of aqueous solution = 200 ml

Volume percentage = 20%

Volume percentage = [Volume of solute / Volume of solution] \times 100

$$20 = [\text{Volume of ethanol}/200] \times 100$$

$$\text{Volume of ethanol} = [20 \times 200] / 100 = 40 \text{ ml}$$



Notes

$$\text{Mass Percentage} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

$$\text{Mass Percentage} = \frac{\text{Mass of the solute}}{\text{Mass of the solute} + \text{Mass of the solvent}} \times 100$$

$$= \frac{25}{25+100} \times 100$$

$$= \frac{25}{125} \times 100$$

$$= 20\%$$

- 6) 16 grams of NaOH is dissolved in 100 grams of water at 25°C to form a saturated solution. Find the mass percentage of solute and solvent.

Mass of the solute (NaOH) = 16 g

Mass of the solvent H₂O = 100 g

(i) Mass percentage of the solute

Mass percentage of solute = $\left[\frac{\text{Mass of the solute}}{\text{Mass of the solute} + \text{Mass of the solvent}} \right] \times 100$

$$\text{Mass percentage of solute} = \frac{\text{Mass of the solute}}{\text{Mass of the solute} + \text{Mass of the solvent}} \times 100$$

$$= \frac{16 \times 100}{16 + 100}$$

$$= \frac{1600}{116}$$

Mass percentage of the solute = 13.79 %

(ii) Mass percentage of solvent

= 100 - (Mass percentage of the solute)

= 100 - 13.79 = 86.21%

- 7) Find the amount of urea which is to be dissolved in water to get 500 g of 10% w/w aqueous solution?

$$\text{Mass percentage (w/w)} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

$$10 = \frac{\text{Mass of the urea}}{500} \times 100$$

Mass of urea = 50g



Notes

Review Questions

- 1) 1.5 g of solute is dissolved in 15 g of water to form a saturated solution at 298K. Find out the solubility of the solute at the temperature.

Mass of the solvent = 15 g

Solubility of the solute = [Mass of the solute/ Mass of the solvent] × 100

$$\begin{aligned} \text{Solubility of the solute} &= [1.5/15] \times 100 \\ &= 10 \text{ g} \end{aligned}$$

- 2) Find the mass of potassium chloride would be needed to form a saturated solution in 60 g of water at 303 K? Given that solubility of the KCl is 37/100 g at this temperature.

Mass of potassium chloride in 100 g of water in saturated solution = 37 g

$$\begin{aligned} \text{Mass of potassium chloride in 60 g of water in saturated solution} &= 37/100 \times 60 \\ &= 22.2 \text{ g} \end{aligned}$$

- 3) What is the mass of sodium chloride that would be needed to form a saturated solution in 50 g of water at 30°C. Solubility of sodium chloride is 36 g at 30°C?

At 30°C, 36 g of sodium chloride is dissolved in 100 g of water.

□ Mass of sodium chloride that would be need for 100 g of water = 36 g

$$\begin{aligned} \square \text{ Mass of sodium chloride dissolved in 50 g of water} &= [36 \times 50] \times 100 \\ &= 18 \text{ g} \end{aligned}$$

- 4) The Solubility of sodium nitrate at 50°C and 30°C is 114 g and 96 g respectively. Find the amount of salt that will be thrown out when a saturated solution of sodium nitrate containing 50 g of water is cooled from 50°C to 30°C?

Amount of sodium nitrate dissolved in 100 g of water at 50°C is 114 g

$$\begin{aligned} \square \text{ Amount of sodium nitrate dissolving in 50 g of water at 50°C} &= [114 \times 50] / 100 \\ &= 57 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Similarly amount of sodium nitrate dissolving in 50g of water at 30°C} &= [96 \times 50] \\ &\times 100 \\ &= 48\text{g} \end{aligned}$$

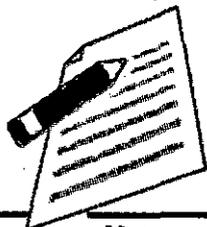
Amount of sodium nitrate thrown when 50g of water is cooled from 50°C to 30°C is

$$57 - 48 = 9 \text{ g}$$

- 5) A solution was prepared by dissolving 25 g of sugar in 100 g of water. Calculate the mass percentage of solute.

Mass of the solute = 25 g

Mass of the solvent = 100 g



Notes

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic symbol	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
Valence electron configuration	[He]2s ² 2p ³	[Ne]3s ² 3p ³	[Ar]3d ¹⁰ 4s ² 4p ³	[Kr]4d ¹⁰ 5s ² 5p ³	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Melting point	210	44.15	817	631	271
Boiling point (°C)	-196	281	603(sublimes)	1587	1564
Density (g/cm ³) at 25°C	1.15(g/L)	1.8	5.7	6.68	9.79
Atomic radius (pm)	56	98	114	133	143
First Ionization energy (kJ/mol)	1402	1012	947	834	703
Common Oxidation state(s)	-3 to +5	+5, +3, -3	+5, +3	+5, +3	+3
Ionic radius (pm)	146(-3)	212(-3)	58(+3)	76(+3)	103(+3)
Electronegativity	3.0	2.2	2.2	2.1	1.9

Some of the trends in the modern periodic table with respect to group 15 elements of the p-Block elements are discussed below.

Electronic Configuration

- The valence shell electronic configuration plays a major role in how an element behaves. The valence electron shell configuration of group 15 elements is ns²np³.
- All the group 15 elements have the same arrangement and this is why they're similar.
- The s-orbital in this group is completely filled and *the p-orbitals are half filled and this makes their configuration extra stable.*

Atomic and Ionic Radii

If you see the electronic configuration of elements in the table above, you will notice that with every step you move downwards, new orbitals are added to the atom. This addition of new orbitals increases both the Atomic and the Ionic radii of group 15 elements. However, we see that from Arsenic to Bismuth only a small increase in ionic radius is observed. This is due to the presence of completely filled d and/or f orbitals in heavier members.

Ionization Enthalpy

Ionization Energy is the amount of energy required to remove an electron from the outermost orbit of the atom. This is basically a measure of how hard the nucleus is holding on to the electron. The closer the electron is to the nucleus the stronger its hold and thus the energy required is more. As we move down the group, the radius of the atom increases and therefore the Ionization energy decreases due to the weaker hold of the nucleus.

Electro negativity

The electro negativity value decreases down the group with increasing atomic size. This again is due to the increasing distance between the nucleus and the valence shell as we move down the group.



Hot Conc. H_2SO_4 liberates SO_2 but the reaction is retarded by the formation of an insoluble layer of lead sulphate.



Concentrated HCl evolves hydrogen and also forms Chloroplumbic acid



Uses: Lead is used

- For making lead pipes,
- For making telegraph and telephone wires,
- In making bullets and lead accumulators,
- In lead chambers, for the manufacture of sulphuric acid,
- For making alloys like solder, pewter and type metal,
- For preparing tetraethyl lead ($\text{Pb}(\text{C}_2\text{H}_5)_4$) which is used as an additive to petrol to prevent knocking

Problem

An element **A** belongs to 14th group and occupies period number 6. **A** reacts with conc. HCl to give **B** an acid. **A** is used to prepare **C** which is used as an antiknock in automobiles. Identify the element **A** and the compounds **B** and **C**. Write the reactions.

Solution

As per the position in the periodic table, the element **A** is lead. Lead with Conc. HCl gives **B**



\square Compound **B** is chloroplumbic acid.

Compound **C** is tetraethyl lead.

What are Group 15 Elements?

Group 15 elements are also called *Nitrogen family* includes nitrogen phosphorus, arsenic, antimony and bismuth elements. The p-block elements are also known as the *Representative Elements* which is placed on the right side of the main periodic table.

The modern periodic table as conceived by *Dimitri Mendeleev* arranges all the elements known to man on the basis of its atomic number, which is unique to every element. The results of such an arrangement were the periodic table. The elements with similar properties were arranged into a column called a group.

Periodic Trends in Group 15 Elements

So in Group 15 elements as you would move down a group, starting with the lightest element and finishing with the heavy ones; you'd notice a general flow in properties as you move down the order. For e.g., Nitrogen is a gas and non-metal but as you move down the group, we encounter metalloids and then at the bottom, metal i.e., Bismuth. These trends in the periodic table help us better understand the behaviour of atoms and also helps us predict new elements.



Purification of Lead

Lead extracted by the above method contains impurities such as silver, copper, tin, bismuth, gold and iron. It is refined by the following processes.

Liquation

The impure metal is heated on a sloping hearth. Lead melts and flows down the slope. The infusible impurities remain on the hearth.

Desilverisation

Silver is removed by either Pattinson's process or Park's process.

Electrolytic refining

Very pure lead is obtained by this process.

Anode - Impure lead

Cathode - Very pure lead

Electrolyte - Lead fluosilicate + Hydrofluosilicic Acid

(PbSiF₆) (H₂SiF₆)

The metallic impurities which are more electropositive than lead, such as iron and tin, go into the solution while the rest of the impurities are thrown down as anode mud.

Physical properties

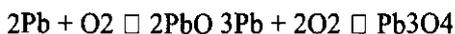
- Lead is a bluish grey metal with a bright luster.
- It is soft and can be cut with a knife and drawn into a wire and rolled into a sheet.
- It is not a good conductor of heat and electricity. It marks paper.

Chemical properties

Action of air

It is unaffected by dry air but in moist air a layer of lead carbonate or lead hydroxide is deposited on its surface which protects it from further action of air.

When heated in air or oxygen, lead is oxidized to litharge (PbO) and red lead (Pb₃O₄)



Action of water

Lead is not attacked by pure water in the absence of air, but water containing dissolved air has a solvent action on it due to the formation of lead hydroxide (a poisonous substance). This phenomenon is called **Plumbo solvency**.



Action of acids

Dilute H₂SO₄ and HCl have no action on lead.

2 Metallurgy of Lead



Notes

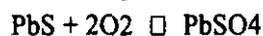
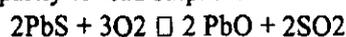
Ores

- Galena PbS
Cerrusite $PbCO_3$
Anglesite $PbSO_4$
Lead ochre PbO

Extraction: Lead is mainly extracted from the sulphide ore galena. Galena contains lead sulphide and small quantities of silver.

Concentration: The ore is concentrated by froth floatation process.

Smelting in a Reverberatory furnace: The concentrated ore is roasted in a reverberatory furnace at a moderate temperature. The temperature of furnace is controlled by regulating the air supply. During roasting, galena is partly oxidized to lead monoxide and partly to lead sulphate.



More of galena is then added. The temperature is raised and simultaneously the air supply is reduced. Lead sulphide reacts with the two oxidised products giving lead.

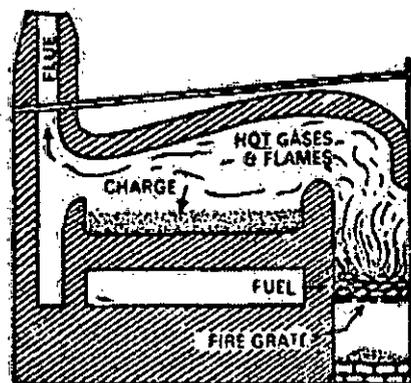
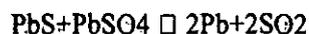
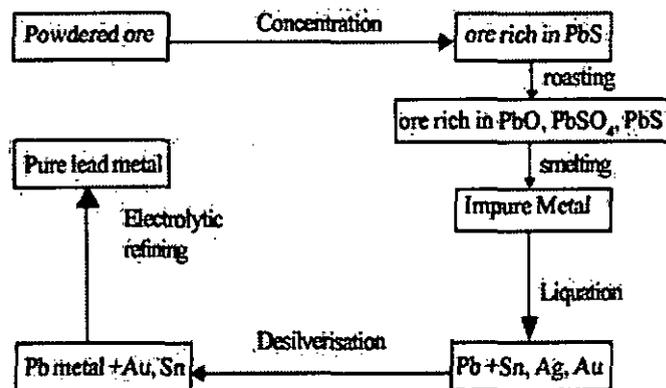
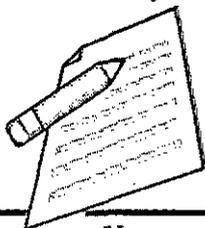


Fig. A reverberatory furnace



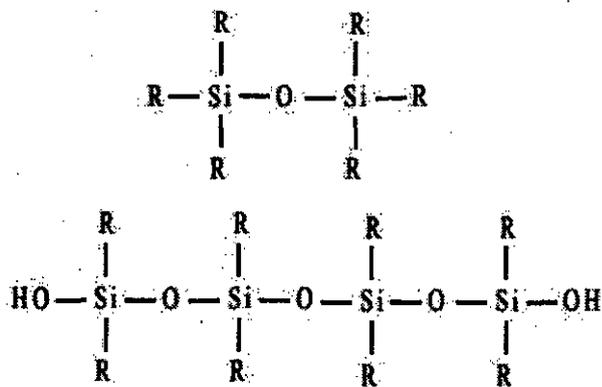
Thus in this process roasting and smelting are carried out in the same furnace, at two different temperatures. About 90% of lead is obtained as metal, the rest passes into slag. Lead is recovered from the slag by heating with lime and powdered coke.



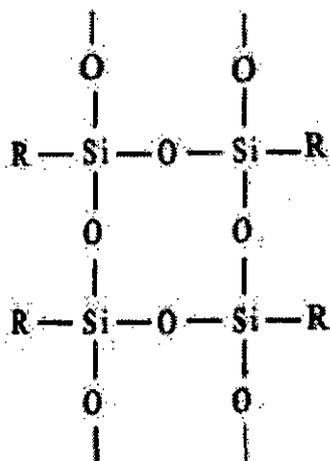


Notes

The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus the hydrolysis of trialkylmonochlorosilane R_3SiCl yields hexa-alkylsiloxane.



The dialkyldichlorosilane R_2SiCl_2 on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerisation continues and the chain increases in length. The hydrolysis of alkyl trichlorosilane $RSiCl_3$ gives a very complex cross-linked polymer.



Uses

- Silicones act as excellent insulators for electric motors and other appliances as they can withstand high temperatures.
- Straight chain polymers of 20 to 500 units are used as silicone fluids. They are water repellent because of the organic side group. These polymers are used in waterproofing textiles, as lubricants and as polish.
- Silicone rubber retain their elasticity even at low temperatures and resist chemical attack. They are mixed with paints to make them damp-resistant.
- Silicone resins, a cross-linked polymer used as non-stick coating for pans and are used in paints and varnish.
- Silicone oils are highly stable and non-volatile even on heating. Hence used for high temperature oil bath, high vacuum pump etc.



General Trends

Electronic configuration: The elements of this group possess $ns^2 np^2$ electronic configuration.

Electronic Configuration of Group 14 elements

Carbon -

Atomic Number : 6 Electronic Configuration : $[\text{He}] 2s^2 2p^2$ Group Number : 14 Period Number : 2

Silicon -

Atomic Number : 14 Electronic Configuration : $[\text{Ne}] 3s^2 3p^2$ Group Number : 14 Period Number : 3

Germanium -

Atomic Number : 32 Electronic Configuration : $[\text{Ar}] 3d^{10} 4s^2 4p^2$ Group Number : 14 Period Number : 4

Tin -

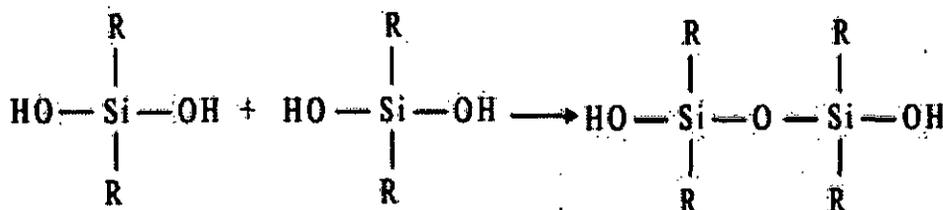
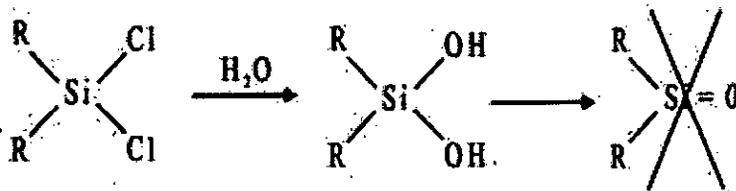
Atomic Number : 50 Electronic Configuration : $[\text{Kr}] 4d^{10} 5s^2 5p^2$ Group Number : 14 Period Number : 5

Lead -

Atomic Number : 82 Electronic Configuration : $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^2$ Group Number : 14 Period Number : 6

1 Silicones - structure and uses

The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses. The complete hydrolysis of SiCl_4 yields silica SiO_2 , which has a very stable three-dimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkyl-substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones.





- Closo-boranes (B_nH_{2n+2})
- Nido-boranes (B_nH_{2n+4})
- Arachno-boranes (B_nH_{2n+6})

Diborane (B_2H_6)

It can be prepared by reacting BCl_3 with hydrogen gas over a Cu-Al catalyst at $450^\circ C$.



Diborane on heating alone or in the presence of hydrogen, higher boranes are obtained.

Structure of Diborane

The total number of valence electrons present in diborane = $3 \times 2 + 1 \times 6 = 12$ electrons.

The number of valence electrons in ethane (C_2H_6) = $4 \times 2 + 1 \times 6 = 14$ electrons.

Therefore, we can see that diborane is electron deficient and hence should be unstable.

From the data obtained from electron diffraction studies, we were able to elucidate the structure of diborane.

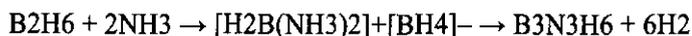
It has two types of hydrogen atoms, terminal and bridged. The four terminal B-H bonds have the same bond length, and they are normal covalent bonds.

The two bridged hydrogen atoms, however, the H-B-H bond are much longer than the terminal B-H bond. The H-B-H bond is unusual as the two bridges involve only one electron from each hydrogen atom giving a total of four electrons. That is, each H-B-H bond has two electrons delocalized over three centres, giving rise to a three-centred two-electron bond.

Borazine

Boron-Nitrogen species that carry only one substituent on each atom, and exist as trimers are called Borazine ($B_3N_3H_6$).

It is prepared by heating diborane and ammonia in 1:2 molar ratio at $-120^\circ C$, which gives ionic species which on heating gives borazine.



Similarities of Borazine with Benzene

Borazine is isoelectric with benzene. i.e. the total number of electrons in benzene = $6 \times 6 + 1 \times 6 = 42$ electrons and the total number of electrons in borazine = $3 \times 5 + 3 \times 7 + 6 \times 1 = 42$ electrons.

Borazine is isosteric with benzene. That is, the total number of atoms are same.

Borazine possesses a cyclic structure of alternating boron and nitrogen atoms.

Both the N and B are sp^2 hybridized.

Properties of Borazine

It readily undergoes addition reaction. This is because the B-N bond is polar unlike the covalent C-C bond, and hence addition reactions happen easily.

Group - 14 elements - the carbon family

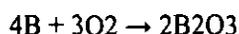
The group 14 (IVA) elements - carbon, silicon, germanium, tin and lead are especially important both in industry and in living organisms. Carbon is an essential constituent of the molecules on which life is based. Silicon is the second most abundant element in the earth's crust. Both silicon and germanium are used in making modern solid-state electronic devices. Tin and lead have been known and used since ancient times.

Compounds of Group 13 Elements

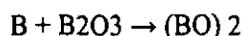
Oxides

All the elements of group 13 form sesquioxides (sesqui means one and a half). The formula of the oxide formed is $MO_{3/2}$ or M_2O_3 .

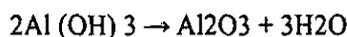
B_2O_3 is formed by heating amorphous boron in air,



Boron suboxide $(BO)_2$ is formed by heating B_2O_3 with boron at $1050^\circ C$.



The oxides of the other elements can be prepared by the thermal decomposition of their nitrates or their hydroxides.



Halides

Boron forms trihalides with Fluorine, Chlorine, and Iodine. All of the trihalides formed are planar molecules and sp^2 hybridized.

Since all the elements of group 13 possess only 6 electrons in their valance shell, they act as Lewis acids.

The order of the Lewis acid character exhibited by the trihalides is,



Reason: This is not in accordance with the normal trend observed, surely, we can claim that BF_3 to be the most acidic as F is the most electronegative.

The reason for the above trend is back bonding, specifically, $p\pi-p\pi$ back bonding. The lone pair on F is given to the empty p -orbital of B making it less electropositive, and thereby, reducing the acidic character.

The overlap of B and F is maximum as their sizes are compatible. Boron cannot form effective back bonding with Cl or Br as they are bigger than B. The halides of Al, Gallium, In and Tl are largely covalent.

Borates

Borates are compounds of group 13 containing discrete $[BO_3]^{3-}$ units. Each unit is sp^2 hybridized. They are classified according to the way the individual units are linked.

Orthoborates: They contain discrete BO_3^{3-} units. For example, $Mg_3(BO_3)_2$.

Pyroborates: Two units of BO_3^{3-} are linked via a common oxygen atom. The formula is $B_2O_5^{4-}$. For example, $Mg_2B_2O_5$.

Metaborates: They have a structure where each unit shares two oxygen atoms. Therefore they are either in the form of chains or cyclic. The general formula is $(BO_2)_n^-$.

Sheet borate: The two-dimensional network of borates where all the three oxygen atoms are shared.

Boron Hydrides

The binary compounds formed by boron and hydrogen are called boranes. The simplest borane known is B_2H_6 . They are classified into three major types,





Ionization Energy

Down the group, the values of Ionization Enthalpy do not decrease smoothly. From Boron to Aluminium, the Ionization Enthalpy increase as expected. But from Aluminium to Gallium, the Ionization Enthalpy increase slightly. The first Ionization Enthalpy of Thallium is greater than Aluminium.

Reason: This trend is observed due to the poor shielding of d and f orbitals. Gallium is smaller than Aluminium due to poor d shielding, therefore, IE1 of Aluminium < IE1 of Gallium. Similarly, Thallium has intervening f orbitals which are very poor at shielding, thereby increasing the IE1 of Thallium.

Element	IE1 (KJmol ⁻¹)
B	801
Al	577
Gallium	579
In	558
Tl	589

Electro negativity

The electronegativity first decreases from B to Al, then it increases slightly from Aluminium to Tl. This can be attributed to the poor shielding of the intervening d and f orbitals.

Electro positivity

The trend expected should be the exact opposite of electro negativity. The metallic character first increases from B to Al, then it decreases slightly from Aluminium to Tl.

This is due to the fact that the group 13 has a very high Ionization Enthalpy. Also, larger the size of the ion, lesser is its Ionization Enthalpy. Therefore Aluminium is the most metallic. This can further be explained using the standard reduction potentials.

Element	B	Al	Ga	In	Tl
M ³⁺ (aq)/M(s)	-0.87	-1.66	-0.56	-0.34	+1.26

This shows that Aluminium is the most metallic and that Tl³⁺ isn't that stable, as the potential is positive, making Gibb's free energy positive. ($\Delta G = -nFE$)

Density

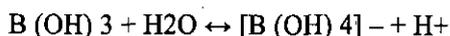
The elements of group 13 have higher densities than group 2 elements. This is because they have smaller sizes, and hence small volumes. The density increases from B to Tl.

Acid-Base Characteristics

The acidic character of oxides of group 13 elements decreases down the group and the basic character increases.

Note: Both Al and Gallium are amphoteric in nature.

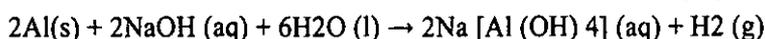
H₃BO₃ is a monobasic acid in water. This is because water acts as a Lewis base and H₃BO₃ acts as a Lewis acid. This results in the release of a proton,





Note: The action of concentrated HNO_3 renders Aluminium and Gallium passive by forming a protective layer of oxide.

Aluminium and Gallium can also react with alkalis liberating hydrogen gas.



Reactivity of Group 13 towards Halogens

They react with halogens at high temperatures to form trihalides MX_3 .



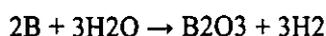
Tl however, only forms TlF_3 and TlCl_3 .

Note: Tl also forms mono-halides.

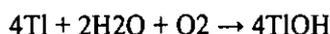
Reactivity of Group 13 towards Water and Metals

Reactivity towards Water :

Boron does not react with water or steam, however, at very high temperatures it reacts with steam.

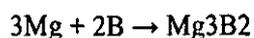


If the oxide layer is absent, Aluminium decomposes cold water to yield hydrogen gas. Gallium and Indium do not react with water unless oxygen gas is present. Thallium forms TlOH in moist air.



Reactivity towards Metals:

Only boron combines with metals to form borides. The rest of the elements of group 13 are reluctant to combine with metals. This portrays the non-metallic character of Boron.



Complex Forming Tendency

Group 13 elements have more tendency to form complexes than s-block elements due to their smaller size and more polarising power.

Boron can form many complexes like $[\text{BF}_4]^-$. It has an sp^3 hybridized orbitals and tetrahedral geometry. Other elements also form complex compounds like $\text{Li}[\text{AlH}_4]$, $[\text{GaCl}_6]^{3-}$.

Physical Properties of Group 13 Elements

Atomic and Ionic Radii

The atomic radii of group 13 elements are lesser than their corresponding group 2 elements. This is because the effective nuclear charge increases which make the size of the atom smaller.

The atomic and ionic radii down the group increases due to the addition of a new shell. There is a deviation, however, on moving from Aluminium (143 pm) to Gallium (135 pm). This arises due to the poor shielding of the intervening d-orbitals in Gallium, making the size smaller than Aluminium.





This can be explained using the inert pair effect. It is the non-participation of the s-orbital during chemical bonding due to the poor shielding of the intervening electrons.

Simply put, for elements like Indium and Thallium, d and f orbitals are filled with electrons. Since the shielding ability of d and f orbitals are very poor, the nuclear charge that seeps through attracts the s orbital closer to the nucleus. This makes the s orbital reluctant to bond, thereby only the p electrons are involved in bonding.

Covalent Character of Group 13 Elements

There are three reasons for the formation of covalent compounds by group 13 elements.

Fajan's rule may be applied. Smaller the cation more is the covalence.

They have very high ionisation enthalpies ($IE_1 + IE_2 + IE_3$) which makes the formation of ionic compounds hard.

They have relatively higher electro negativities and hence the formation of compounds would not result in a higher electro negativity difference.

Reason Behind the Anomalous Behaviour of Boron

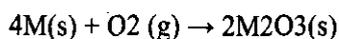
Boron behaves differently from the rest of the elements present in group 13 because of the following reasons.

- It has a very small size
- It has very high ionisation enthalpy
- It has high electro negativity owing to its small size
- The absence of d-orbital in the valence shell

Chemical Properties of Group 13 Elements

Reactivity of Group 13 towards Oxygen

All of the elements of group 13 react at high temperature forming trioxides, M_2O_3 .



Tl besides forming Tl_2O_3 also forms Tl_2O .

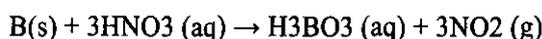
The reactivity of group 13 elements towards oxygen increases down the group.

Boron is unreactive towards oxygen in its crystalline form. Finely divided amorphous boron reacts with oxygen on heating to form B_2O_3 .

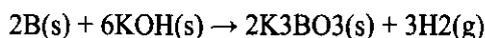
Thermodynamically, Aluminium should react with air, but it is stable. This is because Al_2O_3 forms as a protective layer on the surface of the metal, thereby making it inert.

Reactivity of Group 13 towards Acids and Alkalis

Boron does not react with non-oxidising acids like HCl, but at higher temperatures, it reacts with strong oxidizing acids like a mixture of hot concentrated H_2SO_4 and HNO_3 to give boric acid.



Boron resists the action of alkalis (NaOH and KOH) up to 773 K, above which they form borates.



All the other elements of group 13 react both with non-oxidising and oxidising acids liberating hydrogen gas.



Notes

All the three types of carbides are prepared by heating the element or its oxide with carbon or a hydrocarbon to a high temperature.

- $2\text{Be} + \text{C} \rightarrow \text{Be}_2\text{C}$
- $\text{CaO} + 3\text{C} \rightarrow \text{CaC}_2 + \text{CO}$
- $\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}$

Oxides

The oxides show a marked trend in structure from the molecules of carbon dioxide to giant structures intermediate between ionic and covalent lower down the group.

The +2-oxidation state is the more stable state in the case of lead oxide, and lead (IV) oxide decomposes on heating giving lead(II) oxide, a solid that melts at 886degC. The structure of lead(II) oxide is predominantly ionic.

The oxides at the top of the group (CO_2 and SiO_2) have an acidic nature, the carbonate ion CO_3^{2-} being produced easily in dilute aqueous solutions. The ease of formation of oxoanions (SiO_3^{2-} , GeO_3^{2-} -etc.) decreases down the group as the acidic character decreases. The oxides of germanium, tin and lead are amphoteric, reacting to form simple salts with acids.

Uses of carbon and its compounds

Carbon and its compounds play an enormous role in the global economy, e.g., Fossil fuels.

Halogenated carbon compounds are used as refrigerants, aerosol propellants, fire extinguisher and solvents.

CS_2 is used in the manufacture of viscose rayon (artificial silk) and cellophane.

What are Group 13 Elements?

The group 13 elements are the first group in the p-block of the periodic table. All the elements of group 13 are also called the boron family. The periodic table is segregated into s, p, d and f-blocks. This segregation is done based on the valence electron, if the valence electron falls on the p subshell, it comes in p-block and so on.

The members of Group 13 elements are:

Boron

Aluminium

Gallium

Indium

Thallium

The general electronic configuration for the group 13 elements is $ns^2 np^1$.

Oxidation States and Inert Pair Effect

The general oxidation state exhibited by the group 13 elements in the group are +3, and +1. As we go down the group of Boron family, the tendency to form +1 ion increases. This is due to inert pair effect.

To elucidate, consider B^{3+} and B^+ . It is shown experimentally that B^{3+} is more stable than B^+ . Now consider, Tl^{3+} and Tl^+ . It was seen that Tl^+ is more stable than Tl^{3+} .



General properties

Metallic character

Carbon and silicon are non-metals, germanium is a metalloid while tin and lead are metals. Thus metallic character increases on descending the group since ionization energy decreases on descending the group.

Hydrides

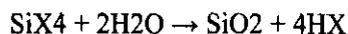
All of these elements form covalent hydrides though the number of hydrides and the ease with which these are formed decreases from carbon to lead. Carbon gives a vast number of hydrides (alkanes), silicon and germanium (silanes and germanes) whereas stannane (SnH_4) and plumbane (PbH_4) are the only hydrides of tin and lead are known.

Unlike alkanes, silanes are strong reducing agents, explode in chlorine and are readily hydrolysed by alkaline solutions. The difference is probably due to the difference in electronegativity between C and Si resulting in difference between C-H and Si-H linkages.

Halides

All these elements give tetrahalides. Tetrachlorides are usually fuming liquids at ordinary temperature. Carbon tetrahalide resists hydrolysis. This is because due to the absence of d-orbitals. Maximum covalency of carbon is only four and there is no possibility of formation of coordinate linkages with H_2O , which could lead to hydrolysis.

Tetrahalides of rest of the elements undergo hydrolysis. For example



Carbon, silicon and germanium form trihalides of the type MHX_3 . Lead and tin do not form trihalides. Silicon, germanium, tin and lead form dihalides.

Chlorides

The chlorides are all simple molecular substances with tetrahedral molecules. The stability of the chlorides decreases down the group and the +2 oxidation state becomes more stable than the +4 state. Only tin and lead form chlorides in which their oxidation state is +2, the other chlorides existing solely in the +4 state. Tin(II) chloride is a solid that is soluble in water, giving a solution which conducts electricity. It is also soluble in organic solvents. Its melting point is 246deg C. Lead(II) chloride is also a solid. It is sparingly soluble in water. The chlorides of the group 14 elements in their +4 oxidation state illustrate further the change in character of the elements from non-metal to metal down the group and giving a solution which conducts electricity, and melts at 501deg C. These observations suggest that tin(II) chloride has both covalent and ionic character, while lead(II) chloride is predominantly ionic.

All the chlorides with +4 oxidation state are readily hydrolysed by water, except tetrachloromethane (CCl_4).

Carbides

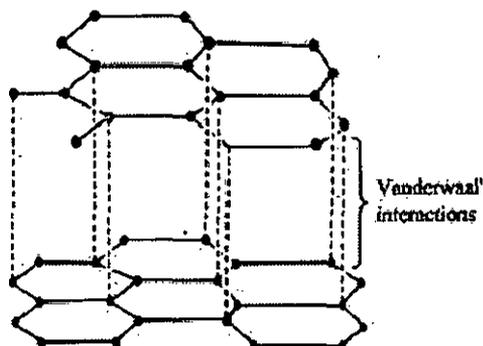
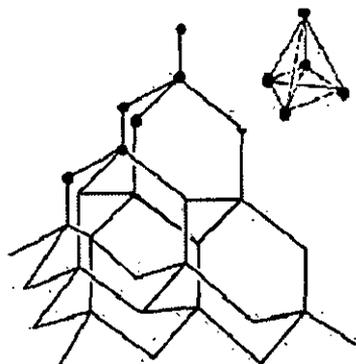
Compounds of carbon with less electronegative elements (e.g., metals, Be, B, Si etc.) are called carbides. These are of three main types.

- Ionic or salt-like e.g., acetylides, methanides, allylides
- Interstitial or metallic e.g., WC and
- Covalent e.g., B_4C , SiC .

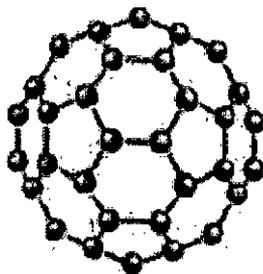
Structure of Buckminster fullerenes

Fullerenes

In 1985, a new allotrope of carbon was discovered by Richard Smalley and Robert Curl of Rice University, Texas, working with Harry Kroto of Sussex University. The first to be identified and the most symmetrical of the family, with 60 atoms and 32 sides (20 hexagons and 12 pentagons), was nick named 'buckyball' and was then named buck minister fullerene, because it resembles the geodesic domes developed by an American inventor called R.Buckminster fuller. The group of spherical carbon molecules is called fullerenes. These compounds have superconducting properties and its potential for opening new areas of chemistry have made study of the 'buckyball' as one of the most rapidly expanding areas of chemical research.



Structure : The structure of graphite.



Fullerene

Amorphous form of carbon

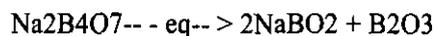
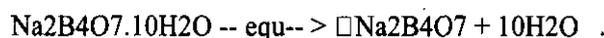
Amorphous carbon is the most reactive form of carbon. It burns relatively easily in air, thereby serving as a fuel, and is attacked by strong oxidising agents. This form has structural features of graphite, such as sheets and layers. It's atomic structure is much more irregular.



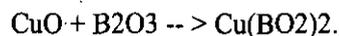


Properties

When borax is heated above its melting point until all the water of crystallization is expelled, it forms a colourless glassy substance known as borax glass. It then decomposes to give sodium meta borate and boron (III) oxide.



When this mixture is fused with metallic oxide it forms characteristic coloured beads. With the help of the colour, the metal ions can be identified. For example



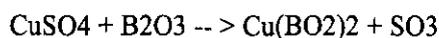
Uses: Borax is used to identify the metallic radicals in the qualitative analysis as a flux in welding metals in the manufacture of glass, soap and porcelain as cleaning and dyeing agent in tanneries as a food preservative.

Borax bead test

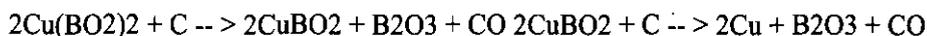
A pinch of borax is heated in a platinum loop, it melts to give a colourless glassy bead. It is then dipped in a coloured metallic salt solution and again heated. Characteristic coloured beads are formed. From the colour of the beads, the basic radicals are identified. Due to the formation of metallic metaborate, the characteristic colours are formed.

Example: Copper salts give blue beads

In an oxidising flame



In a reducing flame



Borax bead test is used to identify the coloured salts.

Carbon group elements

The elements carbon, silicon, germanium, tin and lead constitute the 14th group of the periodic table. These are p-block elements having the configuration ns^2np^2 .

Structure of diamond

In diamond every atom is bonded with the other by covalent links resulting in the formation of giant molecule. Each carbon atom is linked with four neighbouring carbon atoms held at the corners of a regular tetrahedron by covalent bonds. The C-C bonds are very strong. The crystal of diamond is very hard and has high melting and boiling points.

The combined strength of the many carbon-carbon bonds within the structure of diamond give it both great hardness and a lack of chemical reactivity.

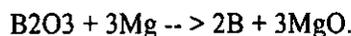
Structure of graphite

It consists of separate layers. The carbon atoms are arranged in regular hexagons in flat parallel layers. There is no strong bonding between different layers, which are, therefore, easily separable from each other. Since there are no covalent linkages between the adjacent planes, graphite can be easily cleaves along the lines of the planes. Whilst the bonds within the layers are strong, those between the layers are not and so they slide over each other easily. This accounts for the softness and lubricating power of graphite.



Notes

acid when a dark brown powder of amorphous boron is obtained as a residue: It is washed with water and dried.



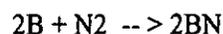
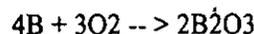
Pure boron is obtained in the crystalline form by passing a mixture of boron tribromide vapours and hydrogen over electrically heated filament of tungsten at 1470K. It may also be prepared by submitting a mixture of boron trichloride vapour and hydrogen to the action of a high tension electric arc, when boron is obtained on cooling as a hard black amorphous mass.

Physical properties

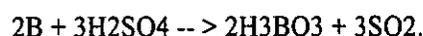
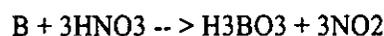
Boron exists in two allotropic forms amorphous and crystalline boron. Boron is a non-metallic element and is a non-conductor of electricity.

Chemical properties

Action of air:- It is unaffected by air at ordinary temperature but when heated in air to about 975K, it burns forming boron trioxide and a little boron nitride, BN



With acids: - Amorphous boron dissolves in hot concentrated sulphuric and in nitric acid to form boric acid.



With caustic alkali:- It dissolves in fused caustic alkali and forms boric acid.

As a reducing agent:- Boron is a powerful reducing agent and can even replace carbon from carbon dioxide and silicon from silica.



With metals:- It combines with metals (except Cu, Ag and Au) at high temperature in the electric furnace to form borides.

With non-metals:- Boron combines with nitrogen, chlorine, bromine and carbon at higher temperature forming boron nitride, BN, boron trichloride, BCl₃, boron tribromide, BBr₃ and boron carbide, B₄C respectively. Boron carbide is probably the hardest substance known.

Compounds of Boron

Borax (or) Sodium tetraborate, Na₂B₄O₇ - Tincal, a crude form of borax, contains 55% of it and is found in the land dried up lakes of Tibet.

Borax can be prepared

From colemanite:- It is boiled with concentrated solution of sodium carbonate.



On filtration and concentration, crystals of borax separate. A current of CO₂ is passed through the mother liquor to convert the metaborate into borax.



The residual sodium carbonate is used again for the treatment of a fresh quantity of colemanite.

From Tincal - Naturally occurring crude borax (Tincal) is dissolved in water, filtered, concentrated and crystallized when pure borax is obtained.



Notes

15

P-BLOCK ELEMENTS AND THEIR COMPOUND - I

- Discuss the concept of p-block.
- Discuss the types of p-block elements.
- Discuss the characteristics of p-block elements.
- Discuss the compound of p-block elements.
- Discuss the characteristics of group 13, 14 and 15.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of p-block elements so that the general characteristics of compounds of p-block elements can be learned.

Introduction**Group 13 - Boron Group (B, Al, Ga, In, Tl)**

Boron does not occur in the free state in nature. In the combined state, it occurs mainly in the form of the salts of boric acid.

Ores of Boron

- Boric acid H_3BO_3
- Borax $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

Extraction

On a large scale, boron is extracted from its minerals, borax $\text{Na}_2\text{B}_4\text{O}_7$ or colemanite $\text{Ca}_2\text{B}_6\text{O}_{11}$. The latter is first converted to borax by boiling with a solution of sodium carbonate in the requisite proportion.

$2\text{Ca}_2\text{B}_6\text{O}_{11} + 3\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 3\text{Na}_2\text{B}_4\text{O}_7 + 3\text{CaCO}_3 + \text{Ca}(\text{OH})_2$ The insoluble calcium carbonate settles down and borax is crystallized from the mother liquor. Boron is isolated from borax in the following two steps.

Preparation of boron trioxide:- Borax is treated with hot concentrated hydrochloric acid, when the sparingly soluble boric acid slowly separates out.



Boric acid is strongly heated when boron trioxide is obtained $2\text{H}_3\text{BO}_3 \rightarrow \text{B}_2\text{O}_3 + 3\text{H}_2\text{O}$

Reduction of boron trioxide:- A mixture of boron trioxide with sodium, potassium or magnesium pieces is heated in a crucible to bright redness. The residual boron is broken up and boiled with concentrated HCl to dissolve out magnesium oxide and excess of boric

10. P_4O_{10} has _____ bridging O atoms

- (a) 4 (b) 5
(c) 6 (d) 2

Answer: (c)

Review Questions

1. Which groups of the 'periodic table' constitute p-block?
2. How does the magnitude of ionization energy of an atom vary along the group in the periodic table?
3. How does electro negativity change along a row of elements in the periodic table?
4. Explain 'Metallic character decreases along a period but increases on moving down a group'.
5. Discuss the trends in the chemistry of p-block elements with respect to:
 - (i) acidic and basic nature of the oxides;
 - (ii) ionic and covalent nature of the hydrides.



CLASS-12**Chemistry***Notes*

2. Graphite has a structural similarity with
(a) B_2H_6 (b) B_4C
(c) B (d) BN
Answer: (d)
3. Which is the correct order of decreasing acidity of lewis acids?
(a) $BBr_3 > BCl_3 > BF_3$ (b) $BF_3 > BCl_3 > BBr_3$
(c) $BCl_3 > BF_3 > BBr_3$ (d) $BBr_3 > BF_3 > BCl_3$
Answer: (a)
4. In the presence of KF , AlF_3 is soluble in HF . Find the complex formed
(a) $K_3[AlF_6]$ (b) AlH_3
(c) $K[AlF_3H]$ (d) $K_3[AlF_3H_3]$
Answer: (a)
5. S-S bond is present in which of the ion pairs
(a) $S_2O_7^{2-}, S_2O_3^{2-}$ (b) $S_4O_6^{2-}, S_2O_7^{2-}$
(c) $S_2O_7^{2-}, S_2O_8^{2-}$ (d) $S_4O_6^{2-}, S_2O_3^{2-}$
Answer: (d)
6. Which is the correct order of decreasing bond dissociation enthalpy?
(a) $F_2 > Cl_2 > Br_2 > I_2$ (b) $I_2 > Br_2 > Cl_2 > F_2$
(c) $Cl_2 > Br_2 > F_2 > I_2$ (d) $Br_2 > I_2 > F_2 > Cl_2$
Answer: (c)
7. Oxygen is not released on heating which of the compounds?
(a) $(NH_4)_2Cr_2O_7$ (b) $K_2Cr_2O_7$
(c) $Zn(ClO_3)_2$ (d) $KClO_3$
Answer: (a)
8. Which of the species has a permanent dipole moment?
(a) SF_4 (b) SiF_4
(c) BF_3 (d) XeF_4
Answer: (a)
9. Which of the statement is incorrect for XeO_4 ?
(a) four $p-d$ bonds are present
(b) four $sp^3 - p$ bonds are present
(c) It has a tetrahedral shape
(d) It has a square planar shape
Answer: (d)

CO₂ SiO₂ GeO₂ SnO PbO

Acidic less acidic amphoteric basic most basic

Acidic character increases across a period

Al₂O₃ SiO₂ P₄O₁₀ SO₂ Cl₂O₇

amphoteric acidic most acidic



Nature of hydrides

Many of the p-block elements form hydrides. The hydrides of non-metals are more stable. Thus in any group the stability of the hydride decreases from top to bottom; its strength as an acid also increases in this order. Thus among all the hydrides, hydrogen iodide forms the strongest acid solution in water. In group 15, nitrogen forms the most stable hydride of all. Thus the order of stability of these hydrides is



Nature of halides

Out of the p-block elements, the non-metals form covalent halides. Metallic halides show a gradation from an ionic character to covalent character. As we move from left to right across the period, ionic character of the halides decreases and covalent character increases. For example, SbCl₃ is partially ionic whereas TeCl₄ is covalent.

In case metals form halides in more than one oxidation state, halides in lower oxidation state are largely ionic and those in higher oxidation state are largely covalent.

Polarizability of a halide ion depends on its size. Iodides and bromides are more covalent while fluorides are more ionic.

SUMMARY

The elements of groups 13, 14, 15, 16, 17 and 18 constitute the p-block of the periodic table. Some of the elements of the p-block are widely and abundantly found in nature, viz., oxygen, silicon, aluminium, etc. Many physical and chemical properties of the p-block main group elements show periodic variation with atomic number. The ionization enthalpy is the energy required to remove the outermost electron from a neutral gaseous atom. The electron gain enthalpy is the energy change when a neutral atom in a gaseous state accepts an electron. Electronegativity is the ability of an atom in a molecule to attract the electrons of a covalent bond to itself. The top element in each group shows a unique behaviour. The reluctance of s-electrons to take part in bond formation is known as "inert pair effect". P-Block elements form a number of oxides on reacting with oxygen. Most of the elements of the p-block form covalent halides. General characteristics of the p-block hydrides, halides and oxides.

EXERCISE

MCQ

1. Find the amphoteric oxide

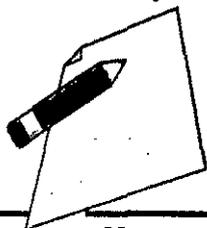
(a) CaO₂

(b) CO₂

(c) SnO₂

(d) SiO₂

Answer: (c)



P-block elements

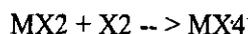
General Characteristics

The elements belonging to the group 13 to 18 of the periodic table, in which p-orbitals are progressively filled are collectively known as p-block elements.

In all these elements while s-orbitals are completely filled, their p-orbitals are incomplete. These are progressively filled by the addition of one electron as we move from group 13 ($ns2np1$) to group 17 ($ns2np5$). In group 18 ($ns2np6$) both s and p-orbitals are completely filled.

p-block elements show a variety of oxidation state both positive and negative. As we go down the group, two electrons present in the valence 's' orbital become inert and the electrons in the 'p' orbital are involved in chemical combination. This is known as 'inert pair effect'.

The inert pair effect is really a name, not an explanation. A full explanation involves the decreasing strength of the M-X bond going down the group (for covalent compounds) or the decreasing lattice energies of compounds containing the M^{4+} ion (for ionic compounds). In this way the energy input needed to form compounds of the formula MX_4 are less likely to be balanced by the energy released when the four M-X bonds are formed, so the equilibrium favours the left hand side.



The existence of a positive oxidation state corresponding to the group number and of another state two units lower is an illustration of the inert pair effect, the term referring to the valence 's' electrons, used in bonding in the higher oxidation state but not in the lower.

With the increase in atomic mass, the ionic character of bonds of the compounds of the group 13 (IIIA) elements increases, and some of the heavier metal ions do exist in the +3 oxidation state in aqueous solution. The stability of such compounds with the +3 oxidation state is, however, lower than those with the +1 oxidation state in the case of heavier members of this group. Thus thallium in +1 oxidation state is more stable than in +3 state. This is because, the s electrons in the ns sub-shell do not prefer to form bonds.

This inertness is found only, i) when the 's' electrons are in the fifth or higher principal quantum number ii) when their loss does not afford a species with a noble gas configuration. This property of stabilising the lower oxidation state keeping the paired electron in the ns orbital is referred to as the 'inert pair effect'. This effect is also observed in the elements of groups 12 (IIB), 14 (IVA) and 15 (VA) where the heavier elements exhibit 0, +2 and +3 oxidation states respectively.

Nature of oxides

Oxides of p-block elements may be basic (in case of metallic elements), amphoteric (in case of metalloids) or acidic (in case of non-metals). Non-metals also form a number of oxyacids. In all the groups, the acidic character of the oxide decreases as we move down the group while it increases in the same period from left to right.

For example

Basic oxide - Bi_2O_3

Amphoteric oxide - SnO , SnO_2 , PbO , Pb_2O_3

Acidic oxides - SO_3 , Cl_2O_7

Oxyacids - HNO_3 , H_2SO_4

Basic character increases down the group



Notes

14

GENERAL CHARACTERISTICS
OF P-BLOCK ELEMENTS

- Discuss the concept of p-block.
- Discuss the types of p-block elements.
- Discuss the characteristics of p-block elements.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of p-block elements so that the general characteristics of p-block elements can be learned.

Introduction

P block elements are in which the last electron enters any of the three p-orbitals of their respective shells. Since a p-subshell has three degenerate p-orbitals each of which can accommodate two electrons therefore in all there are six groups of p-block elements.

P block elements are shiny and usually a good conductor of electricity and heat as they have a tendency to lose an electron. You will find some amazing properties of elements in a P-block element like gallium. It's a metal that can melt in the palm of your hand. Silicon is also one of the most important metalloids of the p-block group as it is an important component of glass.

Do you know where P-block elements are in Periodic Table?

P block elements are nothing but the element in which the last electron enters the outermost p-subshell. P block starts from the 13th group and goes till 18th group in the periodic table.

You must have seen that coal is used in villages to cook food. It is nothing but a P-block element i.e. carbon. Diamonds are used for making beautiful ornaments are also made up of carbon. Aluminium foil made up of aluminium is also made up of the p block element.

Characteristics of p-Block Elements

The *general electronic configuration of p-block elements is ns^2np^{1-6} (except He)*. Whereas the inner core electronic configuration may differ. Just because of this difference the inner core, there are changes in both physical and chemical properties of the elements.

The oxidation state of elements in p – block is maximum when it is equal to a total number of valence electrons i.e. the sum of S and P electrons. One of the most interesting facts about the p-block elements is that it contains both non-metals and metalloids.

The first member of the p block elements differ from other elements in two major respects:

First is the size and each and every property which depends upon the size.

The second difference applies only to the p-block element which arises from the effects of d-orbitals in the valence shell of heavier elements.

CLASS-12

Chemistry



Notes

8. The tendency to lose their valence electron easily by alkali metals makes them
- (a) strong reducing agent (b) weak reducing agent
(c) strong oxidising agent (d) weak oxidising agent

Answer: (a)

9. Which one is known as a fusion mixture?

- (a) $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ (b) $\text{Na}_2\text{CO}_3 + \text{NaOH}$
(c) $\text{Na}_2\text{CO}_3 + \text{K}_2\text{SO}_4$ (d) $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$

Answer: (d)

10. Find the incorrect trend for alkaline earth metals

- (a) atomic size $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr}$
(b) second ionization energy $\text{Be} < \text{Mg} < \text{Ca} < \text{Sr}$
(c) Hydration enthalpy $\text{Sr} < \text{Ca} < \text{Mg} < \text{Be}$
(d) Density $\text{Ca} < \text{Mg} < \text{Be} < \text{Sr}$

Answer: (b)

Review Questions

- Write three general characteristics of the s-block elements which distinguish them from the elements of other blocks.
- The alkali metals follow the noble gases in their atomic structure. What properties of these metals can be predicted from this information?
- What happens when? (a) sodium metal is dropped in water. (b) sodium metal is heated in free supply of air. (c) sodium peroxide dissolves in water.
- Explain why hydrogen is best placed separately in the periodic table of elements.
- Describe the industrial applications of hydrogen.
- Discuss the importance of heavy water in nuclear reactor and how is it prepared from normal water?
- Name the isotopes of hydrogen. What is the importance of heavier isotopes of hydrogen? 8. Why is ice less dense than water and what kind of attractive forces must be overcome to melt ice?
- Show by proper chemical reactions how hydrogen peroxide can function both as an oxidizing and a reducing agent?
- Compare the properties of alkali metals and alkaline earth metals with respect to:
(a) atomic radii (b) ionization energy
(c) melting points (d) reducing behaviour
- Explain the trends of solubility and stability of the carbonates and sulphates of alkaline earth metals.
- Explain the process involved in the manufacture of NaOH , Na_2CO_3 and NaHCO_3 (Give Chemical equations only).
- Explain the biological role of Ca^{2+} and Mg^{2+} .

Biological role of alkali metals. Basic nature of oxides and hydroxides of group 1 and group 2 elements. Thermal stability and solubility of carbonates and sulphates. Manufacture of CaO and CaCO₃. Biological role of alkaline earth metals.



EXERCISE

MCQ

- Which of the compounds is known as Slaked lime?
(a) CaO (b) CaSO₄
(c) Ca(OH)₂ (d) CaCO₃
Answer: (c)
- Which of the ions have maximum hydration energy?
(a) Sr²⁺ (b) Ca²⁺
(c) Mg²⁺ (d) Be²⁺
Answer: (d)
- As compared to K, Na has
(a) higher ionization potential (b) lower melting point
(c) lower electronegativity (d) larger atomic radius
Answer: (a)
- Which one is the most stable carbonate?
(a) BaCO₃ (b) MgCO₃
(c) CaCO₃ (d) BeCO₃
Answer: (a)
- Plaster of Paris (POP) is
(a) CaSO₄ · H₂O (b) CaSO₄ · 2H₂O
(c) CaSO₄ (d) CaSO₄ · 1/2H₂O
Answer: (d)
- Which oxide is amphoteric?
(a) BaO (b) CaO
(c) BeO (d) MgO
Answer: (c)
- Be shows the diagonal relationship with
(a) Na (b) Al
(c) Mg (d) B
Answer: (b)



Plaster of Paris [Calcium hemihydrate, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$]

Naturally, available gypsum is calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). It exists in the monoclinic crystal structure. An aqueous solution of soluble calcium salts like nitrates or chlorides on treatment with dilute sulphuric acid precipitates out hydrous calcium sulphate.

On heating in a carbon-free environment (otherwise calcium sulphate is reduced to calcium sulphite), depending on the temperature monoclinic gypsum undergoes various transformations. It hardens first into another orthorhombic allotropy form.

At 120°C : Some of the water of hydration is lost to yield calcium sulphate hemihydrate, called as Plaster of Paris.

On heating to 200°C : It loses the remaining water and becomes anhydrous calcium sulphate called "dead burnt Plaster".

At 400°C : Calcium Sulphate decomposes into calcium oxide and evolving Sulphur dioxide and oxygen.

Properties

A paste of this hemihydrate with about one-third of water sets to a hard mass, in any moulding, in about 15 minutes. Added water may rehydrate the hemihydrate into dihydrate.

Salts like sodium chloride accelerates the hydration to reduce the setting time, while alum or borax reduce the hydration to increase the setting time of hardening.

It is used much in decorating surfaces, making false ceilings, bondages in surgical treatment, dentistry, etc.

Extraction of Alkaline Earth Metals

Magnesium Extraction

Magnesium occurs naturally and extracted from one of its ores. Some of the ores are,

Magnesite – MgCO_3

Dolomite – $\text{CaMg}(\text{CO}_3)_2$

Epsomite – $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$

Double salts of Carnallite – $2\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Alkaline earth metals have low electrode potentials, and so are obtained by the electrolysis of the fused chlorides. Chlorides and fluorides of alkali and alkaline earth metals are added to reduce the melting point. Since magnesium burns readily in oxygen, the flow of a reducing gas like coal gas is maintained during electrolysis.

SUMMARY

Hydrogen can either be placed with alkali metals or with halogens. Hydrogen exists in three isotopic forms namely hydrogen, deuterium and tritium. Hydrogen is a combustible gas and has reducing property. There are two important oxides of hydrogen: water and hydrogen peroxide. Cage-like structure of ice makes it float on water. Water containing deuterium in place of ordinary hydrogen is known as heavy water. Heavy water can be separated from ordinary water by electrolysis or distillation. Heavy water is used as moderator in nuclear reactors. Hydrogen peroxide acts both as oxidizing and reducing agent. Different types of hydrides i.e. ionic, covalent etc. Hydrogen as fuel. The alkali and alkaline earth metals show regular variation in various properties along a group and period. Alkali metals react with hydrogen, water and halogens to form hydrides, hydroxides and halides respectively. Diagonal relationship between Li^+ Mg^{2+} . Manufacture of NaOH , Na_2CO_3 , NaHCO_3



Unlike other alkaline earth metals, does not liberate hydrogen from acid because of higher electrode potential. Concentrate nitric acid form a coating of oxide, which makes it passive.

Beryllium oxide and hydroxide are amphoteric. Dissolves in acids to form salts and in bases to form beryllate.

- Beryllium forms carbide of a different formula and yields methane and not acetylene like other metal on reaction with water.
- Beryllium nitride is volatile.
- It does not react with atmospheric nitrogen and oxygen.

Diagonal Relationship of Beryllium with Aluminium

- Beryllium of group two resembles more with Aluminium of group three:
- Both beryllium and aluminium occur together in the mineral, "Beryl" $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$
- Both of them do not react with atmospheric oxygen and nitrogen.
- Both of them do not react with water even at high temperatures.
- They do not liberate hydrogen from acid. On treatment with concentrated nitric acid, they become passive.
- Both form polyvalent bridged hydrides of covalent nature.
- Halides of both are polyvalent, bridged, and of low melting points. Halides are Lewis acids.
- Water hydrolyzes both nitrides liberate ammonia.
- Oxides and hydroxides of Be and Al are amphoteric. So, they react with acid as well base.
- Both form carbide, that on hydrolysis yields Methane.
- Carbonates of beryllium and Aluminium are unstable.

Uses of Alkaline Earth Metals

Calcium Carbonate

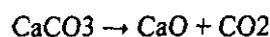
It occurs naturally in many forms as marble, limestone, chalk, coral calcite etc. The pure form is made by:

First, dissolve the mineral in hydrochloric acid,

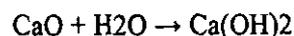
Removing, hydroxide forming impurities like iron, aluminium, by the addition ammonia,

Finally, precipitating the calcium carbonate by the addition of ammonium carbonate.

Limestone on heating decomposes to evolve carbon dioxide and form quick lime (CaO).



Calcium oxide (quick lime) reacts exothermically with water to form calcium hydroxide (lime water or slaked lime).





Nitrates

Nitrates can be prepared by reacting the corresponding oxides, hydroxides and carbonates with nitric acid. Nitrates are soluble in water. On heating, **Beryllium nitrate forms nitrite** and, other nitrates yield oxide, liberating brown fumes of nitrogen dioxide.



Halides

Alkaline earth metals from calcium to barium react with all halogens to form solid ionic halides with a definite crystal structure. Reactivity decreases from fluorine to iodine. **Beryllium halides are an exception with more covalent bonding** because of the high polarization of the small covalent ion on the electron cloud of the halogen anion as indicated by the Fajan's rule.

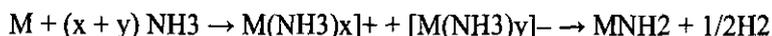
In the gas phase, Beryllium halides exist as individual molecules and in the solid phase, they form chains of Be-X.

Halides of Alkaline Earth Metals

Fluorides are insoluble in water. The **solubility of other halides decreases with increase in ionic size** i.e. from Mg^{2+} to Ba^{2+} . Halides are hygroscopic and have the water of crystallization in their solid state ($CaCl_2 \cdot 6H_2O$). Fused halides are used as dehydrating agents.

Reaction of Alkaline Earth Metals with Liquid Ammonia

Like alkali metals, Alkaline earth metals also form ammonia solvated cation and electrons. The solution is **electrically conductive, reductive and paramagnetic**. The solvated electrons absorb in the visible region and the solution turns blue in colour. The concentrated solution is bronze in colour. On long standing, it decomposes into amide, ammonia and hydrogen.



Complex of Alkaline Earth Metal

Smaller alkaline earth metals form **complexes**. Beryllium forms many complexes with mono, di and tetradentate ligands.

Examples: $[BeF_3]^{-}$, $[BeF_4]^{2-}$, $[Be(H_2C_2O_4)_2]^{2-}$, $[Be_4O(R)_6]$, where R may be NO_3^{-} , $HCOO^{-}$, CH_3COO^{-} etc.

Anomalous behaviour of Beryllium

Beryllium has more covalent nature due to its smallest size, Highest ionization energy, high electropositive nature and strongest polarizing nature. Because of these, **Beryllium differs from other alkaline earth metal properties.**

- It is the hardest metal among alkaline earth metals
- Does not react with water even at red hot conditions.
- **Melting and boiling point** of beryllium is **maximum**.
- It does not react directly with hydrogen to form hydride.

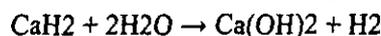


Hydrides of Alkaline Earth Metals

Calcium, strontium and barium react with hydrogen to form metallic hydrides. Metallic hydrides give hydrides ions.



Hydrides react violently with water to release hydrogen. Calcium hydride called "Hydrolith" is used for producing hydrogen.

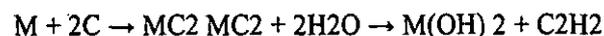


Reaction of Alkaline Earth Metals with Water

Beryllium does not react with water even at higher temperatures. Magnesium reacts with hot water only to form hydroxides and releasing hydrogen. Magnesium gets a protecting coat of its oxide, that prevents any further attack by the water molecules. Other alkaline earth metals react with even cold water to liberate hydrogen.

Carbides

Alkaline earth metals and their oxides, except beryllium, react with carbon to yield carbides. Carbides react with water to liberate acetylene gas and hence used as a source for the gas.



Oxides

Beryllium reacts with oxygen only above 600°C. Magnesium and strontium burn in oxygen to form oxides while Barium forms peroxides.

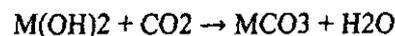
BeO and MgO are more covalent while the other oxides are ionic. Beryllium oxide is amphoteric, magnesium oxide and calcium oxide are weakly basic while other oxides are basic.

Hydroxides

Oxides react with water to ultimately yield hydroxides. The basic nature and the thermal stability of hydroxides increases from beryllium to barium.

Carbonates and Bicarbonates

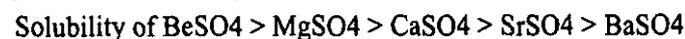
The hydroxides react with carbon dioxide to carbonates.



Bicarbonates are soluble in water and exist only in solution. Carbonates exist as solid and insoluble in water. The solubility of carbonates decreases from Be to Ba. In the presence of carbon dioxide, carbonates dissolve by forming bicarbonates. **Ionic character and the thermal stability of the carbonates increases from Be to Ba.**

Sulphates

Contrary to alkali metal sulphates, beryllium sulphate is water-soluble. The smaller size and the charge density increases the hydration energy of the beryllium sulphate leading to more solubility. In other sulphates, increasing lattice energy and the decreasing hydration energy (due to increasing size) decreases their solubility from BeSO₄ to BaSO₄.





Note: In the same period ionization energy increases due to decreasing the ionic size and increasing nuclear charge.

Why Solubility of Alkaline Earth Metals decreases down the Group?

Beryllium ion is the most soluble and the solubility decreases with increasing size so that Barium ion is the least water-soluble alkaline earth metal ion. Solubility in water is related to the ionic nature and size.

Smaller ions have higher charge density and can be solvated by more water molecules. This releases a higher enthalpy of hydration and makes the hydrated ions more stable.

Example: Solubility of $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$

Reactivity of Alkaline Earth Metals

Reducing ability is inversely related to ionization energy. As ionization energy decreases down the column, reducing property is expected to increase from Beryllium to Barium.

Reduction potential also decreases from beryllium to barium indicating the increasing reducing capacities. But, the alkaline earth metals are weaker reducing agents than alkali metals, due to higher ionization energy.

Flame Colouration

In Alkaline Earth Metals, the energy needed for an electronic transition between the available energy levels falls in the visible spectrum region. So, on heating, **except beryllium and magnesium** produce a characteristic colour to the flame reflective of their emission or absorption spectrum and can be used for their identification.

Example: Ca – Brick Red colour, Sr – Crimson Red colour, and Ba – Apple Green colour.

Melting and Boiling Points

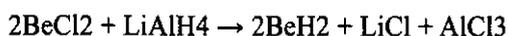
Because of smaller size and strong metallic bonding in close-packed structure, the melting and boiling points of the alkaline earth metals are higher than alkali metals. Among the alkaline earth metals except for magnesium, the **melting and boiling points decrease** regularly from beryllium to barium.

Chemical Properties of Alkaline Earth Metals

The key features of the compounds of alkaline earth metals and their general characteristics are discussed in this subsection.

Hydrides

Beryllium does not react with hydrogen directly. **Beryllium hydride can be prepared** by the reduction of beryllium chloride with lithium aluminium hydride.



Beryllium and magnesium form covalent hydrides where each hydrogen is connected to two metal atoms. This is an example of molecules with three centres sharing only two electrons called “banana Bond”.



Notes

Physical Properties of Alkaline Earth Metals

Down the column, nuclear charge increases and a new orbital is added to each alkaline earth atom.

Atomic and Ionic Radii

Ionic and Atomic radius increases down the column of the periodic table, both radii will be smaller than the alkali metal and larger than other atoms of the same period due to charge and addition of the electron to the same energy level.

Alkaline earth elements can lose both s-electrons and hence become **doubly positive cationic**. The cationic radius is smaller than the neutral atom. Still, the ionic radii increase down the column. For Example, $RBe < RMg < RCa < RSr < RBa$ and $RBe^{2+} < RMg^{2+} < RCa^{2+} < RSr^{2+} < RBa^{2+}$

Why Alkaline Earth Metals are Denser than Alkali Metals?

Radii being smaller, the volume of the atoms are also smaller. In addition, due to the presence of two valence electrons, atoms have stronger metallic bonding. Hence, **alkaline earth metals have more density and harder than alkali metals**.

Density generally increases from magnesium to radium while calcium has the lowest density among the alkaline earth metals.

Ionization Energy

Alkaline earth elements can donate both valence electrons to get a noble gas configuration of octet configuration. Thus, they have two ionization energies:

First Ionization energy

The **first ionization energy** of alkaline earth metals is the energy needed for the removal of the first electron from the neutral atom. It is larger than that of the alkali metal atom for two reasons:

Due to smaller radii and the electrons being held tightly by the higher nuclear charge, and Electron being removed from a fully filled and hence a stable subshell.

Second Ionization Energy

The **second ionization energy** of alkaline earth metals needed for the second electron from the cation will be more than the first ionization energy of the atom, but less than any second ionization of alkali metal. In spite of the high ionization energy, removal of both electrons are feasible because,

Atom gets a noble gas configuration

The smaller size and higher charge help to overcome the higher ionization energy by **higher lattice energy arising due to the close packing of atoms or ions in solids**.

Higher hydration energy in liquids due to larger solvation.

So group two alkaline earth elements are all **divalent electropositive metals** and exhibit a fixed oxidation state of 2. Ionization energy needed for the removal of the valence electron will be highest for the small beryllium atom.

With increasing atomic size, the valence electron gets shielded by the inner electrons and becomes easily removable with less energy requirement. Hence the ionization energy decreases with an increasing atomic number or atomic size.

Example: $IE_{Be} > IE_{Mg} > IE_{Ca} > IE_{Sr} > IE_{Ba}$



Notes

In the presence of nitrogen, lithium and magnesium form their respective nitrides. Superoxides are not formed when lithium and magnesium react with excess oxygen. Carbon dioxide and their respective oxides are formed when carbonates of magnesium and lithium are heated.

Similarities between Beryllium and Aluminium

Aluminium hydroxide and beryllium hydroxide react with excess alkali to form their respective ions.

Both these elements have the capacity to withstand the acid attack due to the presence of an oxide film on the surface of the metal.

Both these metals have the tendency to form complexes.

Chlorides of both these metals possess the capacity to be soluble in organic solvents.

Alkaline Earth Metals

The alkaline earth metals are the elements that correspond to group 2 of the modern periodic table. This group of elements includes **beryllium, magnesium, calcium, strontium, barium, and radium**. The elements of this group are quite similar in their physical and chemical properties. For example, all alkaline earth metals are silvery-white coloured solids under standard conditions. They are also highly lustrous (shiny) and are quite reactive. The general electronic configuration of these elements is ns^2 . Since the alkaline earth metals have a completely full s-orbital in their respective valence shells, they tend to readily lose two electrons to form cations with a charge of +2. Thus, the most common oxidation state exhibited by the alkaline earth metals is +2.

What are Alkaline Earth Metals?

Elements whose atoms have their s-subshell filled with their two valence electrons are called alkaline earth metals. Their general electronic configuration is [Noble gas] ns^2 . They occupy the **second column of the periodic table** and so-called as group two metals also.

Examples of Alkaline earth Metals: Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra).

They occupy successive periods from first to seven of this radium is a radioactive element. Alkaline earth metals form amalgams with mercury.

Overview of Alkaline Earth Metals

Metals	Beryllium	Magnesium	Calcium	Strontium	Barium
Atomic Number	4	12	20	38	56
Configuration	[He]2s ²	[Ne]3s ²	[Ar]4s ²	[Kr]5s ²	[Xe]6s ²
Abundance (ppm)	6	20900	36300	300	250
Atomic size (pm)	112	160	197	215	222
Density g/cm ³	1.85	1.74	1.55	2.63	3.62
Ionization energy kJ/mol	899 & 1757	737 & 1450	590 & 1146	549 & 1064	503 & 965
Hydration enthalpy kJ/mol	-506	-406	-330	-310	-276
Reduction potential (v)	-1.7	-2.37	-2.87	-2.89	-2.9
Flame colour	–	–	Brick red	Crimson red	Apple green



Uses of alkali metals:

- i. Lithium metal is used to make useful alloys. For example with lead it is used to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.
- ii. Lithium is also used to make electrochemical cells.
- iii. Lithium carbonate is used in medicines.
- iv. Sodium is used to make Na/Pb alloy needed to make $Pb(Et)_4$ and $Pb(Me)_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays lead-free petrol in use.
- v. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors. Potassium has vital role in biological systems.
- vi. Potassium chloride is used as a fertilizer. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.
- vii. Caesium is used in devising photoelectric cells.

Physical Properties of S block elements

In the S block elements, the density of the alkali metals increases down the group.

Exception: the density of potassium is less than the density of sodium.

The alkali metals have a low melting and boiling point due to the weak metallic bonding.

Alkali metals and its respective salts have the capability to impart colour to the oxidizing flame due to the heat generated from the flame which excites the valence electrons from one energy level to another energy level. This helps in the detection of alkali metals during the flame test.

Diagonal Relationship within S Block Elements

A diagonal relationship in S block elements exists between adjacent elements which are located in the second and third period of the periodic table. For example, Lithium of group 1A and second period shows similarities with the properties of magnesium which are located in the 2nd group and 3rd period.

Similarly, properties of beryllium which are located in the 2nd group and 2nd period show a likeness with properties of aluminium which is located in the third period and third group. The two elements which show similarities in their properties can be called a **diagonal pair or diagonal neighbours**.

The properties of S block elements vary significantly when compared to the other elements of the sub-group they belong to. The **diagonal neighbours show a lot of similarities**. Such a relationship is exhibited as you move left to right and down the group; the periodic table has opposing factors.

For example, the electronegativity of the S block elements increases as we go across the period and decreases as we go down the group. Therefore, when it is moved diagonally the opposite tendencies cancel out and the value of electronegativity almost remains the same.

Similarities between Lithium and Magnesium

The hardness of lithium and magnesium is higher than the other elements in their respective groups.

Chlorides of lithium and magnesium have the capability to be soluble in ethanol.

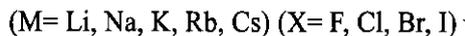
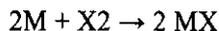
They are lighter when compared to other elements in their groups.

Lithium and magnesium react gently with water. The oxides and hydroxides are less soluble.



Reaction with halogen

Alkali metals combine readily with halogens to form ionic halides MX. Reactivity of alkali metals with halogens increases down the group because of corresponding decrease in ionisation enthalpy.



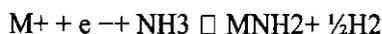
All metal halides are ionic crystals. However Lithium iodide shows covalent character, as it is the smallest cation that exerts high polarising power on the iodide anion. Additionally, the iodide ion being the largest can be polarised to a greater extent by Li^+ ion.

Reaction with liquid ammonia:

Alkali metals dissolve in liquid ammonia to give deep blue solutions that are conducting in nature. The conductivity is similar to that of pure metals (The specific conductivity of Hg is $104 \Omega^{-1}$ and for sodium in liquid ammonia is $0.5 \times 104 \Omega^{-1}$). This happens because the alkali metal atom readily loses its valence electron in ammonia solution. Both the cation and the electron are ammoniated to give ammoniated cation and ammoniated electron.



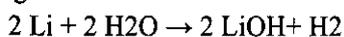
The blue colour of the solution is due to the ammoniated electron which absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of an amide.



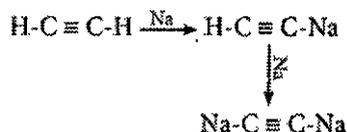
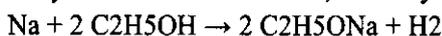
In concentrated solution, the blue colour changes to bronze colour and become diamagnetic.

Reaction with water:

Alkali metals react with water to give corresponding hydroxides with the liberation of hydrogen.



They also react with alcohol, and alkynes which contain active hydrogens.



Reducing activity:

Alkali metals can lose their valence electron readily hence they act as good reducing agents.



Reaction with carbon:

Lithium directly reacts with carbon to form the ionic compound, lithium carbide. Other metals do not react with carbon directly. However, when they are treated with compounds like acetylene, they form acetaldehydes.

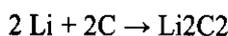


Table 5.6 Similarities between lithium and Magnesium

S.No.	Properties
1	Both lithium and magnesium are harder than other elements in the respective groups
2	Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating.
3	Both form a nitride, Li_3N and Mg_3N_2 , by direct combination with nitrogen
4	They do not give any superoxides and form only oxides, Li_2O and MgO
5	The carbonates of lithium and magnesium decompose upon heating to form their respective oxides and CO_2 .
6	Lithium and magnesium do not form bicarbonates.
7	Both LiCl and MgCl_2 are soluble in ethanol and are deliquescent. They crystallise from aqueous solution as hydrates, $\text{LiCl}\cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2\cdot 8\text{H}_2\text{O}$



Diagonal Relationship:

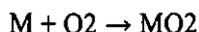
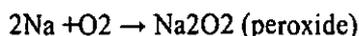
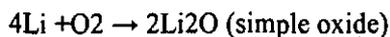
Similarity between the first member of group 1 (Li) and the diagonally placed second element of group 2 (Mg) is called diagonal relationship. It is due to similar size ($r \text{Li}^+ = 0.766 \text{ \AA}$ and $\text{Mg}^{2+} = 0.72 \text{ \AA}$) and comparable electro negativity values ($\text{Li} = 1.0$; $\text{Mg} = 1.2$).

Chemical properties of alkali metals

Alkali metals exhibit high chemical reactivity. The reactivity of alkali metals increases from Li to Cs, since the ionisation energy decreases down the group. All alkali metals are highly reactive towards the more electronegative elements such as oxygen and halogens. Some characteristic chemical properties of alkali metals are described blow.

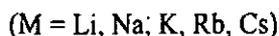
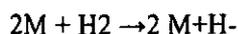
Reaction with oxygen

All the alkali metals on exposure to air or oxygen burn vigorously, forming oxides on their surface. Lithium forms only monoxide, sodium forms the monoxide and peroxide and the other elements form monoxide, peroxide, and superoxides. These oxides are basic in nature.

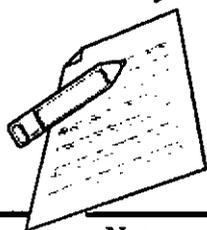


Reaction with hydrogen

All alkali metals react with hydrogen at about 673 K (lithium at 1073 K) to form the corresponding ionic hydrides. Reactivity of alkali metals with hydrogen decreases from Li to Cs.



The ionic character of the hydrides increases from Li to Cs and their stability decreases. The hydrides behave as strong reducing agents and their reducing nature increases down the group.



Electro negativity:

Alkali metals have comparatively smaller value of electro negativity than the other elements in the respective period. When they react with other elements, they usually produce ionic compounds. For example, they react with halogens to form ionic halides.

Flame colour and the spectra:

When the alkali metal salts moistened with concentrated hydrochloric acid are heated on a platinum wire in a flame, they show characteristic coloured flame as shown below.

Table 5.4 Flame colour and wavelength

Element	Colour	Wavelength (nm)
Lithium	Crimson red	670.8
Sodium	Yellow	589.2
Potassium	Lilac	766.5
Rubidium	Reddish violet	780.0
Caesium	Blue	455.5

The heat in the flame excites the valence electron to a higher energy level. When it drops back to its actual energy level, the excess energy is emitted as light, whose wavelength is in the visible region as shown in the above table.

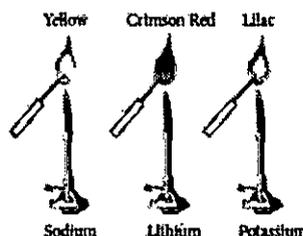


Figure 5.3 Flame colours of alkali metal salts

Distinctive behaviour of lithium

The distinctive behaviour of Li⁺ ion is due to its exceptionally small size, high polarising power, high hydration energy and non-availability of d-orbitals.

Table 5.5 Comparison of properties of lithium with other elements of the group:

Lithium	Other elements of the family
Hard, high melting and boiling point	Soft and Lower melting and boiling point
Least reactive (For example it reacts with oxygen to form normal oxide, forms peroxides with great difficulty and its higher oxides are unstable)	More reactive
Reacts with nitrogen to give Li ₃ N	No reaction
Reacts with bromine slowly	React violently
Reacts directly with carbon to form ionic carbides. For example 2Li + 2C → Li ₂ C ₂	Do not react with carbon directly, but can react with carbon compounds. Na + C ₂ H ₂ → Na ₂ C ₂
Compounds are sparingly soluble in water	highly soluble in water.
Lithium nitrate decomposes to give an oxide	decompose to give nitrites



Atomic and ionic radii

Being the first element of each period, alkali metals have the largest atomic and ionic radii in their respective periods. On moving down the group, there is an increase in the number of shells and, therefore, atomic and ionic radii increase. The monovalent ions (M^+) are smaller than the respective parent atoms as expected.

Table 5.3 Physical properties of alkali metals

Physical property	Li	Na	K	Rb	Cs
Atomic radius / Metallic radius (Å)	1.52	1.86	2.27	2.48	2.65
Ionic radius (Å)	0.76	1.02	1.38	1.52	1.67
Melting point ($^{\circ}$ C)	181	98	63	39	28.5
Boiling point ($^{\circ}$ C)	1347	881	766	688	705
First ionization enthalpy (kJ mol^{-1})	520.2	495.8	418.8	403.0	375.7
Electronegativity (Paulings scale)	1.0	0.9	0.8	0.8	0.7
Density (g cm^{-3})	0.54	0.97	0.86	1.53	1.90
Standard potential E° for M^+/M (V)	-3.04	-2.71	-2.92	-2.93	-2.93
Hydration enthalpy (kJ mol^{-1})	-506	-406	-330	-310	-276

Ionisation enthalpy

Alkali metals have the lowest ionisation enthalpy compared to other elements present in the respective period. As we go down the group, the ionisation enthalpy decreases due to the increase in atomic size. In addition, the number of inner shells also increases, which in turn increases the magnitude of screening effect and consequently, the ionisation enthalpy decreases down the group.

The second ionisation enthalpies of alkali metals are very high. The removal of an electron from the alkali metals gives monovalent cations having stable electronic configurations similar to the noble gas. Therefore, it becomes very difficult to remove the second electron from the stable configurations already attained.

Hydration enthalpy

Lithium salts are more soluble than the salts of other metals of group 1. e.g., LiClO_4 is up to 12 times more soluble than NaClO_4 . KClO_4 , RbClO_4 and CsClO_4 have solubilities only 10^{-3} times of that of LiClO_4 . The high solubility of Li salts is due to strong solvation of small size of Li^+ ion.

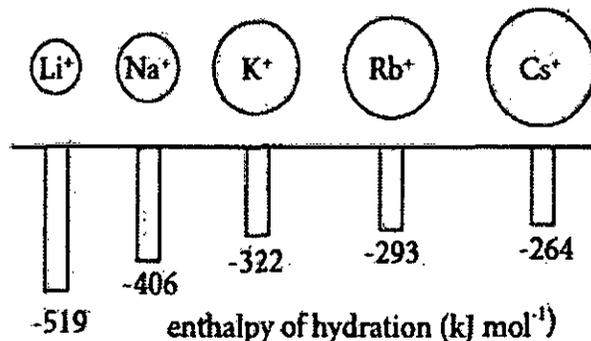


Figure 5.2 Hydration enthalpy of alkali metals



General characteristics of alkali metals:

Alkali metals are highly reactive and are found in nature only as compounds. Rubidium and caesium are found associated in minute quantities with minerals of other alkali metals. Francium is radioactive and does not occur appreciably in nature. Francium is highly radioactive; its longest-lived isotope has a half-life of only 21 minutes.

Table 5.1 Abundance of important alkali metals and their sources

Elements	Abundance in earth crust (%)	Relative Abundance	Mineral source
Lithium	0.0018	35	Spodumene [LiAl(SiO ₃) ₂]
Sodium	2.27	7	Rock Salt [NaCl]
Potassium	1.84	8	Sylvite [KCl]
Rubidium	0.0078	23	No convenient Source (obtained as by product of lithium processing)
Cesium	0.00026	46	

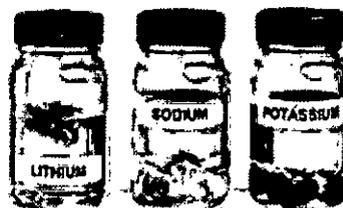


Figure 5.1 Alkali metals Li, Na and K stored under oil

Electronic configuration

The general valence shell electronic configuration of alkali metals is ns^1 , where 'n' represents the period number.

Table 5.2 Electronic configuration of alkali metals

Element	Symbol	Atomic No.	Electronic configuration
Lithium	Li	3	[He]2s ¹
Sodium	Na	11	[Ne]3s ¹
Potassium	K	19	[Ar]4s ¹
Rubidium	Rb	37	[Kr]5s ¹
Caesium	Cs	55	[Xe]6s ¹
Francium	Fr	87	[Rn]7s ¹

Common oxidation state

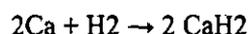
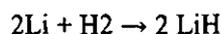
All these elements are highly electropositive in nature. They readily lose their valence electron to give monovalent cations (M⁺). Alkali metals have only one oxidation state which is +1.



hydrides are classified as ionic, covalent and metallic hydrides according to the nature of bonding. Hydrides formed with elements having lower electronegativity than hydrogen are often ionic, whereas with elements having higher electronegativity than hydrogen form covalent hydrides.

Ionic (Saline) hydrides:

These are hydrides composed of an electropositive metal, generally, an alkali or alkaline-earth metal, except beryllium and magnesium, formed by transfer of electrons from metal to hydrogen atoms. They can be prepared by the reaction of elements at about 400° C. These are salt-like, high-melting, white crystalline solids having hydride ions (H⁻) and metal cations (Mⁿ⁺).



Covalent (Molecular) hydrides:

They are compounds in which hydrogen is attached to another element by sharing of electrons. The most common examples of covalent hydrides of non-metals are methane, ammonia, water and hydrogen chloride. Covalent hydrides are further divided into three categories, viz., electron precise (CH₄, C₂H₆, SiH₄, GeH₄), electron-deficient (B₂H₆) and electron-rich hydrides (NH₃, H₂O). Since most of the covalent hydrides consist of discrete, small molecules that have relatively weak intermolecular forces, they are generally gases or volatile liquids.

Metallic (Interstitial) hydrides:

Metallic hydrides are usually obtained by hydrogenation of metals and alloys in which hydrogen occupies the interstitial sites (voids). Hence, they are called interstitial hydrides; the hydrides show properties similar to parent metals and hence they are also known as metallic hydrides. Most of the hydrides are non-stoichiometric with variable composition (TiH_{1.5-1.8} and PdH_{0.6-0.8}), some are relatively light, inexpensive and thermally unstable which make them useful for hydrogen storage applications. Electropositive metals and some other metals form hydrides with the stoichiometry MH or sometimes MH₂ (M = Ti, Zr, Hf, V, Zn).

s-Block Elements

The elements belonging to the group 1 and 2 in the modern periodic table are called s-block elements. The elements belonging to these two groups are commonly known as alkali and alkaline earth metals respectively. In this unit, we study their properties, uses, important compounds and biological importance.

Alkali metals:

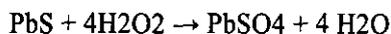
The word "alkali" is derived from the word al-qaliy meaning the plant ashes, referring to the original source of alkaline substances. A water-extract of burnt plant ashes, called potash contain mainly potassium carbonate. Alkali metal group consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are all metals, generally soft and highly reactive. They form oxides and hydroxides and these compounds are basic in nature.



Uses of hydrogen peroxide:

The oxidizing ability of hydrogen peroxide and the harmless nature of its products, i.e., water and oxygen, lead to its many applications. It is used in water treatment to oxidize pollutants, as a mild antiseptic, and as bleach in textile, paper and hair-care industry.

Hydrogen peroxide is used to restore the white colour of the old paintings which was lost due to the reaction of hydrogen sulphide in air with the white pigment $Pb_3(OH)_2(CO_3)_2$ to form black coloured lead sulphide. Hydrogen peroxide oxidises black coloured lead sulphide to white coloured lead sulphate, thereby restoring the colour.



Structure of hydrogen peroxide:

Both in gas-phase and liquid-phase, the molecule adopts a skew conformation due to repulsive interaction of the OH bonds with lone-pairs of electrons on each oxygen atom. Indeed, it is the smallest molecule known to show hindered rotation about a single bond.

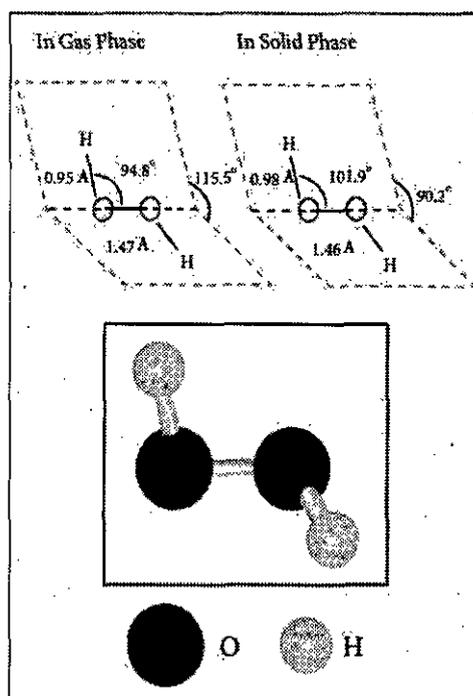
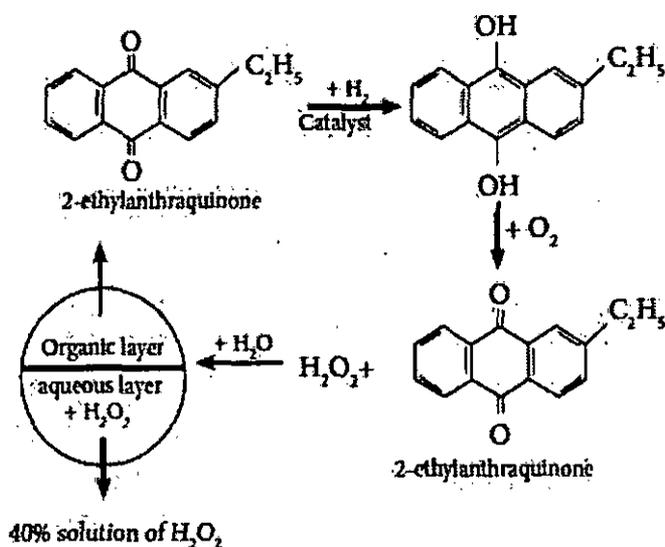


Figure 4.5 structure of H_2O_2

H_2O_2 has a non-polar structure. The molecular dimensions in the gas phase and solid phase differ as shown in figure 4.5. Structurally, H_2O_2 is represented by the dihydroxyl formula in which the two OH-groups do not lie in the same plane. One way of explaining the shape of hydrogen peroxide is that the hydrogen atoms would lie on the pages of a partly opened book, and the oxygen atoms along the spine. In the solid phase of molecule, the dihedral angle reduces to 90.2° due to hydrogen bonding and the O-O-H angle expands from 94.8° to 101.9° .

Hydrides

Hydrogen forms binary hydrides with many electropositive elements including metals and non-metals. It also forms ternary hydrides with two metals, E.g., $LiBH_4$ and $LiAlH_4$. The



Physical properties:

Pure hydrogen peroxide is almost a colourless liquid (pale blue), less volatile and more viscous than water.

A 30 % solution of hydrogen peroxide is marketed as '100-volume' hydrogen peroxide indicating that at S.T.P., 100 ml of oxygen is liberated by 1 ml of this solution on heating.

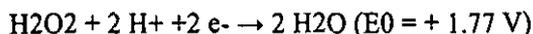
Chemical properties:

Hydrogen peroxide is highly unstable and the aqueous solution spontaneously disproportionate to give oxygen and water. The reaction is, however, slow but is explosive when catalyzed by metal. If it is stored in glass container, it dissolves the alkali metals from the glass, which catalyzes the disproportionation reaction. For this reason, H_2O_2 solutions are stored in plastic bottles.



Hydrogen peroxide can act both as an oxidizing agent and a reducing agent. Oxidation is usually performed in acidic medium while the reduction reactions are performed in basic medium

In acidic conditions:



For example .

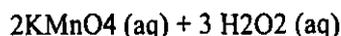


In basic conditions:

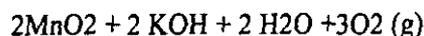


($E^0 = + 0.08 V$)

For Example,



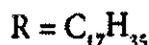
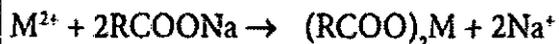
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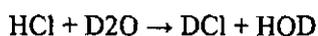
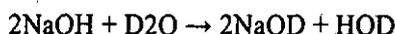
Hard water produces less foam with detergents. Do you know why?

The cleaning capacity of soap is reduced when used in hard water. Soaps are sodium or potassium salts of long chain fatty acids (e.g., coconut oil). When soap is added to hard water, the divalent magnesium and calcium ions present in hard water react with soap. The sodium salts present in soaps are converted to their corresponding magnesium and calcium salts which are precipitated as scum/precipitate.



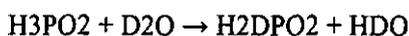
Chemical properties of heavy water:

When compounds containing hydrogen are treated with D₂O, hydrogen undergoes an exchange for deuterium

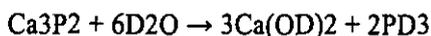
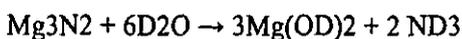
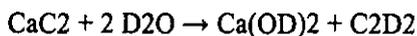
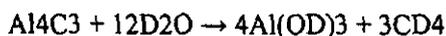


These exchange reactions are useful in determining the number of ionic hydrogens present in a given compound.

For example, when D₂O is treated with of hypo-phosphorus acid only one hydrogen atom is exchanged with deuterium. It indicates that, it is a monobasic acid.



It is also used to prepare some deuterium compounds:

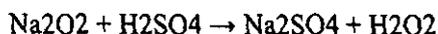
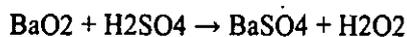


Uses of heavy water:

1. Heavy water is widely used as moderator in nuclear reactors as it can lower the energies of fast neutrons
2. It is commonly used as a tracer to study organic reaction mechanisms and mechanism of metabolic reactions
3. It is also used as a coolant in nuclear reactors as it absorbs the heat generated.

Hydrogen Peroxide:

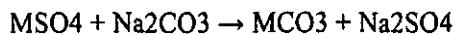
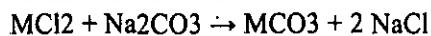
Hydrogen peroxide (H₂O₂) is one of the most important peroxides. It can be prepared by treating metal peroxide with dilute acid.



On an industrial scale, hydrogen peroxide is now prepared exclusively by autoxidation of 2-alkyl anthraquinol.

Permanent Hardness:

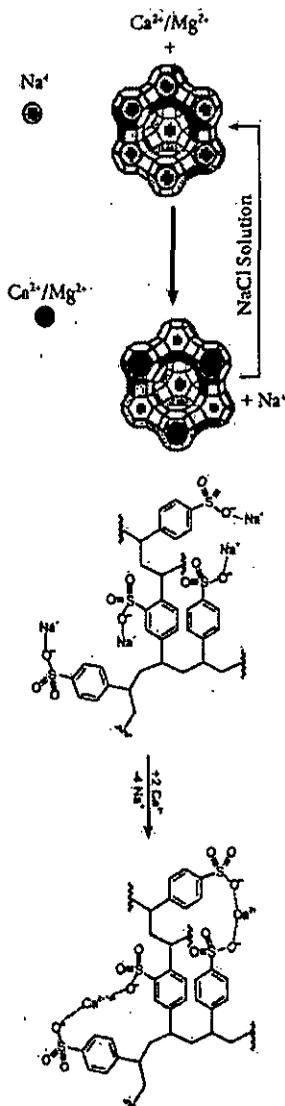
Permanent hardness of water is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in it. It can be removed by adding washing soda, which reacts with these metal ($M = \text{Ca}$ or Mg) chlorides and sulphates in hard water to form insoluble carbonates.



In another way to soften the hard water is by using a process called ion-exchange. That is, hardness can be removed by passing through an ion-exchange bed like zeolites or column containing ion-exchange resin. Zeolites are hydrated sodium aluminosilicates with a general formula, $\text{NaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ($x = 2$ to 10 , $y = 2$ to 6). Zeolites have porous structure in which the monovalent sodium ions are loosely held and can be exchanged with hardness producing metal ions ($M = \text{Ca}$ or Mg) in water. The complex structure can conveniently be represented as $\text{Na}_2\text{-Z}$ with sodium as exchangeable cations.



When exhausted, the materials can be regenerated by treating with aqueous sodium chloride. The metal ions (Ca^{2+} and Mg^{2+}) caught in the zeolite (or resin) are released and they get replenished with sodium ions.



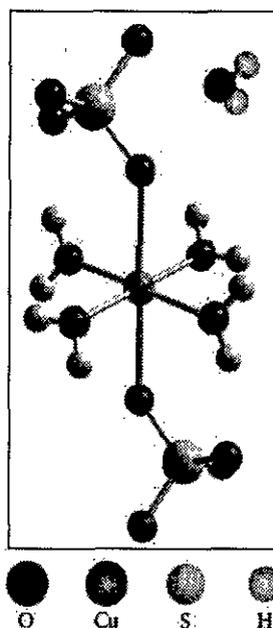


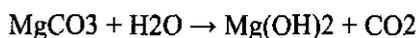
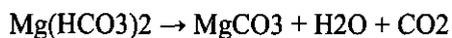
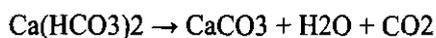
Figure 4.4 structure of copper sulphate pentahydrate

Hard and Soft Water:

Hard water contains high amounts of mineral ions. The most common ions found in hard water are the soluble metal cations such as magnesium & calcium, though iron, aluminium, and manganese may also be found in certain areas. Presence of these metal salts in the form of bicarbonate, chloride and sulphate in water makes water 'hard'. When hard water is boiled carbonates of magnesium and calcium present in it gets precipitated. On the other hand, water free from soluble salts of calcium and magnesium is called soft water. The hardness of water is of two types, viz., temporary hardness and permanent hardness.

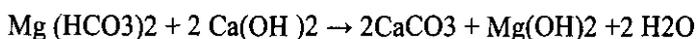
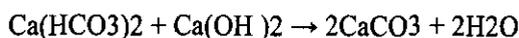
Temporary Hardness and its removal:

Temporary hardness is primarily due to the presence of soluble bicarbonates of magnesium and calcium. This can be removed by boiling the hard water followed by filtration. Upon boiling, these salts decompose into insoluble carbonate which leads to their precipitation. The magnesium carbonate thus formed further hydrolysed to give insoluble magnesium hydroxide.



The resulting precipitates can be removed by filtration.

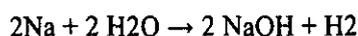
Alternatively, we can use Clark's method in which, calculated amount of lime is added to hard water containing the magnesium and calcium, and the resulting carbonates and hydroxides can be filtered-off.



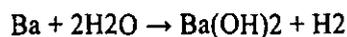


Chemical Properties:

Water reacts with metals, non-metals and other compounds differently. The most reactive metals are the alkali metals. They decompose water even in cold with the evolution of hydrogen leaving an alkali solution.



The group 2 metals (except beryllium) react in a similar way but less violently. The hydroxides are less soluble than those of Group 1.

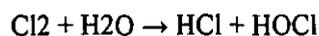


Some transition metals react with hot water or steam to form the corresponding oxides. For example, steam passed over red hot iron results in the formation of iron oxide with the release of hydrogen.

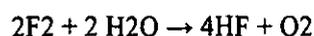


Lead and copper decompose water only at a white heat. Silver, gold, mercury and platinum do not have any effect on water. In the elemental form, the non-metals such as carbon, sulphur and phosphorus normally do not react with water. However, as we have seen earlier, carbon will react with steam when it is red (or white) hot to give water gas.

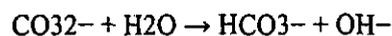
On the other hand, the halogens react with water to give an acidic solution. For example, chlorine forms hydrochloric acid and hypo chlorous acid. It is responsible for the antibacterial action of chlorine water, and for its use as bleach.



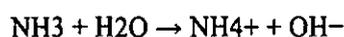
Fluorine reacts differently to liberate oxygen from water.



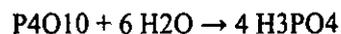
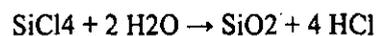
In a similar way, compounds of non-metals react with water to give acidic or alkaline solutions. For example, solutions of carbonates are slightly alkaline.



Water is an amphoteric oxide. It has the ability to accept as well as donate protons and hence it can act as an acid or a base. For example, in the reaction with HCl it accepts proton whereas in the reaction with weak base ammonia it donates proton.



Water dissolves ionic compounds. In addition, it also hydrolyses some covalent compounds.

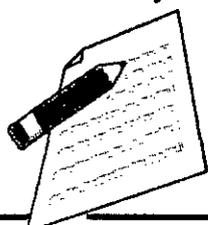


Many salts crystallized from aqueous solutions form hydrated crystals. The water in the hydrated salts may form co-ordinate bond or just present in interstitial positions of crystals.

Examples: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ – All six water molecules form co-ordinate bond

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ – Both the water molecules are present in interstitial positions.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – In this compound four water molecules form co-ordinate bonds while the fifth water molecule, present outside the co-ordination, can form intermolecular hydrogen bond with another molecule. $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$



Rearrangements

The Hofmann and Curtius rearrangements are used to convert a carboxylic acid derivative to a primary amine with the loss of a carbon unit – the original carbonyl group. In both cases the rearrangement reaction involves the alkyl group being transferred from the carbonyl group to the nitrogen atom to form an isocyanate intermediate. Hydrolysis then results in loss of the original carbonyl group. The Hofmann rearrangement involves the treatment of a primary amide with bromine under basic conditions. The Curtius rearrangement involves heating an acyl azide.

Arylamines

Amino groups cannot be directly introduced to an aromatic ring. However, nitro groups can be added directly by electrophilic substitution, then reduced to the amine. Once the amine is present, reactions such as alkylation, acylation, or reductive amination can be carried out as described for alkylamines.

Reduction

Nitriles and amides can be reduced to alkylamines using lithium aluminium hydride. In the case of a nitrile, a primary amine is the only possible product. Primary, secondary, and tertiary amines can be prepared from primary, secondary, and tertiary amides, respectively.

Substitution with NH₂

Primary alkyl halides and some secondary alkyl halides can undergo S_N2 nucleophilic substitution with an azide ion (N₃⁻) to give an alkyl azide.

The overall reaction is equivalent to replacing the halogen atom of the alkyl halide with an NH₂ unit. Another method of achieving the same result is the **Gabriel synthesis** of amines.

This involves treating phthalimide with KOH to abstract the N–H proton (Fig. 2). The N–H proton of phthalimide is more acidic (pK_a 9) than the N–H proton of an amide since the anion formed can be stabilized by resonance with both neighbouring carbonyl groups. The phthalimide ion can then be alkylated by treating it with an alkyl halide in a nucleophilic substitution. Subsequent hydrolysis releases a primary amine (Fig. 3).

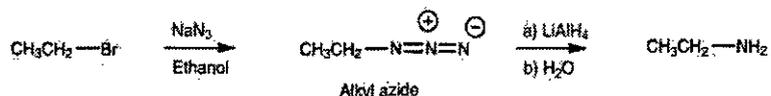


Fig. 1. Synthesis of a primary amine from an alkyl halide via an alkyl azide.

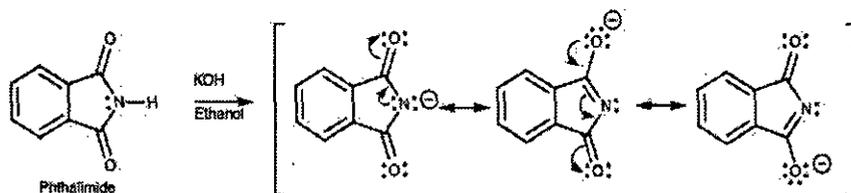


Fig. 2. Ionization of phthalimide.

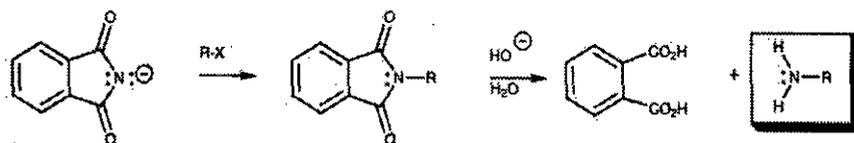


Fig. 3. Gabriel synthesis of primary amines.



Notes

17

COMPOUNDS OF CARBON
CONTAINING NITROGEN

- Understand the concept of nitrogen.
- Discuss the concept of amines.
- Discuss the classification of amines.
- Discuss the concept of alkylamines
- Discuss the characteristics of various nitrogen compounds.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of nitrogen so that the characteristics of various nitrogen compounds like amines etc can be learned.

Introduction**Preparation of amines****Reduction**

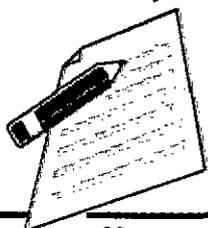
Nitriles can be reduced to primary amines with lithium aluminium hydride (LiAlH_4). Primary, secondary, and tertiary amides can be reduced with LiAlH_4 to primary, secondary, and tertiary amines respectively.

Substitution with NH_2

Nucleophilic substitution of an alkyl halide with an azide ion gives an alkyl azide which can then be reduced with LiAlH_4 to give a primary amine. Alternatively, nucleophilic substitution of an alkyl halide with a phthalimide ion is carried out and the N-alkylated phthalimide is then hydrolyzed to the primary amine. Reductive amination of an aldehyde with ammonia is a third method of introducing an NH_2 group. A fourth possible method is to react an alkyl halide with ammonia, but this is less satisfactory since over-alkylation is possible.

Alkylation of alkylamines

Primary and secondary alkylamines can be alkylated to secondary and tertiary alkylamines, respectively, by reaction with an alkyl halide. Primary alkylamines can also be synthesized if ammonia is used instead of an alkyl-amine. However, these reactions are difficult to control and over-alkylation is common. Reductive amination is a more controlled method of adding an extra alkyl group to an amine, where the amine (or ammonia) is treated with an aldehyde or a ketone in the presence of a reducing agent (sodium cyanoborohydride). Alternatively, primary and secondary amines can be acylated with an acid chloride or acid anhydride and then reduced with LiAlH_4 to give a secondary and tertiary amine, respectively.



8. Which of the following methods is best suited for the separation of a mixture containing naphthalene and benzoic acid
- | | |
|---------------------|--------------------|
| (a) Crystallisation | (b) Chromatography |
| (c) Sublimation | (d) Distillation |

Answer: (c)

9. How many structural isomers are possible if one hydrogen in diphenylmethane is replaced by chlorine?
- | | |
|-------|-------|
| (a) 8 | (b) 4 |
| (c) 7 | (d) 6 |

Answer: (b)

10. Why do we boil the extract with conc. HNO_3 in Lassaig's test for halogens?
- | |
|-----------------------------------------------------------------------------|
| (a) to increase the concentration of NO_3^- ions |
| (b) to increase the solubility product of AgCl |
| (c) it increases the precipitation of AgCl |
| (d) for the decomposition of Na_2S and NaCN formed |

Answer: (d)

Review Questions

- What are hydrocarbons? Explain giving two examples.
- Give two examples of aromatic hydrocarbons.
- Classify the following hydrocarbons as alkanes, alkenes or alkynes and write their IUPAC names. (i) $(\text{CH}_3)_3\text{CH}$ (ii) $\text{CH}_3\text{CH}=\text{CH}_2$ (iii) $(\text{CH}_3)_4\text{C}$ (iv) $\text{CH}_3\text{C}\equiv\text{CH}$ (v) $\text{CH}_3\text{C}\equiv\text{CCH}_3$ (vi) $\text{CH}_2=\text{CH}_2$ (vii) (viii) (ix)
- Write structures of the possible isomers and their IUPAC names of compounds having the following molecular formula: (i) C_5H_{10} and (ii) C_5H_8 .
- Write the structures of the following compounds: (i) Isobutylbenzene (ii) 4-Methyl-2-pentene (iii) Hepta-1,6-diene (iv) Cyclobutene.
- Write the structures for the following compounds: (i) 1-Bromo-3-methylhexane (ii) 3-Chloro-2,4-dimethylpentane (iii) 3-Methylbutanal (iv) Ethyl propanoate (v) 2-Methylbutanenitrile (vi) Cyclohexene (vii) 3-Methylhexan-2-one.
- What are electrophilic aromatic substitution reactions? How will you prepare nitrobenzene from benzene?
- Draw all the possible structural isomers having the molecular formula $\text{C}_4\text{H}_9\text{Cl}$ and give their IUPAC names.
- What is a nucleophilic aliphatic substitution reaction? Give one example.
- Describe the electrophilic addition reaction of an alkene. Write the product obtained by the addition of Br_2 to propene.

EXERCISE

CLASS-12

Chemistry



Notes

MCQ

1. Which is the best-suited method for the separation of para and ortho-nitrophenols from 1:1 mixture?

- (a) crystallisation (b) chromatography
(c) sublimation (d) steam distillation

Answer: (d)

2. Find the incorrect statement for a nucleophile

- (a) A nucleophile is a Lewis acid
(b) Nucleophiles do not seek electron
(c) Ammonia is a nucleophile
(d) Nucleophiles attack low electron density sites

Answer: (a)

3. Which among the following is the most deactivating meta-directing group in aromatic substitution reaction?

- (a) $-\text{COOH}$ (b) $-\text{SO}_3\text{H}$
(c) $-\text{NO}_2$ (d) $-\text{CN}$

Answer: (c)

4. Ammonia evolved from 0.75 g of the soil sample in the Kjeldahl's method for nitrogen estimation, neutralises 10 ml of 1M H_2SO_4 . Find the percentage of nitrogen present in the soil

- (a) 35.33 (b) 37.33
(c) 43.33 (d) 45.33

Answer: (b)

5. The correct order of increasing nucleophilicity is

- (a) $\text{Cl}^- < \text{Br}^- < \text{I}^-$ (b) $\text{Br}^- < \text{Cl}^- < \text{I}^-$
(c) $\text{I}^- < \text{Br}^- < \text{Cl}^-$ (d) $\text{I}^- < \text{Cl}^- < \text{Br}^-$

Answer: (a)

6. Homologous series of alkanols have a general formula

- (a) $\text{C}_n\text{H}_{2n}\text{O}_2$ (b) $\text{C}_n\text{H}_{2n}\text{O}$
(c) $\text{C}_n\text{H}_{2n+1}\text{O}$ (d) $\text{C}_n\text{H}_{2n+2}\text{O}$

Answer: (d)

7. Find the compound which undergoes nucleophilic substitution reaction exclusively by an $\text{S}_\text{N}1$ mechanism

- (a) Benzyl chloride (b) Chlorobenzene
(c) Ethyl chloride (d) Isopropyl chloride

Answer: (a)



Worked out example: 1

0.26g of an organic compound gave 0.039 g of water and 0.245 g of carbon dioxide on combustion. Calculate the percentage of C & H

Weight of organic compound = 0.26g

Weight of water = 0.039g

Weight of CO₂ = 0.245g

Percentage of hydrogen

18 g of water contain 2 g of hydrogen

$$0.039 \text{ g of water contain } \frac{2}{18} \times \frac{0.039}{0.26}$$

$$\% \text{ of hydrogen} = \frac{0.039}{0.26} \times \frac{2}{18} \times 100 = 1.66\%$$

Percentage of carbon

44 g of CO₂ contain 12 g of C

$$0.245 \text{ g of CO}_2 \text{ contains } \frac{12}{44} \times \frac{0.245}{0.26} \text{ g of C}$$

$$\% \text{ of Carbon} = \frac{12}{44} \times \frac{0.245}{0.26} \times 100 = 25.69\%$$

SUMMARY

Organic compounds are classified into aliphatic (open-chain), homocyclic (closed ring) or carbocyclic (alicyclic and aromatic) hydrocarbons and their derivatives, and heterocyclic compounds (contain at least one heteroatom i.e., N, S, O in the ring). Homologous series of organic compounds and IUPAC naming of different classes. The substitution, elimination, additions reactions and molecular rearrangements. Homolytic fission of a covalent bond produces free radicals because each of the parting away atoms takes away its shared electron. Heterolytic fission of a covalent bond produces ions because one of the atoms takes away both the shared electrons. Electrophiles are positively charged or electron deficient species. Nucleophiles are negatively charged or electron rich species. Benzene ring undergoes aromatic substitution reactions. A functional group is an atom or group responsible for specific properties of a compound. The compounds which have the same molecular formula but different structure are called structural isomers. Isomerism is classified into structural isomerism and stereoisomerism. A carbon atom attached to four different groups is called chiral atom or asymmetric carbon atom. The non-superimposable mirror image isomers of a compound are called enantiomers. They are optically active and rotate the plane of plain polarized light in opposite directions. The absolute configuration of a chiral carbon can be specified as R or S.



Notes

(3) **Absorption Apparatus** The combustion products containing moisture and carbon-dioxide are then passed through the absorption apparatus which consists of (i) a weighed U-tube packed with pumice soaked in Conc. H_2SO_4 to absorb water (ii) a set of bulbs containing a strong solution of KOH to absorb CO_2 and finally (iii) a guard tube filled with anhydrous $CaCl_2$ to prevent the entry of moisture from atmosphere.

Procedure:

The combustion tube is heated strongly to dry its content. It is then cooled slightly and connected to the absorption apparatus. The other end of the combustion tube is open for a while and the boat containing weighed organic substance is introduced. The tube is again heated strongly till the substance in the boat is burnt away. This takes about 2 hours. Finally, a strong current of oxygen is passed through the combustion tube to sweep away any traces of carbon dioxide or moisture which may be left in it. The U-tube and the potash bulbs are then detached and the increase in weight of each of them is determined.

Calculation:

Weight of the organic substance taken = w g

Increase in weight of H_2O = x g

Increase in weight of CO_2 = y g

18 g of H_2O contain 2g of hydrogen

$$\therefore x \text{ g of } H_2O \text{ contain } \left(\frac{2}{18} \times \frac{x}{w} \right) \text{ g of hydrogen}$$

$$\text{Percentage of hydrogen} = \left(\frac{2}{18} \times \frac{x}{w} \times 100 \right) \%$$

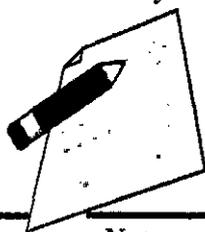
44g of CO_2 contains 12g of carbon

$$\therefore y \text{ g of } CO_2 \text{ contain } \left(\frac{12}{44} \times \frac{y}{w} \right) \text{ g of carbon}$$

$$\text{Percentage of Carbon} = \left(\frac{12}{44} \times \frac{y}{w} \times 100 \right) \%$$

Note:

1. If the organic substance under investigation also contain N, it will produce oxides of nitrogen on combustion. A spiral of copper is introduced at the combustion tube, to reduce the oxides of nitrogen to nitrogen which escapes unabsorbed.
2. If the compound contains halogen as well, a spiral of silver is also introduced in the combustion tube. It converts halogen into silver halide.
3. In case if the substance also contains sulphur, the copper oxide in the combustion tube is replaced by lead chromate. The SO_2 formed during combustion is thus converted to lead sulphate and prevented from passing into the absorption unit.



Notes

v) Test for phosphorous:

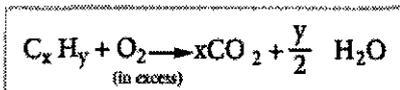
A solid compound is strongly heated with a mixture of Na_2CO_3 & KNO_3 . phosphorous present in the compound is oxidized to sodium phosphate. The residue is extracted with water and boiled with Conc. HNO_3 . A solution of ammonium molybdate is added to the above solution. A canary yellow coloration or precipitate shows the presence of phosphorous.

Estimation of elements

After detecting the various elements present in a given organic compound by qualitative analysis it is necessary to determine their composition by weight. The estimation of carbon, hydrogen, nitrogen, sulphur halogens are discussed here. No dependable method is however available for determination oxygen and hence its amount is always determined by difference.

Estimation of carbon and hydrogen:

Both carbon and hydrogen are estimated by the same method. A known weight of the organic substance is burnt in excess of oxygen and the carbon and hydrogen present in it are oxidized to carbon dioxide and water, respectively.



The weight of carbon dioxide and water thus formed are determined and the amount of carbon and hydrogen in the organic substance is calculated.

The apparatus employed for the purpose consists of three units (i) oxygen supply (2) combustion tube (3) absorption apparatus. (Refer Page 153 Fig. 11.2)

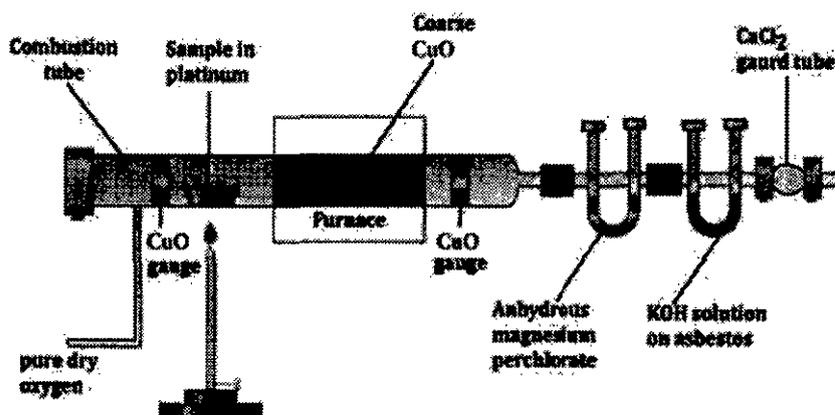


Fig 11.2 Estimation of Carbon and Hydrogen

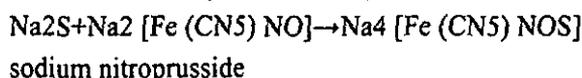
- (1) **Oxygen supply:** To remove the moisture from oxygen it is allowed to bubble through sulphuric acid and then passed through a U-tube containing soda lime to remove CO_2 . The oxygen gas free from moisture and carbon dioxide enters the combustion tube.
- (2) **Combustion tube:** A hard glass tube open at both ends is used for the combustion of the organic substance. It contains (i) an oxidized copper gauze to prevent the backward diffusion of the products of combustion (ii) a porcelain boat containing a known weight of the organic substance (iii) coarse copper oxide on either side and (iv) an oxidized copper gauze placed towards the end of the combustion tube. The combustion tube is heated by a gas burner.



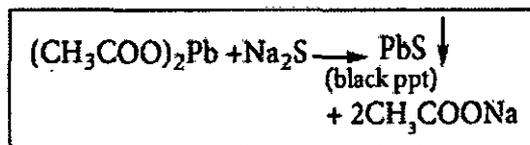
Notes

(iii) Test for sulphur:

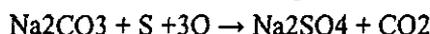
- a) To a portion of the lassaigne's extract, add freshly prepared sodium nitroprusside solution. A deep violet or purple colouration is obtained. This test is also used to detect S²⁻ in inorganic salt analysis



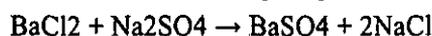
- b) Acidify another portion of lassaigne's extract with acetic acid and add lead acetate solution. A black precipitate is obtained.



- c) **Oxidation test:** The organic substances are fused with a mixture of KNO₃ and Na₂CO₃. The sulphur, if present is oxidized to sulphate.

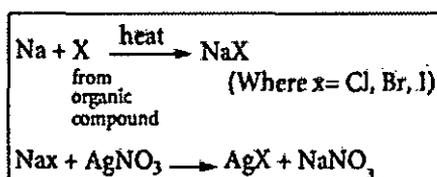


The fused mass is extracted with water, acidified with HCl and then BaCl₂ solution is added to it. A white precipitate indicates the presence of sulphur.

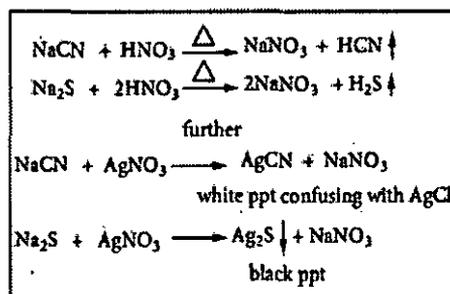
**iv) Test for halogens:**

To another portion of the lassaigne's filtrate add dil HNO₃ warm gently and add AgNO₃ solution.

- a) Appearance of curdy white precipitate soluble in ammonia solution indicates the presence of chlorine.
- b) Appearance of pale yellow precipitate sparingly soluble in ammonia solution indicates the presence of bromine.
- c) Appearance of a yellow precipitate insoluble in ammonia solution indicates the presence of iodine.



If N or S is present in the compound along with the halogen, we might obtain NaCN and Na₂S in the solution, which interfere with the detection of the halogen in the AgNO₃ test. Therefore we boil the lassaigne's extract with HNO₃ which decomposes NaCN and Na₂S as





CuSO₄ which turns anhydrous CuSO₄ blue. This confirms the presence of C and H in the compound.

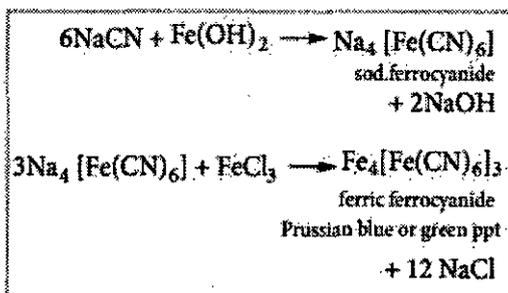
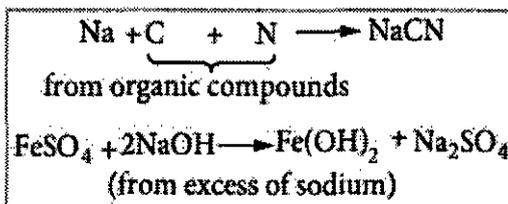
Detection of nitrogen by lassaigne sodium fusion test: This is a good test for the detection of nitrogen in all classes of nitrogenous compound and it involves the preparation of sodium fusion extract

This method involves the conversion of covalently bonded N, S or halogen present in the organic compounds to corresponding water soluble ions in the form of sodium salts For this purpose a small piece of Na dried by pressing between the folds of a filter paper is taken in a fusion tube and it is gently heated.

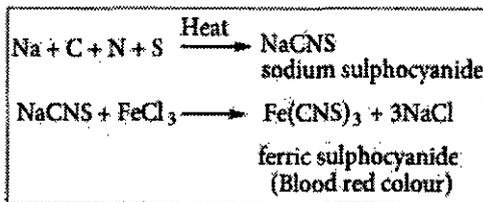
When it melts to a shining globule, put a pinch of the organic compound on it. Heat the tube till reaction ceases and becomes red hot. Plunge it in about 50 mL of distilled water taken in a china dish and break the bottom of the tube by striking against the dish. Boil the contents of the dish for about 10 mts and filter. This filtrate is known as lassaignes extract or sodium fusion extract and it used for detection of nitrogen, sulfur and halogens present in organic compounds.

(ii) Test for Nitrogen:

If nitrogen is present it gets converted to sodium cyanide which reacts with freshly prepared ferrous sulphate and ferric ion followed by conc. HCl and gives a Prussian blue colour or green colour or precipitate. It confirms the presence of nitrogen. HCl is added to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of NaOH on FeSO₄ which would otherwise mark the Prussian blue precipitate. The following reaction takes part in the formation of Prussian blue.

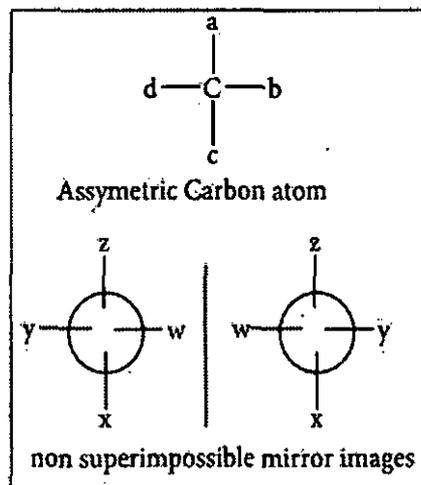


In case if both N & S are present, a blood red colour is obtained due to the following reactions.



Conditions for enantiomerism or optical isomerism

A carbon atom whose tetra valency is satisfied by four different substituents (atoms or groups) is called asymmetric carbon or chiral carbon. It is indicated by an asterisk as C*. A molecule possessing chiral carbon atom and non-super impossible to its own mirror image is said to be a chiral molecule or asymmetric, and the property is called chirality or dissymmetry.



Detection of elements in organic compounds

Introduction

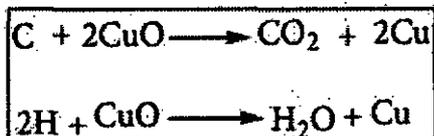
The first step in the analysis of an organic compound is the detection of elements present in it. The principal elements are carbon, hydrogen and oxygen. In addition to these they may contain nitrogen, sulphur and halogens. Phosphorous. Metals like Li, Mg, Zn are present in certain organometallic compounds.

Detection of carbon and hydrogen

If the compound under investigation is organic, there is no need to test for carbon. This test is performed only to establish whether a given compound is organic or not. With the exception of few compounds like CCl₄, CS₂ all organic compounds also contain hydrogen. The presence of both these elements is confirmed by the following common test.

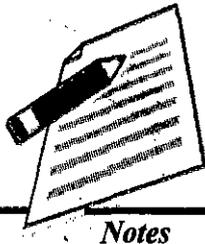
(i) Copper oxide test:

The organic substance is mixed with about three times its weight of dry copper oxide by grinding. The mixture is then placed in a hard glass test tube fitted with a bent delivery tube. The other end of which is dipping into lime water in an another test tube. The mixture is heated strongly and the following reaction take place.



Thus if carbon is present, it is oxidized to CO₂ which turns lime water milky. If hydrogen is also present, it will be oxidized to water which condenses in small droplets on the cooler wall of the test tube and inside the bulb. Water is collected on anhydrous



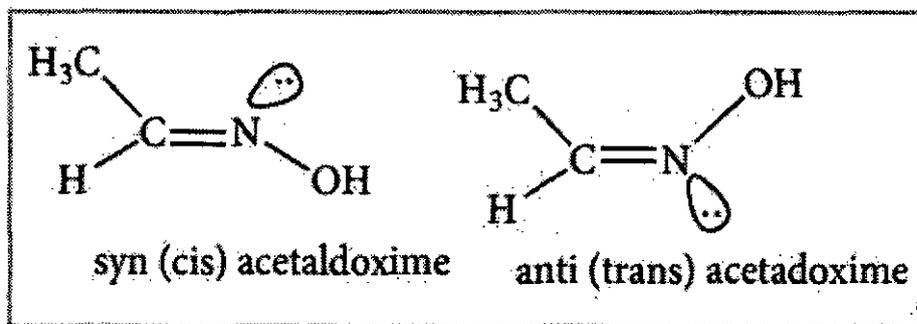


steric repulsion of the groups makes the cis isomers less stable than the trans isomers in which bulky groups are on the opposite side. These cis and trans isomers have different chemical property is. They can be separated by fractional distillation, gas chromatography etc., All alkenes with identical substrate do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded C atom is attached to two different atoms or groups e.g. In propene no geometrical isomers are possible because one of the double bonded carbon has two identical H atoms.

Cis-trans isomerism is also seen around single bond. For e.g.: 1,3-butadiene has two double bonds in conjugation. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. It can exist in infinite number of conformations, but the following two extreme conformations are important.

ii) Oximes and azo compounds:

Restricted rotation around $\text{C}=\text{N}$ (oximes) gives rise to geometrical isomerism in oximes. Here 'syn' and 'anti' are used instead of cis and trans respectively. In the syn isomer the H atom of a doubly bonded carbon and $-\text{OH}$ group of doubly bonded nitrogen lie on the same side of the double bond, while in the anti-isomer, they lie on the opposite side of the double bond. For e.g.:



Optical Isomerism

Compounds having same physical and chemical property but differ only in the rotation of plane of the polarized light are known as optical isomers and the phenomenon is known as optical isomerism.

Some organic compounds such as glucose have the ability to rotate the plane of the plane polarized light and they are said to be optically active compounds and this property of a compound is called optical activity. The optical isomer, which rotates the plane of the plane polarised light to the right or in clockwise direction is said to be dextrorotary (dexter means right) denoted by the sign (+), whereas the compound which rotates to the left or anticlockwise is said to be leavo rotatory (leaves means left) denoted by sign(-). Dextrorotatory compounds are represented as 'd' or by sign (+) and laevorotatory compounds are represented as 'l' or by sign (-).

Enantiomerism and optical activity

An optically active substance may exist in two or more isomeric forms which have same physical and chemical properties but differ in terms of direction of rotation of plane polarized light, such optical isomers which rotate the plane of polarized light with equal angle but in opposite direction are known as enantiomers and the phenomenon is known as enantiomerism. Isomers which are non-super impossible mirror im-ages of each other are called enantiomers.



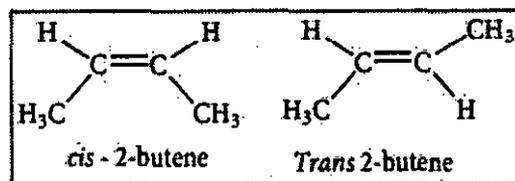
Stereoisomerism:

The isomers which have same bond connectivity but different arrangement of groups or atoms in space are known as stereoisomers. This branch of chemistry dealing with the study of three-dimensional nature (spatial arrangement) of molecules is known as stereochemistry. The metabolic activities in living organisms, natural synthesis and drug synthesis involve various stereoisomers.

Geometrical isomerism:

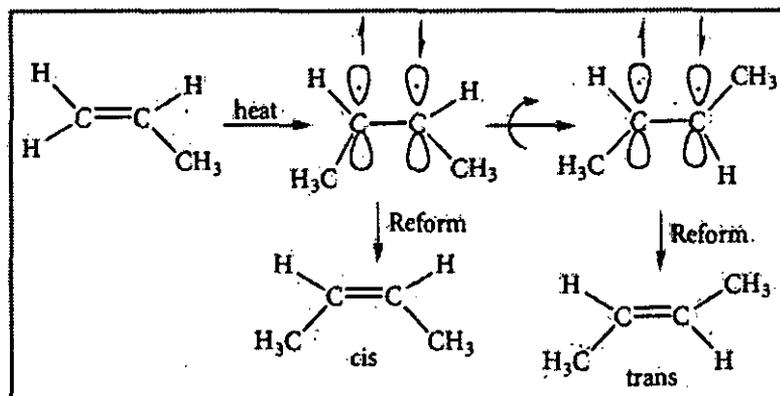
Geometrical isomers are the stereoisomers which have different arrangement of groups or atoms around a rigid frame work of double bonds. This type of isomerism occurs due to restricted rotation of double bonds, or about single bonds in cyclic compounds.

In alkenes, the carbon-carbon double bond is sp^2 hybridized. The carbon-carbon double bond consists of a σ bond and a π bond. The σ bond is formed by the head on overlap of sp^2 hybrid orbitals. The π bond is formed by the side wise overlap of 'p' orbitals. The presence of the π bond lock the molecule in one position. Hence, rotation around C=C bond is not possible. This restriction of rotation about C-C double bond is responsible for geometrical isomerism in alkenes.

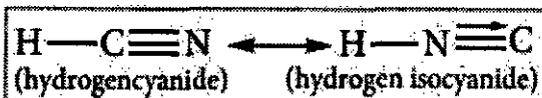


These two compounds are termed as geometrical isomers and are distinguished from each other by the terms *cis* and *trans*. The *cis* isomer is one in which two similar groups are on the same side of the double bond. The *trans* isomers is that in which the two similar groups are on the opposite side of the double bond, hence this type of isomerism is often called *cis-trans* isomerism.

The *cis*-isomer can be converted to *trans* isomer or vice versa is only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62kcal/mole) to break the π bond so that rotation about σ bond becomes possible. Upon cooling, the reformation of the π bond can take place in two ways giving a mixture both *cis* and *trans* forms of *trans*-2-butene and *cis*-2-butane.



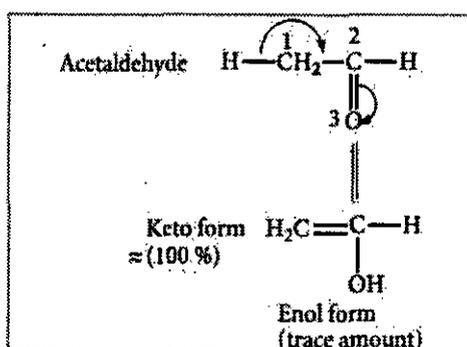
Generally the *trans* isomer is more stable than the corresponding *cis* isomers. This is because in the *cis* isomer, the bulky groups are on the same side of the double bond. The



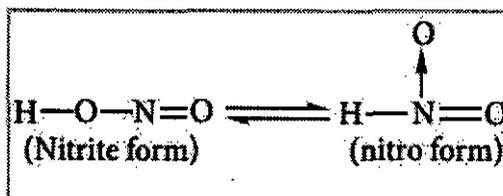
In this example hydrogen atom oscillates between carbon & nitrogen atom

(ii) **Triad system:** In this system hydrogen atom oscillates between three polyvalent atoms. It involves 1,3 migration of hydrogen atom from one polyvalent atom to other within the molecule. The most important type of triad system is keto-enol tautomerism and the two groups of tautomers are ketoform and enol-form. The polyvalent atoms involved are one oxygen and two carbon atoms. Enolisation is a process in which keto-form is converted to enol form. Both tautomeric forms are not equally stable. The less stable form is known as labile form

Example:

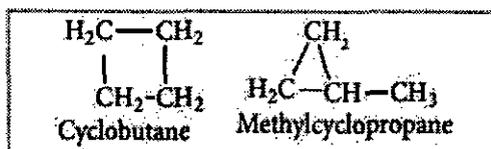
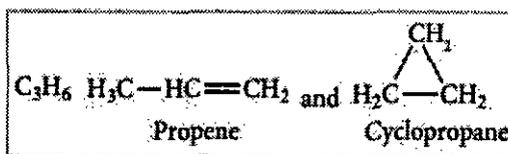


Nitro-aci tautomerism.



(f) Ring chain isomerism:

In this type of isomerism, compounds having same molecular formula but differ in terms of bonding of carbon atom to form open chain and cyclic structures for e.g.:

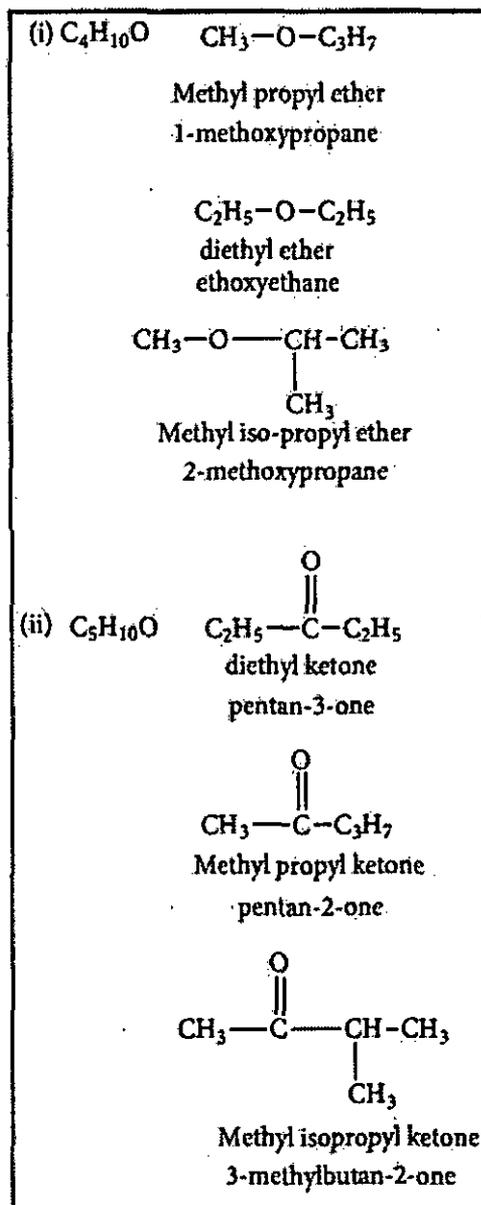




Notes

(d) Metamerism:

This type of isomerism is a special kind of structural isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group or different alkyl groups attached to the either side of the same functional group and having same molecular formula. This isomerism is shown by compounds having functional group such as ethers, ketones, esters and secondary amines between two alkyl groups.

**(e) Tautomerism:**

It is a special type of functional isomerism in which a single compound exists in two readily inter convertible structures that differ markedly in the relative position of at least one atomic nucleus, generally hydrogen. The two different structures are known as tautomer. There are several types of tautomerism and the two important types are dyad and triad systems.

(i) **Dyad system:** In this system hydrogen atom oscillates between two directly linked polyvalent atoms. E.g.:

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Chemistry



Notes

(b) Position Isomerism:

If different compounds belonging to same homologous series with the same molecular formula and carbon skeleton, but differ in the position of substituent or functional group or an unsaturated linkage are said to exhibit position isomerism.

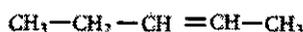
Example:

(i) Molecular formula C_5H_{10}



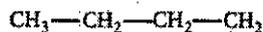
Pent-1-ene

and



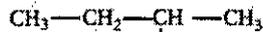
Pent-2-ene

(ii) Mol. formula C_4H_9Cl



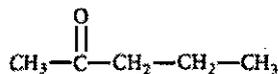
1-chlorobutane

and



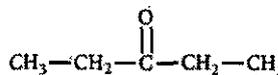
2-chlorobutane

(iii) Mol. formula $C_5H_{10}O$



Pent-2-one

and



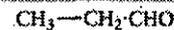
Pent-3-one

(c) Functional Isomerism:

Different compounds having same molecular formula but different functional groups are said to exhibit functional isomerism.

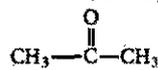
Example:

(i) C_3H_6O



Propanal

(aldehyde group)



Propanone

(keto group)

(ii) $C_3H_6O_2$



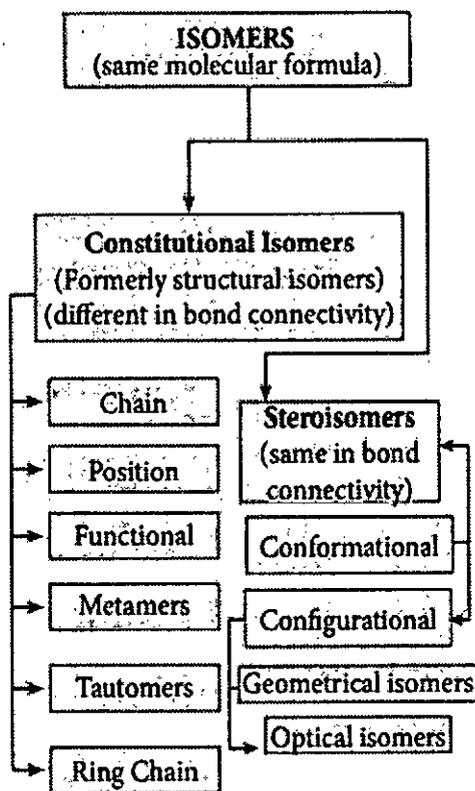
Propanoic acid

acid group



Methyl acetate

(ester group)



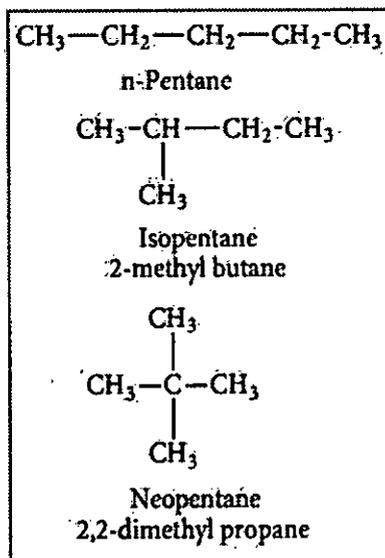
अणुसंरचना
में अंतर

Constitutional Isomers (Formerly structural isomers):

This type of isomers have same molecular formula but differ in their bonding sequence. Structural or constitutional isomerism is further classified into following types.

(a) Chain or nuclear or skeletal Isomerism:

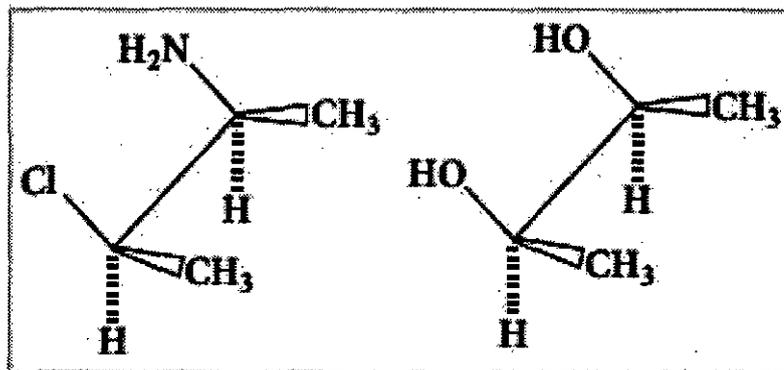
These isomers differ in the way in which the carbon atoms are bonded to each other in a carbon chain or in other words isomers have similar molecular formula but differ in the nature of the carbon skeleton (i.e., Straight or branched)





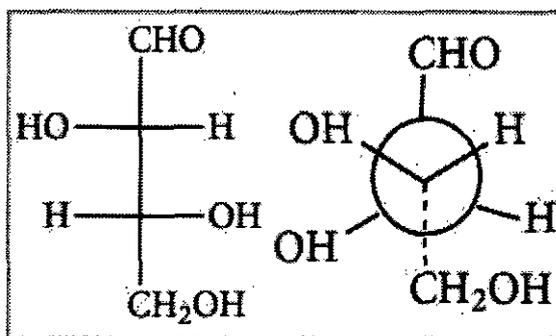
Sawhorse projection formula:

Here the bond between two carbon atoms is drawn diagonally and slightly elongated. The lower left hand carbon is considered lying towards the front and the upper right hand carbon towards the back. The Fischer projection inadequately portrays the spatial relationship between ligands attached to adjacent atoms. The sawhorse projection attempts to clarify the relative location of the groups.



Newman projection formula:

In this method the molecules are viewed from the front along the carbon-carbon bond axis. The two carbon atom forming the σ bond is represented by two circles. One behind the other so that only the front carbon is seen. The front carbon atom is shown by a point where as the carbon lying further from the eye is represented by the origin of the circle. Therefore, the C-H bonds of the front carbon are depicted from the circle while C-H bonds of the back carbon are drawn from the circumference of the circle with an angle of 120° to each other.



Isomerism in organic compounds:

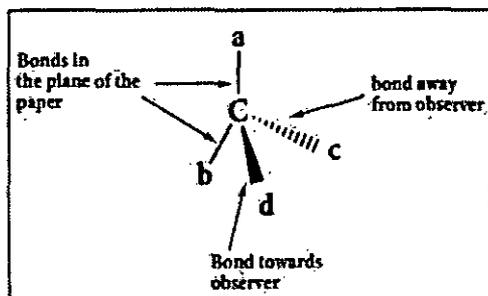
The term 'isomerism' was given by Berzelius, and it represents the existence of two or more compounds with the same molecular formula but different structure and properties (physical, chemical, or both). Compounds exhibiting this isomerism are called isomers. The difference in properties of two isomers is due to the difference in (bond connectivity or spatial arrangement) the arrangement of atoms within their molecules. Isomerism is broadly divided into two types: i. Constitutional isomerism, ii. stereoisomerism.



metal and are commercially available. (i) Frame work model (ii) Ball and stick model & (iii) space filling model. In the frame work model only the bonds connecting the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of the atom. In the ball and stick model, both the atoms and the bonds are shown. Ball represent atoms and the stick a bond. Compounds containing C=C can be best represented by using springs in place of sticks and this model is termed as ball and spring model. The space filling model emphasizes the relative size of each atom based on its Vander Waals radius.

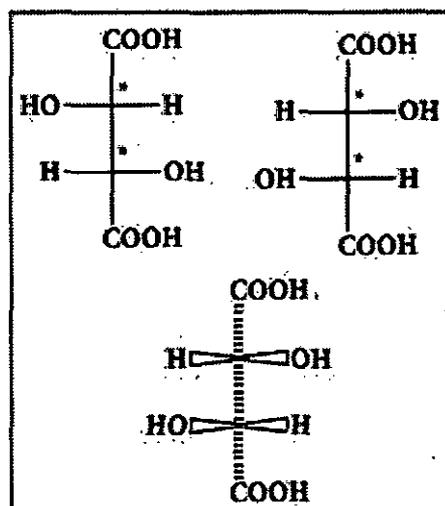
Three dimensional representations of organic molecules:

The simplest convention is solid and dashed wedge formula in which 3-D image of a molecule can be perceived from two dimensional picture. In this representation a tetrahedral molecule with four atoms or group a,b,c and d bonded to it can be represented by a wedge formula as follows. A solid wedge () (or a heavy line) is used to indicate a bond projecting above the plane of the paper and the dashed wedge () (or a dashed line) is used to depict the bond below the plane. The bonds lying in the plane of the paper are shown by normal lines.



Fisher projection formula:

This is a method of representing three dimensional structures in two dimension. In this method, the chiral atom(s) lies in the plane of paper. The horizontal substituents are pointing towards the observer and the vertical substituents are away from the observer. Fisher projection formula for tartaric acid is given below.





We know how to draw the Lewis structure for a molecule. The line bond structure is obtained by representing the two electron covalent bond by a dash or line (-) in a Lewis structure. A single line or dash represents single σ covalent bond, double line represents double bond (1σ bond, 1π bond) and a triple line represents triple bond (1σ bond, 2π bond). Lone pair of electrons on heteroatoms may or may not be shown. This represents the complete structural formula. This structural formula can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula.

For further simplification, organic chemists use another way of representing the structures in which only lines are used. In this type of representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are shown in a zigzag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. These representations can be easily understood by the following illustration.

Molecular formula	Complete structural formula (dash line structure)	Condensed Structure	Bond line Structure
n-propanol C_3H_8O		$CH_3-CH_2-CH_2-OH$	
1,3-butadiene C_4H_6		$CH_2=CH-CH=CH_2$	
t-butyl chloride C_4H_9Cl		$CH_3-C(CH_3)_2-Cl$	
1,3-dimethyl cyclopentane C_7H_{14}			

Molecular models

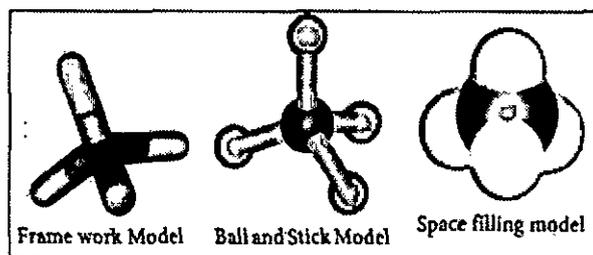


Fig 11.3 Methane - Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three dimensional shapes of organic molecules. These are made of wood, plastic or



Notes

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{C} & =\text{CH} & -\text{C} & -\text{CH}_3 \\ & & & & \\ & \text{CH}_3 & & \text{O} & \end{array}$ <p>4-methylpent-3-en-2-one</p>	4-methyl	pent	3-enyl	2-one
$\begin{array}{c} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{CH}_2 & -\text{C} & -\text{C} & \equiv\text{CH} \\ & & & & \\ & & \text{O} & & \end{array}$ <p>pent-1-yne-3-one</p>	-	pent	1-ynyl	3-one
<p>3-phenyl prop-2-enoic acid</p>	3-phenyl	prop	2-enyl	oic acid
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_3$ <p>N-methylpropan-1-amine</p>	N-methyl	prop	anyl	1-amine
$\begin{array}{c} 1 \\ \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{NH}-\text{CH}_3 \\ \\ 3 \end{array}$ <p>N-methylpropan-2-amine</p>	N-methyl	prop	anyl	2-amine
$\begin{array}{c} \text{CH}_3 \\ \\ 3 \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_3 \\ \\ 1 \end{array}$ <p>N,N-dimethylpropan-1-amine</p>	N,N-dimethyl	prop	anyl	1-amine
$\begin{array}{c} \text{CH}_3 \\ \\ 3 \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_3 \\ \\ 1 \end{array}$ <p>N-ethyl-N-methylpropan-1-amine</p>	N-ethyl-N-methyl	prop	anyl	1-amine
<p>N,N-dimethylbenzamine</p>	N,N-dimethyl	benzene		amine
$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ 6 \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-\text{COOH} \\ \quad \\ 4 \quad 3 \quad 2 \quad 1 \\ \text{OH} \end{array}$ <p>4-hydroxy-3-(2-hydroxyethyl)hexanoic acid</p>	4-hydroxy-3-(2-hydroxyethyl)	hexa	anyl	oic acid

Structural representation of organic compounds

Molecular formula of a compound is the simplest, least informative representation, showing the ratio of atoms present. The structure of an organic compound can be represented using any one of the below mentioned methods.

1. Lewis structure or dot structure,
2. Dash structure or line bond structure,
3. Condensed structure
4. Bond line structure



Notes

Compound Structure and IUPAC Name	Prefix with position number	Root word	Primary suffix	Secondary suffix
$\begin{array}{cccccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ 6 & 5 & 4 & 3 & 2 & 1 \\ & & & \text{CH}_3 & & \end{array}$ <p>3-methylhexane</p>	3-methyl	hex	ane	-
$\begin{array}{cccc} \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & 2 & 3 & 4 \\ & & & \\ & \text{CHO} & & \end{array}$ <p>2-methylbutanal</p>	2-Methyl	but	anal	al
$\begin{array}{cccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}=\text{CH}_2 \\ & & 2 & 3 & 4 \\ & & & & \\ & & \text{COOH} & & \end{array}$ <p>2-ethylbut-3-enoic acid</p>	2-ethyl	but	3-enyl	oic acid
$\begin{array}{cccccc} \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & \text{CN} \\ 6 & 5 & 4 & 3 & 2 & 1 \\ & & & \text{CH}_3 & & \end{array}$ <p>4-methylhexanenitrile</p>	4-methyl	hex	enyl	nitrile
$\begin{array}{cccc} \text{CH}_2=\text{CH} & -\text{CH} & -\text{CH}_3 \\ & 4 & 3 & 2 \\ & & & \\ & & \text{CONH}_2 & \end{array}$ <p>2-methylbut-3-enamide</p>	2-methyl	but	3-enyl	amide
$\begin{array}{cccccc} \text{OH} & & & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}=\text{CH} & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 & 6 \end{array}$ <p>hex-4-en-2-ol</p>		hex	4-enyl	2-ol
$\begin{array}{cccccc} \text{CH}_3 & & \text{C}_2\text{H}_5 & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{array}$ <p>3-ethyl-5-methylheptane</p>	3-ethyl 5-methyl	hept	ane	-
$\begin{array}{cccccc} \text{CH}_3 & & & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH} & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 & 6 \\ & & & & & \\ & & \text{C}_2\text{H}_5 & & & \end{array}$ <p>3-ethyl-2-methylhexane</p>	3-ethyl-2-methyl	hex	ane	-
$\begin{array}{cccccc} \text{CH}_3 & & \text{C}_2\text{H}_5 & & & \\ & & & & & \\ \text{CH}_3 & -\text{CH}_2 & -\text{C} & -\text{CH} & -\text{CH}_2 & -\text{CH}_3 \\ & & & 3 & 2 & 1 \\ & & \text{CH}_3 & -\text{CH}_2 & -\text{CH}_3 \\ & & 5 & 6 & 7 \end{array}$ <p>3,4-diethyl-4-methylheptane</p>	3,4-diethyl- 4-methyl	hept	ane	-
$\begin{array}{cccccc} \text{CH}_3 & & & & \text{CH}_3 & \\ & & & & & \\ \text{CH}_3 & -\text{C} & =\text{CH} & -\text{CH} & -\text{CH}_3 \\ 1 & 2 & 3 & 4 & 5 \end{array}$ <p>2,4-dimethylpent-2-ene</p>	2,4-dimethyl	pent	2-ene	-

Side chain substituted

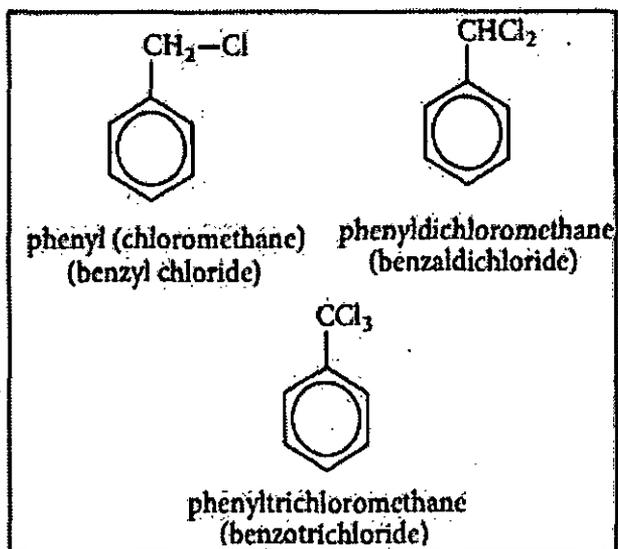
CLASS-12

Chemistry

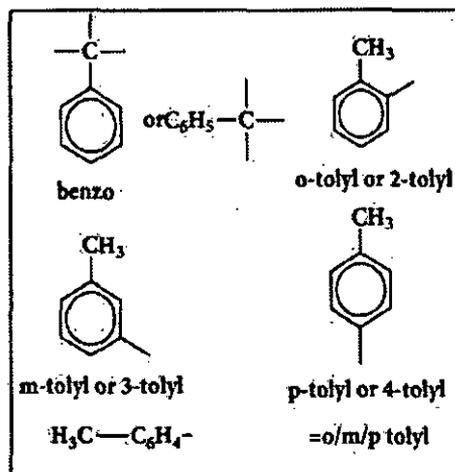
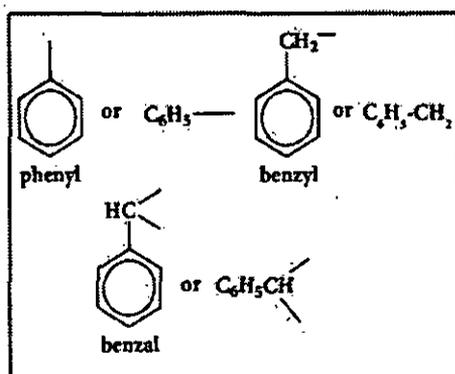


Notes

Side chain substituted



Aryl groups



Selection of parent hydrocarbon out of side chain and benzene ring is based on (more or less) some rule as for the alicyclic compounds.

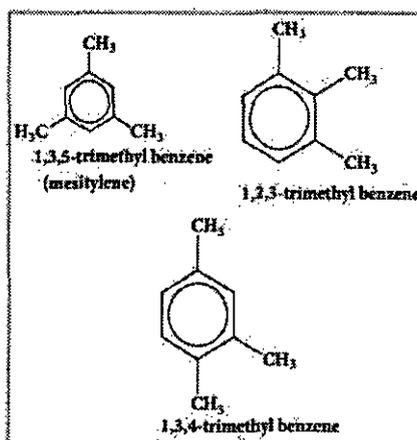
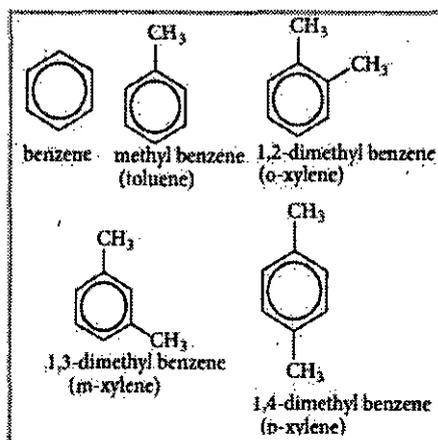
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Chemistry



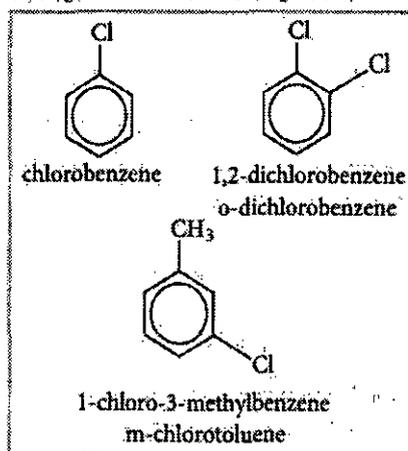
Notes

1. Nuclear substituted aromatic compounds: These are the compounds in which the functional group is directly attached to the benzene ring. They are named as derivatives of benzene.



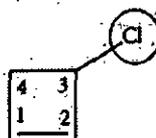
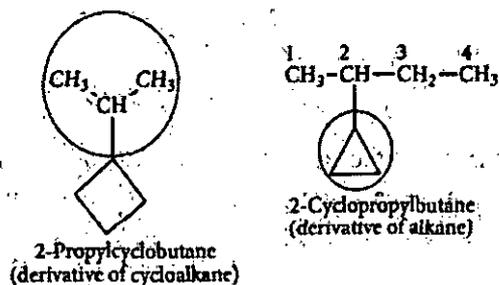
Nuclear substituted aromatic Halogen derivatives compounds.

Nuclear substituted aromatic Halogen derivatives compounds.



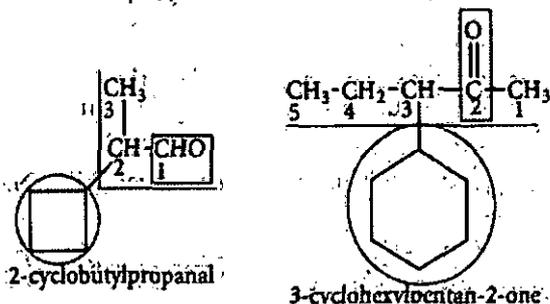
2. Side chain substituted aromatic compounds: These are the compounds in which the functional group is present in the side chain of the benzene ring. These are named as phenyl derivatives of the corresponding aliphatic compounds.

If the ring contains lesser number of carbon atoms than that of alkyl group attached to it, the compound is named as derivative of alkane and the ring is considered as a substituent to the alkane, otherwise it is named as derivative of cycloalkane

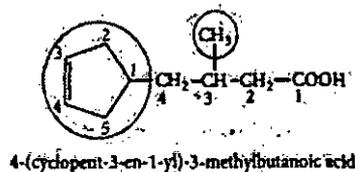
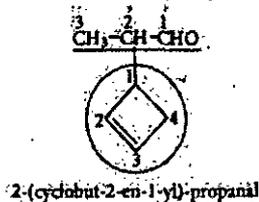


Chlorocyclobut-1-ene.
Double bond get preference over substituent-Cl for numbering)

If the side chain contains a multiple bond or a functional group, then the alicyclic ring is treated as the substituent irrespective of the size of the ring



If the alicyclic ring contains a multiple bond and the side chain contains a functional group the compound is named as derivative of the side chain and the ring is treated as substituent



If both ring as well as the side chain contain the functional group, then parent hydrocarbon is decided on the basis of principal group which is further based on preferential order of functional groups



CLASS-12

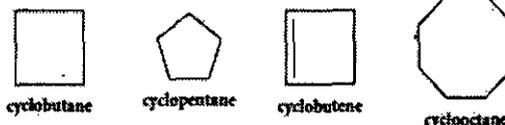
Chemistry



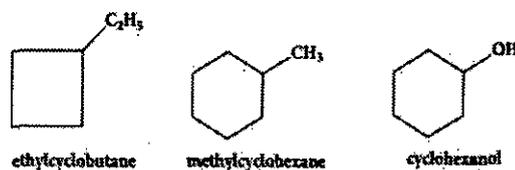
Notes

Rule	Illustration
If both alicyclic ring and the side chain contain same functional group, the parent hydrocarbon is selected on the basis of number of carbon atoms in the ring and side chain	<p>2-(2-hydroxypropyl)cyclohexan-1-ol</p>
If more than one alicyclic rings are attached to the single chain of carbon atoms, the compound is named as a derivative of alkane and alicyclic rings are treated as substituent irrespective of the number of atom in the ring or chain	<p>1-(cyclobutyl)-2-(cyclopropyl)ethane</p>
If the alicyclic ring is directly attached to the benzene ring the compound is named as a derivative of benzene	<p>cyclopentylbenzene</p>
If the alicyclic ring has a functional group along with some substituent on the ring, then the appropriate prefixes and suffixes are used to represent such groups, and numbering is done in such a way that the functional group is not counted for word root rather appropriate suffixes are used to represent such groups	<p>cyclohexanecarboxylic acid</p> <p>2-carbamoylcyclobutane-1-carboxylic acid</p>

In the naming of such compounds a prefix *cyclo* is added to the word root



If only one substituent is present on the ring, then it is not required to give its position



If two or more substituents are present on the ring, the numbering of ring is done according to lowest set of locant rule. Alicyclic compounds also follow the numbering rules of acyclic compounds

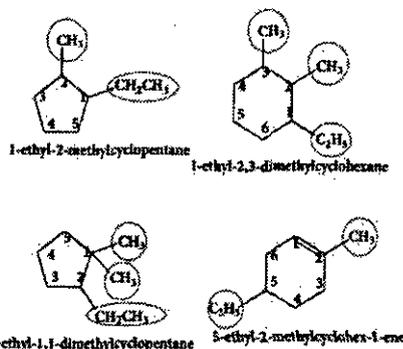


Table 11.6 Rules for naming of alicyclic compounds:



Notes

Table 11.6 Rules for naming of alicyclic compounds:

Rule	Illustration
In the naming of such compounds a prefix cyclo is added to the word root	<p>cyclobutane cyclopentane cyclohexane cyclooctane</p>
If only one substituent is present on the ring, then it is not required to give its position	<p>ethylcyclobutane methylcyclohexane cyclohexanol</p>
If two or more substituents are present on the ring, the numbering of ring is done according to lowest set of locant rule. Alicyclic compounds also follow the numbering rules of acyclic compounds	<p>1-ethyl-3-methylcyclopentane 1-ethyl-2,3-dimethylcyclohexane 1-ethyl-1,3-dimethylcyclopentane 1-ethyl-2-methylcyclohexane</p>

Rule	Illustration
If the ring contains lesser number of carbon atoms than that of alkyl group attached to it, the compound is named as derivative of alkane and the ring is considered as a substituent group to the alkane; otherwise it is named as derivative of cycloalkane	<p>2-Propylcyclobutane (derivative of cycloalkane) 2-Cyclopropylbutane (derivative of alkane)</p> <p>Chlorocyclobut-1-ene double bond gets preference over substituent-Cl for numbering</p>
If the side chain contains a multiple bond or a functional group, then the alicyclic ring is treated as the substituent irrespective of the size of the ring	<p>2-cyclobutylpropanal 3-cyclohexylpentan-2-one</p>
If the alicyclic ring contains a multiple bond and the side chain contains a functional group the compound is named as derivative of the side chain and the ring is treated as substituent	<p>2-(cyclobut-2-en-1-yl)propanal 4-(cyclopent-3-en-1-yl)-3-methylbutanoic acid</p>
If both ring as well as the side chain contain the functional group, then parent hydrocarbon is decided on the basis of principal group which is further based on preferential order of functional groups	<p>3-(3-nitrocyclopentyl)prop-2-enoic acid</p>



Notes

Step No.	Conditions	Rule	Illustrations
	When more than one functional group have same locant the following order of priority should be followed.	Order of precedence of functional group is -COOH > -SO ₃ H > -COOR, -COX > -CONH ₂ > -CN > -CHO > -CO- > -OH > -SH, -NH ₂ > -C=C > -C≡C > -C-C > -O- > -X > -NO ₂ .	
	Two substituents are present on identical position with respect to the parent chain end.	Assign the lowest number according to the alphabetical order of the name of the substituent.	
	Naming the substituents / functional group / side chain using the prefixes / suffixes given in table 11.3 primary suffix for various saturated and unsaturated carbon chains, Table 11.4 Secondary suffix and prefixes for some functional groups and table 11.5 prefix name for some substituents.		
4. Arrange the substituents in the alphabetical order	Two or more substituents are present on the parent chain.	These substituent prefixed with their position number are arranged in alphabetical order (irrespective of the position number) before root word. (The prefixes di-, tri-, etc. are not taken into consideration for grouping alphabetically)	

The following are guide lines for writing IUPAC of the organic compound.

1. The IUPAC names are always written as single word, with notable exception of organic salts, acids and acid derivatives.
2. Commas are used between two adjacent number or letter symbols, and hyphens are used to separate numbers and letter symbol in names **E.g.:** 2,2-Dimethyl-3-hexene
N,N-Dimethyl methanamide
3. Structural prefix such as, meso-, cis-, trans-, are italicised and joined to the name by a hyphen. These prefixes are omitted in alphabetising compound names or in capitalising names at the beginning of a sentence. **Eg:** *trans*-2-Butene
4. Structural prefixes such as di, tri, tetra are treated as a part of the basic name and therefore are neither italicised nor separated by a hyphen. These prefixes are not taken into account in alphabetising compound names **e.g.:** 4-Ethyl-2,2-dimethyl hexane.
5. To name alicyclic compounds, the additional rules should be followed as illustrated in the table 11.x

IUPAC rules for nomenclature of organic compounds

The following steps should be followed for naming an organic compound as per IUPAC nomenclature.

1. Choose the longest carbon chain. (Root word). Consider all the other groups attached to this chain as substituents.
2. Numbering of the longest carbon chain
3. Naming of the substituents (prefixes or suffixes)
4. Arrange the substituents in the alphabetical order
5. Write the name of the compound as below

“prefix + root word + primary suffix + secondary suffix”



Step No.	Conditions	Rule	Illustrations
Choose the longest carbon chain (parent chain)			<p> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ 4C Chain longest chain of 5 C atom </p> <p> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ 6C Chain longest chain of 7 C atom </p>
Two chains of equal lengths.	Choose the chain with maximum number of substituents		<p> $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_2-\text{CH}_3 \end{array}$ 5C Chain Two Substituent Correct </p> <p> $\begin{array}{c} \text{CH}_3-\text{CH} \\ \\ \text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ 5C Chain Wrong One Substituent </p>
Compound contains functional group or multiple bond	i) If any of the functional groups (-OH, -CHO, -COOH, -CN, -COOR, -CONH ₂ , -NH ₂ , -COR, -COX, -SO ₂ H, -SH, -SR) are present, choose the longest carbon chain in such a way that it contains functional groups. ii) If more than one functional group is present, the one with highest precedence should be part of the parent chain. Order of precedence of functional group is -COOH > -SO ₂ H > -COOR, -COX > CONH ₂ > -CN > -CHO > -CO- > -OH > -SH, -NH ₂ > -C=C- > -C≡C- > -O- > -X > -NO ₂	<p> Correct 4C Chain with COOH and double bond. $\begin{array}{c} \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{COOH} \\ \\ \text{CH}_3 \end{array}$ 5C Chain without COOH Wrong 4C Chain with COOH - Wrong </p> <p> Correct 4C Chain with CHO $\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ 5C Chain without CHO Wrong 4C Chain without CHO Wrong </p> <p> Correct 7C chain with COOH group $\begin{array}{c} \text{CH}_3 \\ \\ \text{HOOC}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}-\text{OH} \\ \quad \quad \\ \text{CH}_3 \quad \text{COOH} \quad \text{CH}_3 \end{array}$ 7C chain without COOH group 7C chain with COOH group Correct </p> <p> Correct 7C chain with CHO group $\begin{array}{c} \text{CHO} \\ \\ \text{HOOC}-\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ 7C chain without CHO group 7C chain with COOH group Correct </p>	



Notes

Table 11.5 List of substituents and their Prefix names

Table 11.5 List of substituents and their Prefix names

Substituent group	Prefix
-F	Fluoro
-Cl	Chloro
-Br	Bromo
-I	Iodo
-NO ₂	Nitro
-NO	Nitroso
+ —N=N	Diazo
-OR	Alkoxy
-OCH ₃ (or) -OMe	Methoxy
-OC ₂ H ₅ (or) -OEt	Ethoxy
-CH ₃ (or) -Me	Methyl
-C ₂ H ₅ (or) -Et	Ethyl
-CH ₂ -CH ₂ -CH ₃	1-propyl (n-propyl)
-CH(CH ₃) ₂	2-propyl (iso-propyl)
-CH ₂ -CH ₂ -CH ₂ -CH ₃	1-butyl (n-butyl)

Substituent group	Prefix
-CH ₂ -CH(CH ₃)-CH ₃	2-methyl propyl (iso-propyl)
-C(CH ₃) ₃	1,1-dimethyl ethyl (tert-butyl)
-CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₃	1-pentyl (n-pentyl)
-CH ₂ -CH(CH ₃)-CH ₂ -CH ₃	2-methyl butyl
CH ₂ -CH(CH ₃) ₂	2,2-dimethyl propyl (neopentyl)

Secondary suffix: It is used to denote the nature of functional group present in the organic compound. It is added to the primary suffix by removing its terminal 'e'. Secondary suffix names for some functional groups is listed below in table 11.4



Table 11.4 Secondary suffix and prefixes for some functional groups:

Table 11.4 Secondary suffix and prefixes for some functional groups:

Class of organic compounds	Functional group	Prefix	Secondary suffix
Alcohols	—OH	hydroxy-	-ol
Thioalcohols	—SH	mercapto	-thiol
Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array}$	formyl-	-al
Ketones	$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	oxo-	-one
Carboxylic acid	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$	carboxy-	-oic acid
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OR} \end{array}$	Alkoxy- Carbonyl	-oate
Acid chlorides	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—X} \end{array}$	chloro- carbonyl	-oyl chloride
Acid amines	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—NH}_2 \end{array}$	Carbamoyl	-amide
Amines	—NH_2	amino-	-amine
Nitriles	$\text{—C}\equiv\text{N}$	cyano-	-nitrile
Sulphonic acid	$\text{—SO}_3\text{H}$	sulpho-	-sulphonic acid

Prefix: Substituents that are attached to the parent carbon chain are denoted by adding prefix names before the root word. The prefix names for some common substituents are listed below. If the functional groups are not part of the parent chain, they are considered as substituents. In such cases its prefix name is added before the root word. Prefix names for some functional groups mentioned along with their secondary prefix are listed in table 11.4

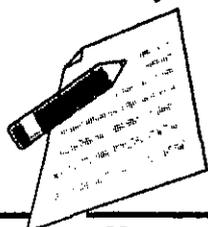


Table 11.2 Number of carbons in parent chain and the corresponding root words

Table 11.2 Number of carbons in parent chain and the corresponding root words

Chain length (or) no. of carbon atoms	Root word	Chain length (or) no. of carbon atoms	Root word
C ₁	Meth-	C ₁₇	Heptadec-
C ₂	Eth-	C ₁₈	Octadec-
C ₃	Prop-	C ₁₉	Nonadec-
C ₄	But-	C ₂₀	Eicos-
C ₅	Pent-	C ₂₁	Henecos
C ₆	Hex-	C ₂₂	Docos
C ₇	Hept-	C ₂₃	Triacont-
C ₈	Oct-	C ₂₄	Hentriacont
C ₉	Non-	C ₂₅	Ditriacont
C ₁₀	Dec-	C ₂₆	Tetracont-
C ₁₁	Undec-	C ₂₇	Pentacont-
C ₁₂	Dodec-	C ₂₈	Hexacont-
C ₁₃	Tridec-	C ₂₉	Heptacont-
C ₁₄	Tetradec-	C ₃₀	Octacont-
C ₁₅	Pentadec-	C ₃₁	Nonacont-
C ₁₆	Hexadec-	C ₃₂	Hect-

Suffix: There are two types of suffix. They are primary suffix and secondary suffix

Primary suffix: It denotes the saturation/ unsaturation of organic compounds. It is added immediately after the root word. Primary suffix for various saturated and unsaturated carbon chains are as follows:

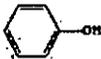
Table 11.3 Primary suffix for various saturated and unsaturated carbon chains

Table 11.3 Primary suffix for various saturated and unsaturated carbon chains

Name & type of carbon chain	Primary suffix
Saturated, C-C	ane
Unsaturated carbon chain	
one C=C bond	ene
Two C=C bonds	diene
Three C=C bonds	triene
One C≡C bond	yne
Two C≡C bonds	diyne



Notes

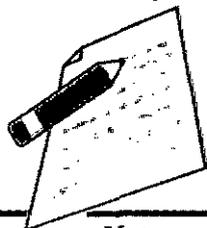
S. No.	Class of compounds	Functional group	General formula (R - Alkyl group)
16	Cyanide (Nitrile)	$\text{—C}\equiv\text{N}$	R-CN
17	Isocyanide	—NC	R-NC
18	Cyanate	—OCN	R-OCN
19	Isocyanate	—NCO	R-NCO
20	Thiocyanate	—SCN	R-SCN
21	Isothiocyanate	—NCS	R-NCS
23	Thioalcohols or thiols	—SH	R-SH
24	Thioethers	—S—R	R-S-R'
25	Imines	=NH	R-CH=NH
26	Nitroso compounds	—NO	R-NO
27	Hydrazines	—NH—NH_2	R-NH-NH ₂
28	Hydrazo compounds	—NH—NH—	R-NH-NH-R
29	Phenols		C ₆ H ₅ OH
30	Imide		RCON(R)COR

Nomenclature of organic compounds:

The International Union of Pure and Applied Chemistry (IUPAC) is the world authority on chemical nomenclature and terminology, naming of new elements in the periodic table standardized methods for measurement; atomic weights, and many other critically-evaluated data. According to IUPAC recommendations to name any organic compound, it is considered as a derivative of its parent saturated hydrocarbon. The IUPAC name of an organic compound consists of three parts.

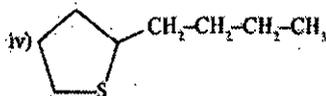
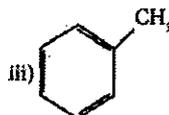
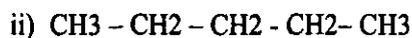
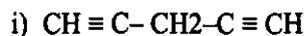
prefix + root word + suffix

Root word denotes the number of carbon atoms in the longest continuous chain in molecules. Prefix denotes the group(s) attached to the main chain which is placed before the root. Suffix denotes the functional group and is placed after the root word.



Based on the above classification let us classify the following compounds.

1. Classify the following compounds based on the structure



Solutions:

- (i) Unsaturated open chain compound
- (ii) saturated open chain compound
- (iii) aromatic benzenoid compound
- (iv) alicyclic compound

Classification based on functional groups:

Table 11.1 Class of compounds and their functional group

S. No.	Class of compounds	Functional group	General formula (R = Alkyl group)
1	Alkene	-	C_nH_{2n}
2	Alkyne	-	$\text{C}_n\text{H}_{2n-2}$
3	Alkyl halide	---X	R-X
4	Alcohol	---OH	R-OH
5	Ether	---O---	R-O-R'
6	Aldehyde		R-CHO
7	Ketone		R-CO-R'
8	Carboxylic acid		R-COOH
9	Ester		RCOOR'
10	Acid anhydride		R-CO-O-CO-R
11	Acyl chloride		R-COX
12	Sulphonic acid	$\text{---SO}_3\text{H}$	$\text{R-SO}_3\text{H}$
13	Nitro alkane	---NO_2	R-NO_2
14	Amine	---NH_2	R-NH_2
15	Amide		R-CO-NH_2



Carbon forms multiple (double and triple) bonds in certain compounds. These can be explained by sp^2 and sp hybridisation of carbon. The carbon forms relatively short bonds which enable the lateral overlap of unhybridised $2p$ orbitals of sp^2 and sp hybridised carbon to form one and two pi bonds respectively.

Molecular structure can be derived from the type of hybridisation. An sp^3 hybridised carbon will have a tetrahedral geometry, a sp^2 hybridised carbon will have trigonal planar geometry, and sp hybridised carbon will have a linear geometry.

Characteristics of organic compounds:

All organic compounds have the following characteristic properties.

1. They are covalent compounds of carbon and generally insoluble in water and readily soluble in organic solvent such as benzene, toluene, ether, chloroform etc...
2. Many of the organic compounds are inflammable (except CCl_4). They possess low boiling and melting points due to their covalent nature
3. Organic compounds are characterised by functional groups. A functional group is an atom or a specific combination of bonded atoms that react in a characteristic way, irrespective of the organic molecule in which it is present. In almost all the cases, the reaction of an organic compound takes place at the functional group. They exhibit isomerism which is a unique phenomenon.
4. **Homologous series:** A series of organic compounds each containing a characteristic functional group and the successive members differ from each other in molecular formula by a CH_2 group is called homologous series. e.g.

Alkanes: Methane (CH_4), Ethane (C_2H_6), Propane (C_3H_8) etc..

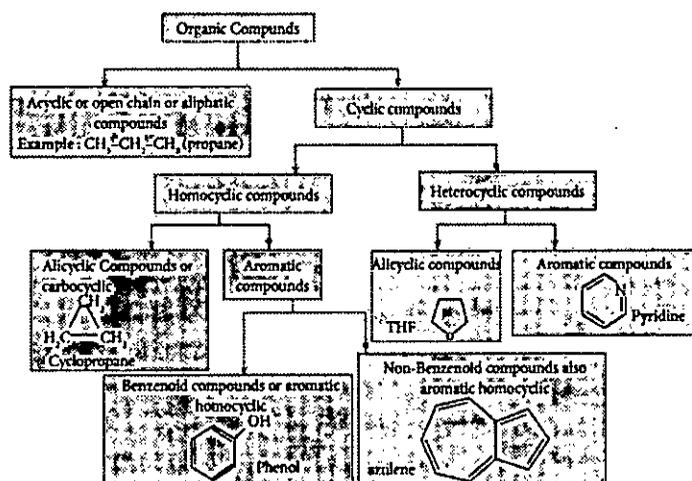
Alcohols: Methanol (CH_3OH), Ethanol (C_2H_5OH), Propanol (C_3H_7OH) etc..)

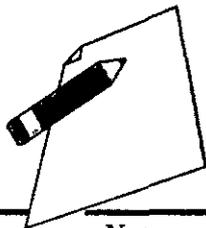
Compounds of the homologous series are represented by a general formula Alkanes C_nH_{2n+2} , Alkenes C_nH_{2n} , Alkynes C_nH_{2n-2} and can be prepared by general methods. They show regular gradation in physical properties but have almost similar chemical property.

Classification of organic compounds

The existing large number of organic compounds and ever-increasing number have made it necessary to classify them. They may be classified based on their structure or the functional group.

Classification based on the structure:





Notes

16 NOMENCLATURE AND GENERAL PRINCIPLES

- Understand the concept of organic compounds.
- Discuss the nomenclature of organic compound.
- Understand the general principles of organic compound.
- Characteristics of organic compounds.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of organic compounds so that the nomenclature and general principles of organic compounds can be learned.

Introduction

Organic chemistry is the study of compounds of carbon. Carbon has a tendency to form more compounds with itself and other atoms (H, O, N, S and halogens) than any other elements. The tendency of an atom to form a chain of bonds with the atoms of the same element is called catenation. The high strength of C-C bond is responsible for its catenation property.

The word 'organic' means 'derived from living organisms'. Organic compounds were thought to be found only in living things. Cell the basic unit of living things, consumes, creates and consists of mainly organic compounds. DNA, the genetic material, the lipids, that forms our cell membrane and the glycogen the energy reserve stored in our liver are all organic compounds. Except few inorganic compounds like salt, water etc... all others such as food, medicine, clothing, cosmetics, fuel etc... are compounds of carbon. All the essential biochemical reactions are also organic in nature leading to the formation various essential bioorganic molecules such as lipoproteins, phospholipids, glycolipids etc...

Synthesis of acetic acid by Kolbe and methane by Berthelot, confirmed that organic compounds can be synthesized in laboratory. Since then, millions of organic compounds were synthesized and characterised. The field of organic chemistry is very vast and its principles find applications in many industries including food, textile, petrochemical, pharmaceutical, dye, polymers, fertiliser, cosmetics etc... Discussing the importance of organic chemistry is just like describing a drop of water in a mighty ocean.

The knowledge of chemical bonding and molecular structure will help in understanding the properties of organic compounds. We know that, the carbon has four valence electrons and its ground state electronic configuration is $1s^2 2s^2 2p^2$. An atom can attain noble gas electronic configuration either by transferring or sharing of electrons. It is not possible for the carbon to form either C^{4+} or C^{4-} ions to attain the nearest noble gas configuration, as it requires large amount of energy. This implies that carbon cannot form ionic bond. Almost in all compounds of carbon, it forms four covalent bonds.

The formation of four covalent bonds can be explained as below. During bond formation, one of the electrons from 2s orbital is promoted to 2p_z orbital. The formation of four sigma bonds by carbon can be explained on the basis of sp³ hybridisation of carbon.



10. P_4O_{10} has _____ bridging O atoms
- (a) 4 (b) 5
(c) 6 (d) 2

Answer: (c)

Review Questions

1. Why is boric acid not a protonic acid?
2. Discuss the structure of boric acid.
3. Draw the Lewis structure of CO and CO₂ molecules.
4. Why does BF₃ act as a Lewis acid?
5. What is catenation? Why does carbon show catenation but silicon does not?
6. Compare the structure of CO₂ and SiO₂.
7. Describe briefly the Haber process for the manufacture of ammonia.
8. Why is graphite a conductor of electricity but diamond is not?
9. Explain different types of silicones.
10. Explain ortho and pro silicates.

CLASS-12

Chemistry



Notes

2. Graphite has a structural similarity with
(a) B_2H_6 (b) B_4C
(c) B (d) BN
Answer: (d)
3. Which is the correct order of decreasing acidity of Lewis acids?
(a) $BBr_3 > BCl_3 > BF_3$ (b) $BF_3 > BCl_3 > BBr_3$
(c) $BCl_3 > BF_3 > BBr_3$ (d) $BBr_3 > BF_3 > BCl_3$
Answer: (a)
4. In the presence of KF , AlF_3 is soluble in HF . Find the complex formed
(a) $K_3[AlF_6]$ (b) AlH_3
(c) $K[AlF_3H]$ (d) $K_3[AlF_3H_3]$
Answer: (a)
5. S-S bond is present in which of the ion pairs
(a) $S_2O_7^{2-}$, $S_2O_3^{2-}$ (b) $S_4O_6^{2-}$, $S_2O_7^{2-}$
(c) $S_2O_7^{2-}$, $S_2O_8^{2-}$ (d) $S_4O_6^{2-}$, $S_2O_3^{2-}$
Answer: (d)
6. Which is the correct order of decreasing bond dissociation enthalpy?
(a) $F_2 > Cl_2 > Br_2 > I_2$ (b) $I_2 > Br_2 > Cl_2 > F_2$
(c) $Cl_2 > Br_2 > F_2 > I_2$ (d) $Br_2 > I_2 > F_2 > Cl_2$
Answer: (c)
7. Oxygen is not released on heating which of the compounds?
(a) $(NH_4)_2Cr_2O_7$ (b) $K_2Cr_2O_7$
(c) $Zn(ClO_3)_2$ (d) $KClO_3$
Answer: (a)
8. Which of the species has a permanent dipole moment?
(a) SF_4 (b) SiF_4
(c) BF_3 (d) XeF_4
Answer: (a)
9. Which of the statements is incorrect for XeO_4 ?
(a) four $p-d$ bonds are present
(b) four $sp^3 - p$ bonds are present
(c) It has a tetrahedral shape
(d) It has a square planar shape
Answer: (d)



Notes

Problem

An element 'A' occupies group number 15 and period number 3 reacts with chlorine to give B which further reacts with chlorine to give C at 273 K. Both B and C are chlorinating agent for organic compounds. C is a better chlorinating agent because it chlorinates metals also. B reacts with SO₃ and reduces it to SO₂. B has a pyramidal shape. C has trigonal bipyramidal shape by sp³d hybridisation. Identify the element A and the compounds B and C.

Write the reactions.

- The element which occupies group number 15 and period number 3 is phosphorus. Therefore A is phosphorus. Phosphorus reacts with chlorine to give PCl₃. Therefore compound B is phosphorus trichloride and it has a pyramidal shape.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$
- PCl₃ further reacts with Cl₂ to give PCl₅. Therefore, the compound C is phosphorus pentachloride and it has a trigonal bipyramidal shape.

$$PCl_3 + Cl_2 \rightarrow PCl_5$$
- PCl₃ and PCl₅ are chlorinating agents for organic compounds. So, both reacts with C₂H₅OH gives C₂H₅Cl. PCl₃ + 3C₂H₅OH → 3C₂H₅Cl + H₃PO₃ PCl₅ + C₂H₅OH → C₂H₅Cl + POCl₃ + HCl
- PCl₅ is a better chlorinating agent. So it chlorinates copper. PCl₅ + 2Cu → 2CuCl + PCl₃
- PCl₃ reacts with SO₃ and reduces it to SO₂. PCl₃ + SO₃ → POCl₃ + SO₂

SUMMARY

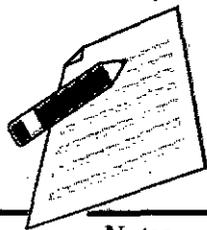
General Characteristic of Group 13, 14, & 15. Method of preparation of boric acid. The acidic nature and structure of boric acid. Method of preparation and uses of borax. Methods of preparation and uses of boron trifluoride and diborane. The Lewis character and use of boron trifluoride. Preparation of aluminium trichloride and its structure. Method of preparation of alums and uses. The comparison of diamond and graphite. The structure and properties of carbon monoxide, carbon dioxide and silicon dioxide and their uses. Comparison of the hydrolytic behaviour of carbon tetrachloride and silicon tetrachloride. Preparation and uses of silicon carbide (carborundum) Preparation and uses of silicones. Preparation and structure of silicates and zeolites. Preparation, properties and uses of nitrogen. Structure of oxides of nitrogen. The methods of preparation, properties and uses of ammonia and nitric acid. Structure of the oxides and oxoacids of nitrogen Halides of phosphorus Allotropic forms of phosphorus oxyacids of phosphorous.

EXERCISE**MCQ**

- Find the amphoteric oxide

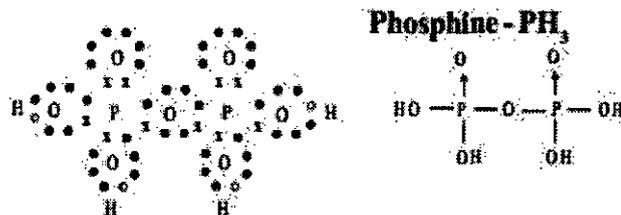
(a) CaO ₂	(b) CO ₂
(c) SnO ₂	(d) SiO ₂

Answer: (c)



Notes

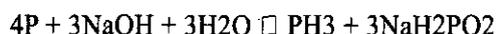
Structure: The Structure of pyrophosphoric acid is represented as:



d) Phosphine - PH₃

Phosphine is the best known hydride of phosphorus.

Laboratory preparation: It is usually obtained by boiling white phosphorus with 30-40% solution of caustic soda in an inert atmosphere of CO₂.



Sodium hypophosphite

Phosphine so obtained is impure. It is passed into an aqueous solution of hydrogen iodide, PH₄I is formed. PH₄I is heated with KOH or NaOH, pure phosphine is obtained.



Physical properties

Phosphine is colourless gas with rotten fish odour.

Chemical properties

- Dissociation:** Phosphine dissociates at about 723 K and gives red phosphorus.
- Action of air:** It burns with oxygen and produces phosphorus pentoxide.
- Action of chlorine:** Phosphine burns in chlorine spontaneously forming PCl₃ and PCl₅.



- Reducing properties:** PH₃ is a powerful reducing agent. When it is passed through the salt solutions, corresponding metal is formed.

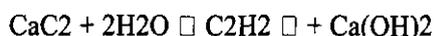
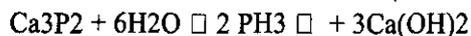


Uses

- Smoke screens

When PH₃ burns it produces smoke which is dense enough to serve as smoke screens.

- Holme's signal :** Containers which have a perforated bottom and a hole at the top are filled with calcium phosphide and calcium carbide. These are thrown into the sea. Water enters the container through the bottom and reacts with calcium carbide and calcium phosphide to give acetylene and phosphine. Phosphine gets ignited spontaneously as it comes in contact with air and also ignites acetylene. Thus a bright red flame is produced which is accompanied by huge smoke due to the burning of phosphine. This serves as a signal to the approaching ships.

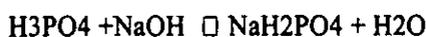




Notes

Chemical properties

1. It is a tribasic acid. It combines with alkalis like NaOH to form three series of salts.



Sodium Di hydrogen Phosphate



Disodium hydrogen Phosphate

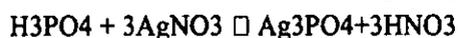


Sodium Phosphate

2. On heating it gives pyrophosphoric acid at 523 K and at 589 K gives metaphosphoric acid



3. On reaction with silver nitrate, it gives yellow precipitate of silver phosphate.

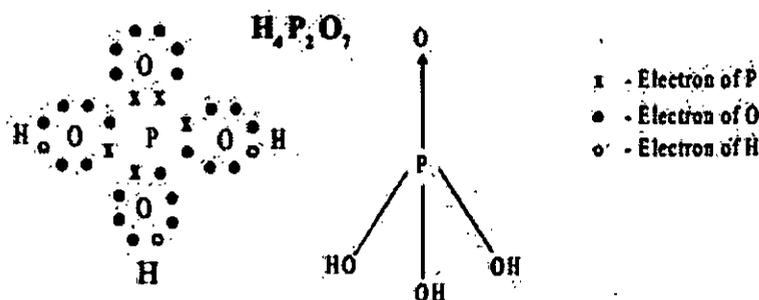


Uses

1. It is used in the preparation of HBr and HI as a substitute for sulphuric acid.
2. It is used as souring agent in the preparation of soft drinks.
3. It is used in the preparation of phosphate salts of sodium, potassium and ammonium.
4. It is used in the manufacture of phosphatic fertilisers.

Structure

Being a tribasic acid, the structure of phosphoric acid is represented as



III. B. Pyrophosphoric acid, $\text{H}_4\text{P}_2\text{O}_7$

Preparation: Pyrophosphoric acid is prepared by heating orthophosphoric acid to 523 K - 533 K.



Physical Properties

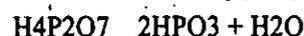
It is a colourless crystalline solid.

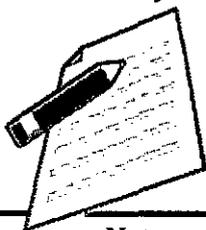
Chemical Properties

1. It is reconverted to orthophosphoric acid on boiling with water



2. When heated strongly, it yields metaphosphoric acid





Notes

Physical properties

It is a white crystalline solid with garlic taste.

Chemical Properties

1. **Acidic nature:** It is a dibasic acid and gives salts of two types.

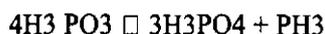


Sodium dihydrogen Phosphite



Disodium hydrogen Phosphite

2. When it is heated it undergoes auto-oxidation and reduction to form phosphoric acid and phosphine.

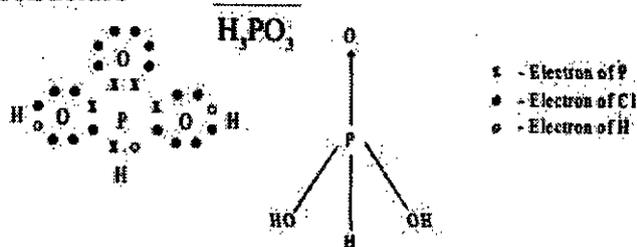


3. It is a powerful reducing agent because it has P-H bond. It reduces silver nitrate solution into silver.



Electronic structure

Electronic structure



Use: It is used as a reducing agent

II. Ortho phosphoric Acid, H₃PO₄

Preparation

1. It is prepared by dissolving phosphorus pentoxide in water and boiling the solution.



2. **Laboratory preparation:** In the laboratory orthophosphoric acid can be prepared by boiling a mixture of red phosphorus with 50% nitric acid in a flask fitted with a reflux condenser on a water bath till no more oxides of nitrogen are liberated. Iodine acts as a catalyst. The product is evaporated below 453 K and then cooled in a vacuum desiccator surrounded by freezing mixture when crystals of orthophosphoric acid are deposited.



Physical properties

1. It is a deliquescent crystalline solid.
2. It is soluble in water.



Notes

b) Oxides of phosphorus

I Phosphorus trioxide P₂O₃ or P₄O₆

It is obtained by the combustion of phosphorus in a limited supply of air.



Physical properties

1. It is a white waxy substance
2. It has a garlic odour.

Chemical properties

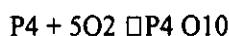
1. It reacts with cold water, gives phosphorus acid.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$
2. It reacts with hot water vigorously to form inflammable phosphine.

$$2P_2O_3 + 6H_2O \rightarrow PH_3 \uparrow + 3H_3PO_4$$

II Phosphorus pentoxide P₂O₅ or P₄O₁₀

Phosphorus pentoxide can be prepared by burning phosphorus with sufficient supply of air.



Physical properties

It is a white solid and an acidic oxide.

Chemical properties

1. It reacts with moisture to form metaphosphoric acid.

$$P_4O_{10} + 2H_2O \rightarrow 4HPO_3$$

When the solution is boiled, the metaphosphoric acid is changed to orthophosphoric acid.

$$HPO_3 + H_2O \rightarrow H_3PO_4$$

or

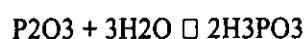
$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$
2. Phosphorus pentoxide extracts water from many inorganic compound including sulphuric acid, nitric acid and several organic compounds. It is therefore, used as a powerful dehydrating agent.

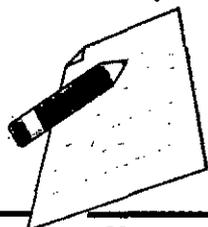
Use: It is used as a dehydrating agent.

c) Oxy-Acids of Phosphorus

I. Phosphorus acid - H₃PO₃

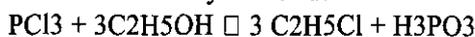
It is prepared by the action of cold water on phosphorus (III) oxide or phosphorus (III) chloride.





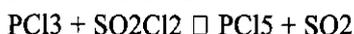
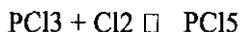
Notes

Acetic Acid Acetyl Chloride

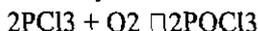


Ethyl alcohol Ethyl Chloride

- It reacts with chlorine or sulphuryl chloride forming phosphorus pentachloride.



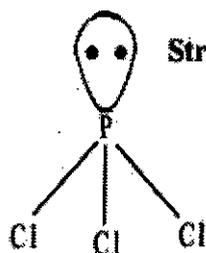
- It readily combines with oxygen forming phosphorus oxychloride



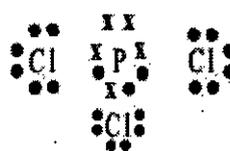
- It reacts with SO_3 to form phosphorus oxychloride and SO_2



Structure: PCl_3 molecule has a pyramidal shape, which arises from sp^3 hybridisation of phosphorus atom. One of the tetrahedral positions is occupied by a lone pair of electrons.



Structure: PCl_3 molecule

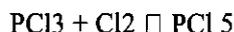


x - Electron of p

• - Electron of Cl

II. Phosphorus pentachloride, PCl_5

Preparation: Phosphorus pentachloride is usually prepared by the action of an excess of chlorine on phosphorus trichloride.

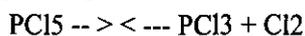


Physical properties

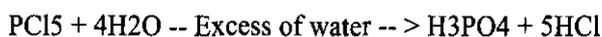
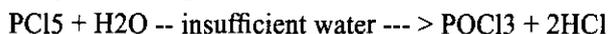
- Phosphorus pentachloride is a yellowish white crystalline solid.
- It sublimes on heating at 473 K and melts at 318 K under pressure.

Chemical properties

Phosphorus pentachloride dissociates on heating into phosphorus trichloride and chlorine.

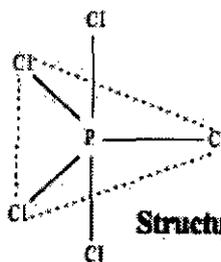
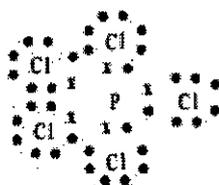


It is violently hydrolysed by water giving phosphorus oxychloride or phosphoric acid depending upon the quantity of water.



Structure

PCl_5 molecule has trigonal bipyramidal shape in vapour state which arises from sp^3d hybridisation of phosphorus atom.



x - Electron of p

• - Electron of Cl

Structure PCl_5 molecule



Physical Properties

All the elements of the group exist in a polyatomic state. The first, Nitrogen is gas but as you move down there is a significant increase in the metallic character of the elements. Nitrogen and Phosphorus are non-metals, Arsenic and Antimony are metalloids and Bismuth is a metal. These changes can be attributed to the decrease in Ionization enthalpy and increase in atomic size. Boiling points also, in general, show an increasing trend as you move down. Except for Nitrogen, all the other elements have allotropes.

Chemical Properties

- The valence shells of the p-Block elements have a configuration of $ns^2 np^3$.
- So the elements here can either lose 5 electrons or gain 3.
- The common oxidation states of these elements are -3, +3 and +5.
- With a decrease in the Ionization enthalpy and electro negativity, due to the increasing atomic radius, the tendency to gain three electrons to create a -3 oxidation state decreases down the group.
- In fact, Bismuth hardly forms any compounds with -3 oxidation state.
- As we go down, the stability of the +5 state decreases and that of +3 increases due to inert pair effect.

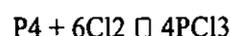
Compounds of Phosphorus

a) Halides of Phosphorus

Phosphorus combines with all the halogens forming phosphorus halides which are all covalent compounds. Phosphorus chlorides are more important. Tri and pentachlorides of phosphorus are most common.

I. Phosphorus Trichloride, PCl_3

Preparation: PCl_3 is prepared by heating white phosphorus in a current of dry chlorine.



Dry white phosphorus is placed in the retort and gently heated on a water bath. A current of pure, dry chlorine is led over the phosphorus. The phosphorus trichloride formed being volatile distills over and is collected in a water cooled receiver.

The phosphorus trichloride obtained as above contains some PCl_5 as impurity. This is removed by distilling the PCl_3 over white phosphorus.

Physical properties

1. Colourless low boiling liquid
2. It fumes in moist air
3. It has pungent odour.

Chemical Properties

1. It is violently hydrolysed by water giving phosphorus acid and hydrochloric acid gas.



In a similar manner it reacts with organic compounds containing hydroxyl (OH) group, such as acids and alcohols.





A third possible method is to react an alkyl halide with ammonia, but this is less satisfactory since over-alkylation is possible (see below). The reaction of an aldehyde with ammonia by reductive amination is a fourth method of obtaining primary amines (see below).

Alkylation of alkylamines

It is possible to convert primary and secondary amines to secondary and tertiary amines respectively, by alkylation with alkyl halides by the S_N2 reaction. However, over-alkylation can be a problem and better methods of amine synthesis are available.

Reductive amination is a more controlled method of adding an extra alkyl group to an alkylamine (Fig. 4). Primary and secondary alkylamines can be treated with a ketone or an aldehyde in the presence of a reducing agent called sodium cyanoborohydride. The alkylamine reacts with the carbonyl compound by nucleophilic addition followed by elimination to give an imine or an iminium ion which is immediately reduced by sodium cyanoborohydride to give the final amine. Overall, this is the equivalent of adding one extra alkyl group to the amine. Therefore, primary amines are converted to secondary amines and secondary amines are converted to tertiary amine. The reaction is also suitable for the synthesis of primary amines if ammonia is used instead of an alkylamine. The reaction goes through an imine intermediate if ammonia or a primary amine is used (Fig. 4a). When a secondary amine is used, an iminium ion intermediate is involved (Fig. 4b).

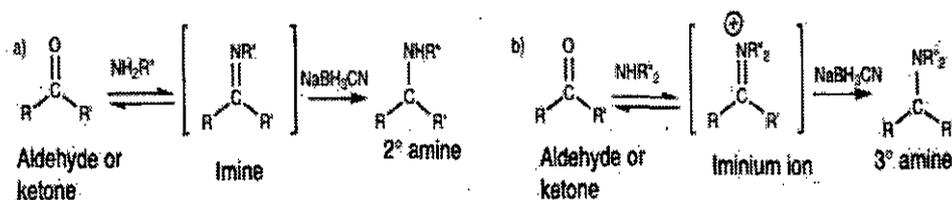


Fig. 4. Reductive amination of an aldehyde or ketone.

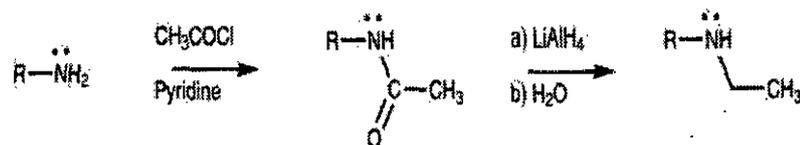


Fig. 5. Alkylation of an amine via an amide.

An alternative way of alkylating an amine is to acylate the amine to give an amide, and then carry out a reduction with $LiAlH_4$. Although two steps are involved, there is no risk of over-alkylation since acylation can only occur once.

Rearrangements

There are two rearrangement reactions which can be used to convert carboxylic acid derivatives into primary amines where the carbon chain in the product has been shortened by one carbon unit (Fig. 6). These are known as the Hofmann and the Curtius rearrangements. The Hofmann rearrangement involves the treatment of a primary amide with bromine under basic conditions, while the Curtius rearrangement involves heating an acyl azide. The end result is the same – a primary amine with loss of the original carbonyl group.



Notes

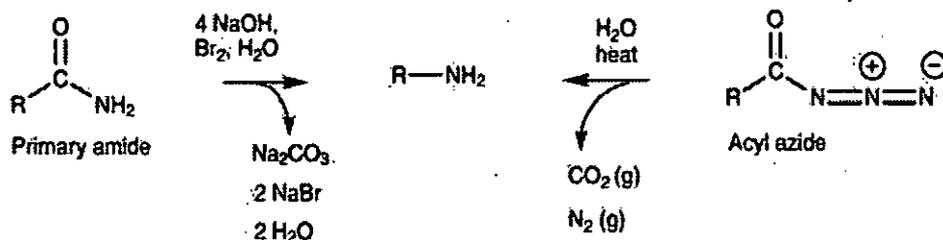


Fig. 6. Hofmann rearrangement (left) and Curtius rearrangement (right).

In both reactions, the alkyl group (R) is transferred from the carbonyl group to the nitrogen to form an intermediate isocyanate (O=C=N-R). This is then hydrolyzed by water to form carbon dioxide and the primary amine. The Curtius rearrangement has the added advantage that nitrogen is lost as a gas which helps to drive the reaction to completion.

Arylamines

The direct introduction of an amino group to an aromatic ring is not possible. However, nitro groups can be added directly by electrophilic substitution and then reduced to the amine. The reduction is carried out under acidic conditions resulting in an arylaminium ion as product. The free base can be isolated by basifying the solution with sodium hydroxide to precipitate the arylamine.

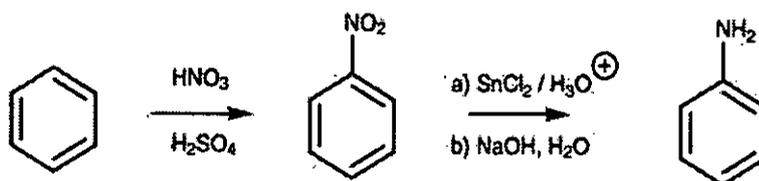


Fig. 7. Introduction of an amine to an aromatic ring.

Once an amino group has been introduced to an aromatic ring, it can be alkylated with an alkyl halide, acylated with an acid chloride or converted to a higher amine by reductive amination as described for an alkylamine.

Properties of amines

Structure

Amines consist of an sp^3 hybridized nitrogen linked to three substituents by σ bonds. The functional group is pyramidal in shape with bond angles of approximately 109° . If the substituents are alkyl groups, the amine is aliphatic or an alkylamine. If one or more of the substituents is aromatic, the amine is aromatic or an arylamine. If the amine has only one alkyl or aryl substituent, it is defined as primary. If there are two such substituents, the amine is secondary, and if there are three such groups, the amine is tertiary.

Pyramidal inversion

Amines can be chiral if they have three different substituents. However, it is not possible to separate enantiomers since they can easily interconvert by pyramidal inversion. The process



involves a planar intermediate where the nitrogen has changed from sp^3 hybridization to sp^2 hybridization and the lone pair of electrons are in a p orbital. Pyramidal inversion is not possible for chiral quaternary ammonium salts and enantiomers of these structures can be separated.

Physical Properties

Amines are polar compounds with higher boiling points than comparable alkanes. They have similar water solubilities to alcohols due to hydrogen bonding, and low molecular weight amines are completely miscible with water. Low molecular weight amines have an offensive fishy smell.

Basicity

Amines are weak bases which are in equilibrium with their ammonium ion in aqueous solution. The basic strength of an amine is indicated by its pK_b value. There are two main effects on basic strength. Alkyl groups have an inductive effect which stabilizes the ammonium ion and results in increased basicity. Solvation of the ammonium ion by water stabilizes the ion and increases basicity. The more hydrogen bonds which are possible between the ammonium ion and water, the greater the stability and the greater the basicity. The alkyl inductive effect is greatest for ammonium ions formed from tertiary amines, whereas the solvation effect is greatest for ammonium ions formed from primary amines. *In general, primary and secondary amines are stronger bases than tertiary amines. Aromatic amines are weaker bases than aliphatic amines since nitrogen's lone pair of electrons interacts with the π system of the aromatic ring, and is less likely to form a bond to a proton. Aromatic substituents affect basicity. Activating substituents increase electron density in the aromatic ring which helps to stabilize the ammonium ion and increase basic strength. Deactivating groups have the opposite effect. Substituents capable of interacting with the aromatic ring by resonance have a greater effect on basicity if they are at the ortho or para positions.*

Reactivity

Amines react as nucleophiles or bases since they have a readily available lone pair of electrons which can participate in bonding. Primary and secondary amines can act as weak electrophiles or acids with a strong base, by losing an N-H proton to form an amide anion (R_2N^-).

Spectroscopic analysis

Evidence for primary and secondary amines include N-H stretching and bending absorptions in the IR spectrum as well as a D_2O exchangeable proton in the 1H nmr spectrum.

Structure

Amines consist of an sp^3 hybridized nitrogen linked to three substituents by three bonds. The substituents can be hydrogen, alkyl, or aryl groups, but at least one of the substituents has to be an alkyl or aryl group. If only one such group is present, the amine is defined as primary. If two groups are present, the amine is secondary. If three groups are present, the amine is tertiary. If the substituents are all alkyl groups, the amine is defined as being an alkylamine. If there is at least one aryl group directly attached to the nitrogen, then the



Notes

amine is defined as an arylamine.

The nitrogen atom has four sp^3 hybridized orbitals pointing to the corners of a tetrahedron in the same way as an sp^3 hybridized carbon atom. However, one of the sp^3 orbitals is occupied by the nitrogen's lone pair of electrons. This means that the atoms in an amine functional group are pyramidal in shape. The C-N-C bond angles are approximately 109° which is consistent with a tetrahedral nitrogen. However, the bond angle is slightly less than 109° since the lone pair of electrons demands a slightly greater amount of space than a σ bond.

Pyramidal inversion

Since amines are tetrahedral, they are chiral if they have three different substituents. However, it is not possible to separate the enantiomers of a chiral amine since amines can easily undergo pyramidal inversion – a process which interconverts the enantiomers (Fig. 1). The inversion involves a change of hybridization where the nitrogen becomes sp^2 hybridized rather than sp^3 hybridized. As a result, the molecule becomes planar and the lone pair of electrons occupy a p orbital. Once the hybridization reverts back to sp^3 , the molecule can either revert back to its original shape or invert.

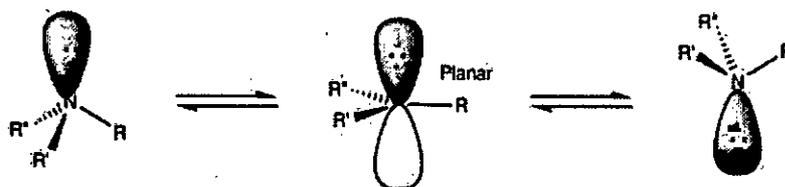


Fig. 1. Pyramidal inversion.

Although the enantiomers of chiral amines cannot be separated, such amines can be alkylated to form quaternary ammonium salts where the enantiomers can be separated. Once the lone pair of electrons is locked up in a σ bond, pyramidal inversion becomes impossible and the enantiomers can no longer interconvert.

Physical properties

Amines are polar compounds and intermolecular hydrogen bonding is possible for primary and secondary amines. Therefore, primary and secondary amines have higher boiling points than alkanes of similar molecular weight. Tertiary amines also have higher boiling points than comparable alkanes, but have slightly lower boiling points than comparable primary or secondary amines since they cannot take part in intermolecular hydrogen bonding.

However, all amines can participate in hydrogen bonding with protic solvents, which means that amines have similar water solubilities to comparable alcohols.

Low molecular weight amines are freely miscible with water. Low molecular weight amines have an offensive fish-like odour

Basicity

Amines are weak bases but they are more basic than alcohols, ethers, or water. As a result, amines act as bases when they are dissolved in water and an equilibrium is set up between the ionized form (the ammonium ion) and the unionized form (the free base; Fig. 2).



Fig. 2. Acid-base reaction between an amine and water.

The basic strength of an amine can be measured by its pK_b value. The lower the value of pK_b , the stronger the base. The pK_b for ammonia is 4.74, which compares with pK_b values for methylamine, ethylamine, and propylamine of 3.36, 3.25 and 3.33, respectively. This demonstrates that larger alkyl groups increase base strength. This is an inductive effect whereby the ion is stabilized by dispersing some of the positive charge over the alkyl group (Fig. 3). This shifts the equilibrium of the acid base reaction towards the ion, which means that the amine is more basic. The larger the alkyl group, the more significant this effect.



Fig. 3. Inductive effect of an alkyl group on an alkylammonium ion.

Further alkyl substituents should have an even greater inductive effect and one might expect secondary and tertiary amines to be stronger bases than primary amines. This is not necessarily the case and there is no direct relationship between basicity and the number of alkyl groups attached to nitrogen. The inductive effect of more alkyl groups is counterbalanced by a **solvation effect**.

Once the ammonium ion is formed, it is solvated by water molecules – a stabilizing factor which involves hydrogen bonding between the oxygen atom of water and any N–H group present in the ammonium ion (Fig. 4). The more hydrogen bonds which are possible, the greater the stabilization. As a result, solvation and solvent stabilization is stronger for alkylammonium ions formed from primary amines than for those formed from tertiary amines. The solvent effect tends to be more important than the inductive effect as far as tertiary amines are concerned and so tertiary amines are generally weaker bases than primary or secondary amines.

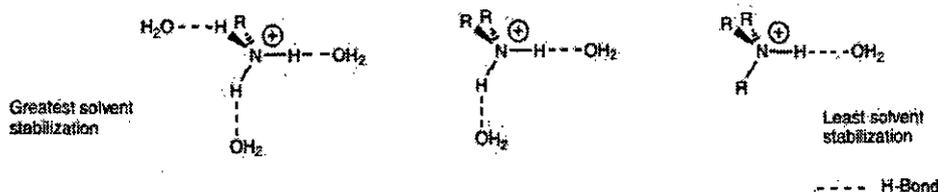


Fig. 4. Solvent effect on the stabilization of alkylammonium ions.

Aromatic amines (arylamines) are weaker bases than alkylamines since the orbital containing nitrogen's lone pair of electrons overlaps with the π system of the aromatic ring. In terms of resonance, the lone pair of electrons can be used to form a double bond to the aromatic ring, resulting in the possibility of three **zwitterionic** resonance structures (Fig. 5). (A zwitterion is a molecule containing a positive and a negative charge.) Since nitrogen's lone pair of electrons is involved in this interaction, it is less available to form a bond to a proton and so the amine is less basic.

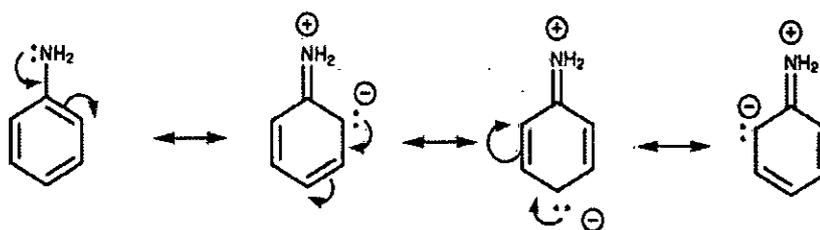


Fig. 5. Resonance interaction between nitrogen's lone pair and the aromatic ring.

The nature of aromatic substituent also affects the basicity of aromatic amines. Substituents which deactivate aromatic rings (e.g., NO_2 , Cl , or CN) lower electron density in the ring, which means that the ring will have an electron-withdrawing effect on the neighbouring ammonium ion. This means that the charge will be destabilized and the amine will be a weaker base. Substituents which activate the aromatic ring enhance electron density in the ring which means that the ring will have an electron-donating effect on the neighbouring charge. This has a stabilizing effect and so the amine will be a stronger base. The relative position of aromatic substituents can be important if resonance is possible between the aromatic ring and the substituent. In such cases, the substituent will have a greater effect if it is at the ortho or para position. For example, para-nitroaniline is a weaker base than meta-nitroaniline. This is because one of the possible resonance structures for the para isomer is highly disfavoured since it places a positive charge immediately next to the ammonium ion (Fig. 6). Therefore, the number of feasible resonance structures for the para isomer is limited to three, compared to four for the meta isomer. This means that the para isomer experiences less stabilization and so the amine will be less basic.

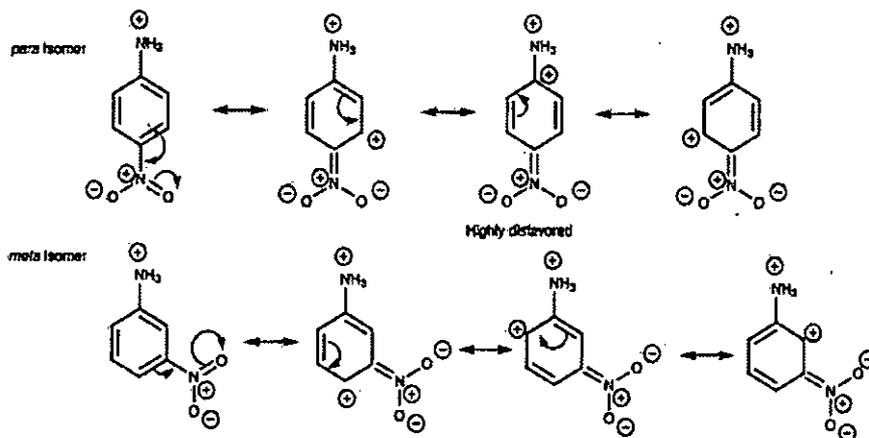


Fig. 6. Resonance structures for para-nitroaniline and meta-nitroaniline.

If an activating substituent is present, capable of interacting with the ring by resonance, the opposite holds true and the para isomer will be a stronger base than the meta isomer. This is because the crucial resonance structure mentioned above would have a negative charge immediately next to the ammonium ion and this would have a stabilizing effect.

Reactivity

Amines react as nucleophiles or bases, since the nitrogen atom has a readily available lone pair of electrons which can participate in bonding (Fig. 7). As a result, amines react with acids to form water soluble salts. This allows the easy separation of amines from other

compounds. A crude reaction mixture can be extracted with dilute hydrochloric acid such that any amines present are protonated and dissolve into the aqueous phase as water-soluble salts. The free amine can be recovered by adding sodium hydroxide to the aqueous solution such that the free amine precipitates out as a solid or as an oil.

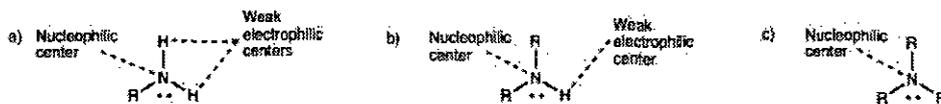


Fig. 7. Nucleophilic and electrophilic centers in (a) primary, (b) secondary, and (c) tertiary amines.

Amines will also react as nucleophiles with a wide range of electrophiles including alkyl halides, aldehydes, ketones, and acid chlorides.

The N-H protons of primary and secondary amines are weakly electrophilic or acidic and will react with a strong base to form amide anions. For example, diisopropylamine ($pK_a \sim 40$) reacts with butyllithium to give lithium diisopropylamide (LDA) and butane.

Spectroscopic analysis

Primary and secondary amines are likely to show characteristic absorptions due to N-H stretching and N-H bending. The former occurs in the region $3500-3300\text{ cm}^{-1}$, and in the case of primary amines two absorptions are visible. The absorptions tend to be sharper but weaker than O-H absorptions which can occur in the same region. N-H bending occurs in the region $1650-1560\text{ cm}^{-1}$ for primary amines and $1580-1490\text{ cm}^{-1}$ for secondary amines although the latter tend to be weak and unreliable. These absorptions occur in the same region as alkene and aromatic C=C stretching absorptions, and care has to be taken in assigning them.

Naturally, these absorptions are not present for tertiary amines. For aromatic amines, an absorption due to Ar-N stretching may be visible in the region $1360-1250\text{ cm}^{-1}$.

The ^1H nmr spectrum of a primary or secondary amine will show a broad signal for the N-H proton in the region $0.5-4.5\text{ ppm}$ which will disappear from the spectrum if the sample is shaken with deuterated water. For aromatic amines this signal is typically in the range $3-6\text{ ppm}$. The chemical shifts of neighbouring groups can also indicate the presence of an amine group indirectly. For example, an N-methyl group gives a singlet near 2.3 ppm in the ^1H spectrum and appears in the region $30-45\text{ ppm}$ in the ^{13}C spectrum.

If the molecular ion in the mass spectrum has an odd number, this indicates that an odd number of nitrogen atoms are present in the molecule. This supports the presence of an amine but does not prove it, since there are other functional groups containing nitrogen. Amines undergo α -cleavage when they fragment (i.e. cleavage next to the carbon bearing the amine group).

REACTIONS OF AMINES

Alkylation

Ammonia, primary amines, and secondary amines can be alkylated with alkyl halides to give primary, secondary, and tertiary amines, respectively. However, over-alkylation usually occurs and mixtures are obtained. The method is best used for converting tertiary amines to quaternary ammonium salts. A better method of alkylating a primary or secondary





amine is to treat the amine with an aldehyde or ketone in the presence of a reducing agent. Reaction of the amine with the carbonyl compound produces an intermediate imine which is reduced to the amine. No over-alkylation takes place.

Acylation

Primary and secondary amines can be acylated with an acid chloride or acid anhydride to give secondary and tertiary amides, respectively.

Sulfonylation

Primary and secondary amines can be sulfonylated with a sulfonyl chloride to give a sulfonamide.

Elimination

Primary amines can be converted to alkenes if the amine is first methylated to a quaternary ammonium salt, then treated with silver oxide. Elimination of triethylamine takes place to give the least substituted alkene. The reaction is known as the Hofmann elimination. The reaction can also be carried out on secondary and tertiary amines although a mixture of alkenes may be formed depending on the substituents present. Aromatic amines will also react if they contain a suitable N-alkyl substituent.

Electrophilic aromatic substitution

Aromatic amines undergo electrophilic aromatic substitutions. The amino group is strongly activating and directs substitution to the ortho and para positions. Nitration, sulfonation, and bromination are all possible, but bromination may occur more than once. Friedel-Crafts alkylation and acylation are not possible since the amino group complexes the Lewis acid involved in the reaction. The problems of excess bromination and Lewis acid complexation can be overcome by converting the amine to an amide before carrying out the substitution reaction. The amide can be hydrolyzed back to the amine once the substitution reaction has been carried out.

Diazonium salts

Aromatic primary amines can be converted to diazonium salts on treatment with nitrous acid. These salts are extremely important in aromatic chemistry since they can be converted to a variety of other substituents. Diazonium salts also react with phenols or aromatic amines in a process called diazonium coupling to produce a highly conjugated system which is usually coloured. Such products are often used as dyes.

Alkylation

Ammonia, primary amines, and secondary amines (both aromatic and aliphatic) can undergo the S_N2 reaction with alkyl halides to produce a range of primary, secondary, and tertiary amines. Primary, secondary, and tertiary amines are produced as ammonium salts which are converted to the free amine by treatment with sodium hydroxide (Fig. 1a).

In theory, it should be possible to synthesize primary amines from ammonia, secondary amines from primary amines, and tertiary amines from secondary amines. In practice,



over-alkylation is common. For example, reaction of ammonia with methyl iodide leads to a mixture of primary, secondary, and tertiary amines along with a small quantity of the quaternary ammonium salt (Fig. 2).

Alkylation of tertiary amines by this method is a good way of obtaining quaternary ammonium salts (Fig. 1b) since no other products are possible. However, alkylation of lower order amines is not so satisfactory.

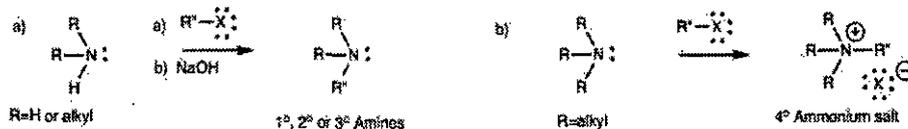


Fig. 1. Alkylation of amines.

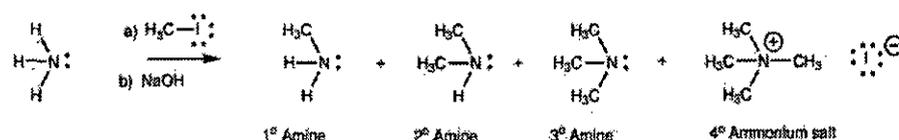


Fig. 2. Alkylation of ammonia with methyl iodide.

A better method of alkylating a primary or secondary amine is to treat the amine with a ketone or an aldehyde in the presence of a reducing agent – sodium cyanoborohydride. This reaction is known as a **reductive amination**. Over-alkylation cannot occur by this method.

Acylation

Primary and secondary amines (both aromatic and aliphatic) can be acylated with an acid chloride or acid anhydride to form secondary and tertiary amides, respectively. This reaction can be viewed as the acylation of an amine or as the nucleophilic substitution of a carboxylic acid derivative.

Sulfonylation

In a similar reaction to acylation, primary and secondary amines (both aromatic and aliphatic) can be treated with a sulfonyl chloride to give a sulfonamide (Fig.3). Tertiary amines do not give a stable product and are recovered unchanged.

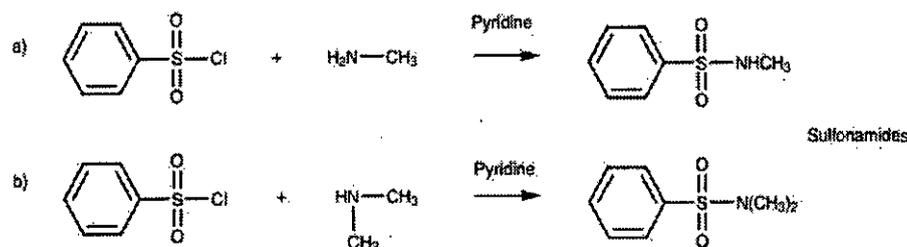


Fig. 3. Reaction of benzenesulfonyl chloride with (a) primary amine; (b) secondary amine.

Elimination

Primary amines could be converted to alkenes if it was possible to eliminate ammonia from the molecule. However, the direct elimination of ammonia is not possible. A less direct method of achieving the same result is to exhaustively methylate the amine by the



Notes

SN₂ reaction to give a quaternary ammonium salt. Once this is formed, it is possible to eliminate triethylamine in the presence of silver oxide and to form the desired alkene. The reaction is called the **Hofmann elimination** (Fig. 4). The silver oxide provides a hydroxyl ion which acts as the base for an E₂ elimination. However, unlike most E₂ eliminations, the less substituted alkene is preferred if a choice is available (Fig. 6). The reason for this preference is not fully understood, but may have something to do with the large bulk of the triethylamine leaving group hindering the approach of the hydroxide ion such that it approaches the least hindered β-carbon.)



Fig. 4. Hofmann elimination.

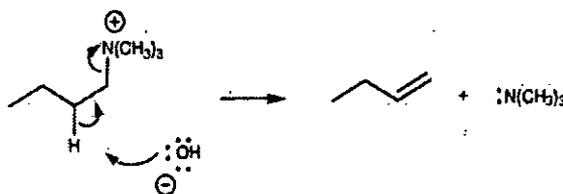


Fig. 5. Mechanism of the Hofmann elimination.

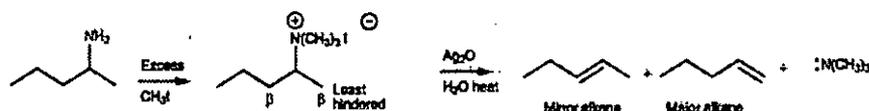


Fig. 6. The less substituted alkene is preferred in the Hofmann elimination.

Secondary and tertiary amines can also be exhaustively methylated then treated with silver oxide. However, mixtures of different alkenes may be obtained if the N-substituents are different alkyl groups (Fig. 7).

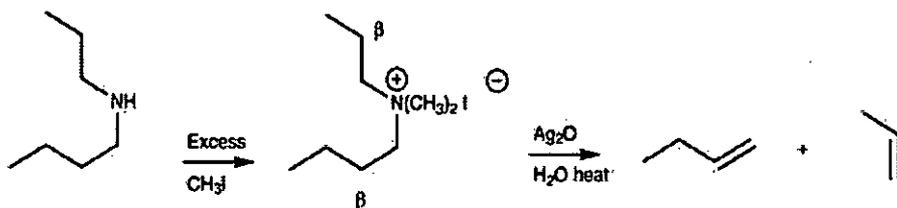


Fig. 7. Hofmann elimination of a secondary amine.

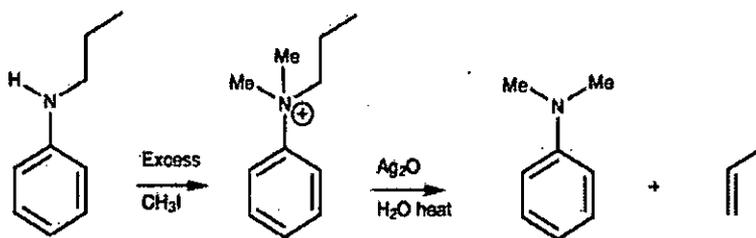


Fig. 8. Hofmann elimination of an aromatic amine.

The Hofmann elimination is not possible with primary arylamines, but secondary and tertiary arylamines will react if one of the substituents is a suitable alkyl group. Elimination of the aromatic amine can then occur such that the alkyl substituent is converted to the alkene (Fig. 8).

Electrophilic aromatic substitution

Aromatic amines such as aniline undergo electrophilic substitution reactions where the amino group acts as a strongly activating group, directing substitution to the ortho and para positions. Like phenols, the amino group is such a strong activating group that more than one substitution may take place. For example, reaction of aniline with bromine results in a tribrominated structure as the only product. This problem can be overcome by converting the amine to a less activating group. Typically, this involves acylating the group to produce an amide. This group is a weaker activating group and so mono-substitution takes place. Furthermore, since the amide group is bulkier than the original amino group, there is more of a preference for para substitution over ortho substitution. Once the reaction has been carried out, the amide can be hydrolyzed back to the amino group.

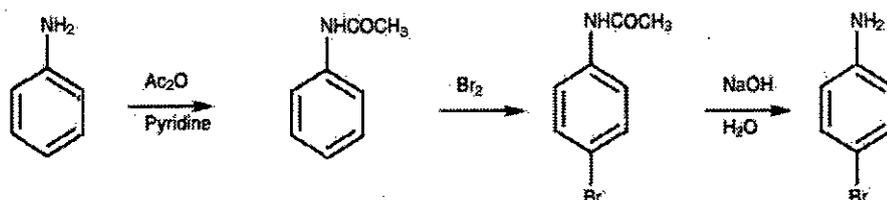
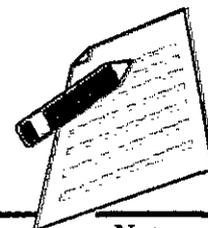


Fig. 9. Synthesis of para-bromoaniline.

Anilines can be sulfonated and nitrated, but the Friedel-Crafts alkylation and acylation are not possible since the amino group forms an acid base complex with the Lewis acid required for this reaction. One way round this is to convert the aniline to the amide as above before carrying out the reaction.

Diazonium salts

Primary arylamines or anilines can be converted to diazonium salts, which in turn can be converted to a large variety of substituents (Fig. 10).

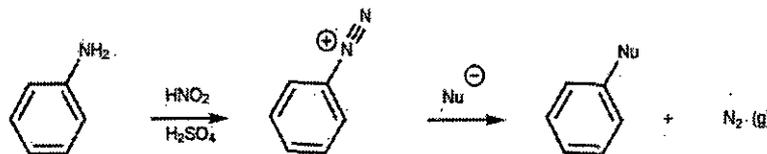


Fig. 10. Synthesis and reactions of diazonium salts.

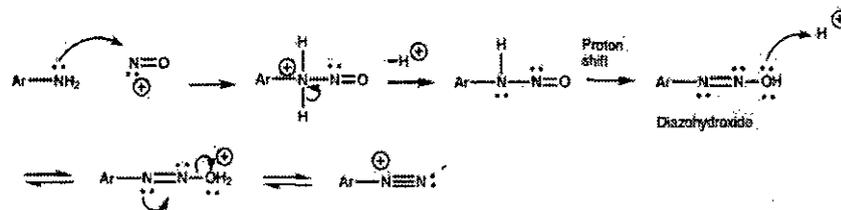


Fig. 11. Mechanism of diazotization.

Reaction of an aniline with nitrous acid results in the formation of the stable diazonium salt in a process called **diazotization** (Fig. 11). In the strong acid conditions used, the nitrous acid dissociates to form an $+NO$ ion which can then act as an electrophile. The aromatic amine uses its lone pair of electrons to form a bond to this $+NO$ ion. Loss of a proton from the intermediate formed, followed by a proton shift leads to the formation of a diazohydroxide. The hydroxide group is now protonated turning it into a good leaving



group, and a lone pair from the aryl nitrogen forms a second π bond between the two nitrogen atoms and expels water.

Once the diazonium salt has been formed, it can be treated with various nucleophiles such as Br^- , Cl^- , I^- , $-\text{CN}$ and $-\text{OH}$ (Fig. 12). The nucleophile displaces nitrogen from the aromatic ring and the nitrogen which is formed is lost from the reaction mixture as a gas, thus helping to drive the reaction to completion. Those reactions involving Cu(I) are also known as the Sandmeyer reaction.

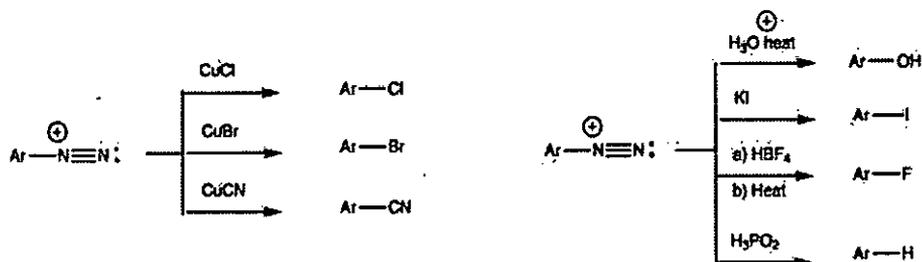


Fig. 12. Reactions of diazonium salts.

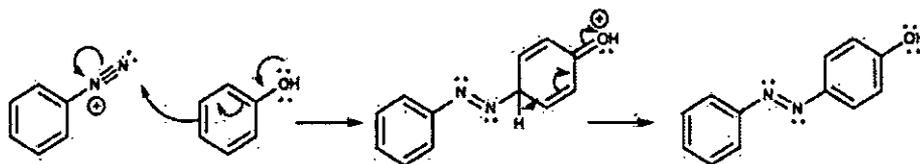


Fig. 13. Diazonium coupling.

Diazonium salts are also used in a reaction called **diazonium coupling** where the diazonium salt is coupled to the para position of a phenol or an arylamine (Fig. 13). The azo products obtained have an extended conjugated system which includes both aromatic rings and the $\text{N}=\text{N}$ link. As a result, these compounds are often coloured and are used as dyes.

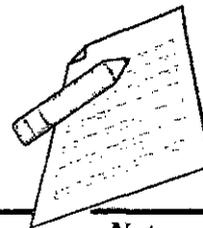
The above coupling is more efficient if the reaction is carried out under slightly alkaline conditions (NaOH) such that the phenol is ionized to a phenoxide ion (ArO^-). Phenoxide ions are more reactive to electrophilic addition than phenols themselves. Strong alkaline conditions cannot be used since the hydroxide ion adds to the diazonium salt and prevents coupling. If the para position of the phenol is already occupied, diazo coupling can take place at the ortho position instead.

Aliphatic amines, as well as secondary and tertiary aromatic amines, react with nitrous acid, but these reactions are less useful in organic synthesis.

SUMMARY

Amines are considered as derivatives of ammonia. They are classified as primary, secondary or tertiary based on how many alkyl groups have replaced the hydrogen atoms of ammonia. Reaction of alkyl halides with ammonia produces a mixture of primary, secondary or tertiary amines along with quaternary ammonium salts. Reduction of nitriles, amides and nitro compounds gives amines having the same number of carbon atoms. In Hofmann bromamide reaction, the amine formed has one carbon less than the starting amide. Both aliphatic and aromatic amines are basic in nature. But aromatic amines are less basic and aliphatic amines are more basic than ammonia. An aliphatic secondary amine is more basic than primary and tertiary amines. Primary amines can be differentiated from secondary and tertiary amines by carbylamine reaction. Aliphatic primary amines undergo diazotisation to

form alcohols whereas aromatic primary amines form diazonium salts. The amino group ($-NH_2$) is an activating and ortho-, para-directing group. Compounds towards the electrophilic aromatic substitution reactions. Nitroalkanes are obtained by the reaction of alkyl halides with alcoholic silver nitrite. Nitrobenzene is obtained by the direct nitration of benzene with conc. HNO_3 in the presence of conc. H_2SO_4 . Primary nitroalkanes are hydrolysed in acidic medium to give carboxylic acids whereas secondary nitroalkanes give ketones. All nitro compounds are reduced into amino compounds by (i) hydrogen in presence of catalyst or (ii) tin or iron in presence of hydrochloric acid. Nitro group is deactivating and meta-directing group towards electrophilic aromatic substitution reactions.



EXERCISE

MCQ

- In this reaction acetamide is converted to methenamine
 - Gabriel phthalimide synthesis
 - Carbylamine reaction
 - Stephen's reaction
 - Hoffmann bromamide reaction
- Which of the following is true for the basicity of amines?
 - Alkylamines are generally less basic than arylamines because N is sp hybridised
 - Arylamines are generally more basic than alkylamines due to aryl group
 - Arylamines are generally less basic than alkylamines due to delocalisation of lone pair of electrons in the benzene ring
 - Alkylamines are generally less basic than arylamines because lone pair of electrons on N in the arylamines are not delocalised in the benzene ring
- How many structural isomers are possible for C_3H_9N ?
 - 4
 - 2
 - 5
 - 3
- Which of the following is incorrect for primary amines?
 - On reaction with nitrous acid alkylamines produce alcohol
 - On reaction with nitrous acid arylamines produce phenol
 - Alkylamines are more basic than ammonia
 - Alkylamines are more basic than arylamines
- Aniline is less basic than
 - Benzylamine
 - Triphenylamine
 - p-Nitroaniline
 - Diphenylamine
- Which of the following is formed when an alkyl primary amine reacts with nitrous acid?
 - Alkyl nitrite
 - Secondary amine
 - Nitroalkane
 - Alcohol

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Chemistry



Notes

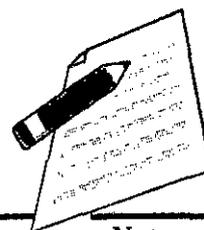
7. In which of the following reactions does amide get converted to amine?
- (a) Claisen (b) Hoffmann
(c) Kekule (d) Perkin
8. This on reduction with LiAlH_4 produces secondary amine
- (a) Methyl cyanide (b) Nitroethane
(c) Methyl isocyanide (d) Acetamide
9. Which of the following compounds is formed on the electrolytic reduction of nitrobenzene in presence of strong acid?
- (a) Azoxybenzene (b) Aniline
(c) Azobenzene (d) p-aminophenol
10. Which of the following is formed in the reaction of an aldehyde and primary amine?
- (a) Ketone (b) Aromatic acid
(c) Schiff's base (d) Carboxylic acid

Answer

1. (d) 2. (c) 3. (a) 4. (b) 5. (a)
6. (d) 7. (b) 8. (c) 9. (d) 10. (c)

Review Questions

1. Write the structural formula of the following compounds :
- (i) 2-Methylpropan - 2-amine
(ii) Butan - 2-amine
(iii) N-Ethyl - N-methylbutan - 1-amine
(iv) 2-Methyl - 2-nitropropane (v) 4-Nitrotoluene.
2. What do you understand by diazotisation? Write the product of following reactions.
- (i) $\text{NH}_2\text{CH}_3 + \text{NaNO} / \text{HCl} \xrightarrow{273-278\text{ K}}$
(ii) $\text{NO}_2\text{NH}_2 + \text{NaNO} / \text{HCl} \xrightarrow{273-278\text{ K}}$
(iii) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2 + \text{NaNO} / \text{HCl} \xrightarrow{273-278\text{ K}}$
3. How will you prepare butan-1-amine starting from a suitable amide? Name the reaction involved.
4. What different reagents can be used for the following conversion?
5. Arrange the following amines in increasing order of their basicities : Ethanamine, N-Methylethanamine, Aniline.
6. How will you prepare sulphanilic acid from nitrobenzene?
7. What happens when ethanamine is treated with excess of chloroethane?
8. Write the reaction sequence to convert nitromethane into ethanamine.
9. How will you prepare para-bromoaniline from nitrobenzene? Can this compound be obtained by direct bromination of aniline with aqueous solution of bromine? Explain.



Notes

18 DRUGS AND MEDICINES

- Understand the concept of drugs.
- Discuss the types of drugs.
- Discuss the concept of medicines.
- Discuss the types of medicines.
- Discuss the characteristics and uses of various types of medicines.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of drugs and medicines so that the characteristics and uses of various types of drugs and medicines can be learned.

Introduction

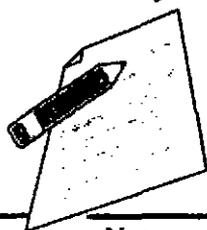
A **medication** (also referred to as **medicine**, **pharmaceutical drug**, or simply **drug**) is a drug used to diagnose, cure, treat, or prevent disease. Drug therapy (pharmacotherapy) is an important part of the medical field and relies on the science of pharmacology for continual advancement and on pharmacy for appropriate management.

Drugs are classified in multiple ways. One of the key divisions is by level of control, which distinguishes prescription drugs (those that a pharmacist dispenses only on the order of a physician, physician assistant, or qualified nurse) from over-the-counter drugs (those that consumers can order for themselves). Another key distinction is between traditional small-molecule drugs, usually derived from chemical synthesis, and biopharmaceuticals, which include recombinant proteins, vaccines, blood products used therapeutically (such as IVIG), gene therapy, monoclonal antibodies and cell therapy (for instance, stem-cell therapies). Other ways to classify medicines are by mode of action, route of administration, biological system affected, or therapeutic effects. An elaborate and widely used classification system is the Anatomical Therapeutic Chemical Classification System (ATC system). The World Health Organization keeps a list of essential medicines.

Drug discovery and drug development are complex and expensive endeavours undertaken by pharmaceutical companies, academic scientists, and governments. As a result of this complex path from discovery to commercialization, partnering has become a standard practice for advancing drug candidates through development pipelines. Governments generally regulate what drugs can be marketed, how drugs are marketed, and in some jurisdictions, drug pricing. Controversies have arisen over drug pricing and disposal of used drugs.

A sampling of classes of medicine includes:

1. Antipyretics: reducing fever (pyrexia/pyresis)
2. Analgesics: reducing pain (painkillers)



Notes

3. Antimalarial drugs: treating malaria
4. Antibiotics: inhibiting germ growth
5. Antiseptics: prevention of germ growth near burns, cuts and wounds
6. Mood stabilizers: lithium and valpromide
7. Hormone replacements: Premarin
8. Oral contraceptives: Enovid, "biphasic" pill, and "triphase" pill
9. Stimulants: methylphenidate, amphetamine
10. Tranquilizers: meprobamate, chlorpromazine, reserpine, chlordiazepoxide, diazepam, and alprazolam
11. Statins: lovastatin, pravastatin, and simvastatin

Introduction to Drugs

Drugs, the word is not new to us. However, the word generally creates a frightful response amongst many. So far we have heard that drugs are the substance of addiction and a reason for the spoiled generation. This is mainly because people have been abusing the substance which has led to the death of even popular people as well.

Yes, they are addictive but did you know that all of them are not harmful. *Biologically speaking, drugs mostly target our brains and switch the mood and physiological conditions of our bodies.* However, since there are various types of drugs including legal as well as illegal drugs, the latter is causing most of the problems.

Having said that, on this page we will be discussing mainly the legal drugs and their classifications.

What are Drugs?

By definition, drugs are chemical substances that affect or alter the physiology when taken into a living system. They can either be natural or synthetic.

Chemically, they are low atomic mass and molecular mass structures. When a drug is therapeutically active and is used for the diagnosis, treatment or prevention of a disease, it is called medicine (legal drugs). They target the macromolecules inside the body and generate a biological response. Most of them interrupt the nervous system (especially brain) for the generation of a proper biological response. However, they can be toxic in higher doses and generally referred to as lethal dose.

Classification of Drugs

Classification of drugs can be done on the basis of certain criteria. Some of them are given below.

Classification of Drugs on the basis of the Pharmacological Effect:

- How a drug or medicine affects or influences the cells of an organism is referred to as the pharmacological effect. Different types of drugs have various pharmacological effects on an organism.
- For example, an analgesic reduces pain while an anti-inflammatory drug reduces the inflammation of the body. Thus, drugs can be classified based on the pharmacological effect.

Classification of Drugs on the basis of Drug Action:

- Different drugs act differently i.e., each drug has its own way of generating a response called drug action.
- Drug action is more specified according to how it generates a response. For example, there are lots of medicines to treat hypertension but each type of drug has different drug actions.
- All the hypertension medicines reduce the blood pressure but in a different pathway.



Classification of Drugs on the basis of Chemical Structure:

- This is a common classification of drugs. Generally, drugs that have the same drug action and pharmacological effect have a basic skeletal structure and a minute variation in the branching.
- This is why some drugs have more potential than the other. For example, all sulphonamides have the same skeletal structure.

Classification of Drugs on the basis of Molecular Targets:

- Drugs target the macromolecules inside the body to generate a biological response.
- Such macromolecules are called target molecules or drug targets. Drugs that have the same mechanism of action will have the same target.
- This basis for the classification of drugs is more helpful during clinical trials.

SUMMARY

Medicines are the chemicals or mixture of chemicals used for the prevention, cure, and treatment, management of diseases and disorders or recovery of patients. Medicines are obtained from plants or parts of plants or synthesized in laboratories. Medicines may contain only one chemical compound or it may be a mixture of several compounds. Drugs may be the crude mixtures and the identity of all the chemical components and their amount present in them may not be accurately known. Antipyretics are used to reduce body temperature for example aspirin and paracetamol. Analgesics reduce body pain for example aspirin and morphine. Antiseptics kill microorganisms and are safe to be used on a living tissue while disinfectants are used on inanimate objects. Aqueous solution (less than 0.2 percent) of phenol is used as an antiseptic. In higher concentrations phenol is used as a disinfectant. z Antibiotics are the metabolic products produced by certain microorganisms which can kill some microorganisms. For example penicillin, streptomycin, tetracycline, etc. Broad spectrum antibiotics can kill several different microorganisms, therefore, can cure several diseases. On storage the taste and smell are changed and become rancid. Certain chemical substances are added to control oxidation spoilage and rancidity. Butylated hydroxyl toluene (BHT) and Butylated hydroxyl anisole (BHA). Common Salt, sugar and oils are natural food preservatives. Sodium benzoate is familiar food preservative. Aspartame is unstable at cooking temp. So used in cold drinks and soft drinks. Alitame is more stable at cooking temp. Suerolose is mare stable at cooling tamp and easy to control the sweetness of food.

EXERCISE

MCQ

1. Consumption of this causes increase in the fat synthesis, dilation of blood vessels, low blood sugar and stomach-inflammation

(a) drug addiction and tobacco	(b) alcohol
(c) tobacco	(d) drug addiction

Answer: (a)

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Chemistry



Notes

2. This causes tunnel vision
- (a) Smoking (b) Alcohol
(c) Barbiturates (d) Vitamin A deficiency
- Answer: (b)
3. After drinking alcohol, consumption of this leads to death
- (a) Morphine (b) Opium
(c) Barbiturate (d) All of these
- Answer: (c)
4. This drug along with alcohol generates marked drowsiness otherwise does not produce sedative effect
- (a) Marijuana (b) Valium
(c) Antihistamine (d) Barbiturate
- Answer: (c)
5. Constituent of alcoholic beverage is
- (a) Propyl alcohol (b) Methyl alcohol
(c) Ethyl alcohol (d) Mix of all of these
- Answer: (c)
6. This is a result of the appearance of the fatty liver syndrome
- (a) synthesis of fatty acids, fat and glycerols
(b) synthesis of fat from alcohol
(c) synthesis of fat from amino acids
(d) excessive synthesis of fat from fatty acids
- Answer: (b)
7. Alcoholism causing fatty acid syndrome is called
- (a) Cirrhosis (b) Neuritis
(c) Gastritis (d) Nephritis
- Answer: (a)
8. This is a withdrawal symptom of alcohol consumption
- (a) Delirium (b) Nausea and vomiting
(c) swollen and patchy face (d) all of these
- Answer: (b)
9. This causes the maximum accumulation of fat in the liver
- (a) meat and egg (b) alcohol
(c) saturated fat (d) starch
- Answer: (b)

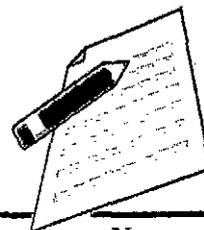
10. This is a consequence of alcohol addiction

- (a) psychosis, hypertension and fatty liver syndrome
- (b) cardiovascular diseases, hypertension and fatty liver syndrome
- (c) ulcers, all types of mental illness, vitamin deficiency, cardiovascular diseases
- (d) all of these

Answer: (b)

Review Questions

1. How are medicines classified?
2. Who isolated the first antibiotic?
3. Name a medicine, which is used as analgesic as well as antipyretic.
4. What is a non-narcotic analgesic?
5. Why is 2.0 percent aqueous solution of phenol used as a disinfectant?
6. What do you understand by allergic reactions of antibiotics?
7. What are scheduled drugs?
8. Which medicines can you purchase without the prescription from a doctor?
9. What is self-medication? Describe some of its ill effects.





Notes

19 SOAPS, DETERGENTS AND POLYMERS

- Understand the concept of soaps.
- Discuss the types of soaps.
- Discuss the concept of detergents.
- Discuss the types of detergents.
- Discuss the characteristics and uses of various types of polymers.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of soaps, detergents and polymers so that the characteristics and uses of various types of polymers can be learned.

Introduction

Soaps and the Detergents are materials that are used by us for cleaning purposes because pure water alone cannot remove all types of dirt or any oily substance from our body or clothes. They contain 'surfactants', which are compounds with molecules that line up around water to break the 'surface tension'. Both of them having a different chemical nature. **Soap** is a cleaning agent that is composed of one or more salts of fatty acids. **Detergent** is a chemical compound or a mixture of chemical compounds, which is used as a cleaning agent, also. They perform their cleaning actions in certain specific conditions. You will learn more about this in detail, in the following units.

1. Soap

Soaps are sodium or potassium salts of some long chain carboxylic acids, called fatty acids. Soap requires two major raw materials: i) fat and ii) alkali. The alkali, most commonly used in the preparation of soap is sodium hydroxide. Potassium hydroxide can also be used. A potassium-based soap creates a more water-soluble product than a sodium-based soap. Based on these features, there are two types of soaps:

A. Hard soap

Soaps, which are prepared by the *saponification of oils or fats with caustic soda* (sodium hydroxide), are known as hard soaps. They are usually used for washing purposes.

B. Soft soap

Soaps, which are prepared by the *saponification of oils or fats with potassium salts*, are known as soft soaps. They are used for cleansing the body.



Notes

Manufacture of soap

KETTLE PROCESS:

This is the oldest method. But, it is still widely used in the small scale preparation of soap. There are mainly, two steps to be followed in this process.

i) Saponification of oil:

The oil, which is used in this process, is taken in an iron tank (kettle). The alkaline solution (10%) is added into the kettle, a little in excess. The mixture is boiled by passing steam through it. The oil gets hydrolysed after several hours of boiling. This process is called Saponification

ii) Salting out of soap:

Common salt is then added to the boiling mixture. Soap is finally precipitated in the tank. After several hours the soap rises to the top of the liquid as a 'curdy mass'. The neat soap is taken off from the top. It is then allowed to cool down.

Effect of hard water on soap

Hard water contains calcium and magnesium ions (Ca^{2+} and Mg^{2+}) that limit the cleaning action of soap. When combined with soap, hard water develops a thin layer (precipitates of the metal ions) called 'scum', which leaves a deposit on the clothes or skin and does not easily rinse away. Over time, this can lead to the deterioration of the fabric and eventually ruin the clothes. On the other hand, detergents are made with chemicals that are not affected by hard water.

2. Detergents

Development of synthetic detergents is a big achievement in the field of cleansing. These soaps possess the desirable properties of ordinary soaps and also can be used with hard water and in acidic solutions. These are salts of sulphonic acids or alkyl hydrogen sulphates in comparison to soap, which are salts of carboxylic acids. The detergents do not form precipitates with Ca^{2+} and Mg^{2+} present in hard water. So, the cleansing action of detergents is better than that of soaps.

Preparation of detergents

Detergents are prepared by adding sulphuric acid to the processed hydrocarbon obtained from petroleum. This chemical reaction result in the formation of molecules similar to the fatty acid in soap. Then, an alkali is added to the mixture to produce the 'surfactant molecules', which do not bond with the minerals present in the hard water, thus preventing the formation of their precipitates.

In addition to a 'surfactant', the modern detergent contains several other ingredients. They are listed as follows:

- i) Sodium silicate, which prevents the corrosion and ensures that the detergent does not damage the washing machine.
- ii) Fluorescent whitening agents that give a glow to the clothes.
- iii) Oxygen bleaches, such as 'sodium perborate', enable the removal of certain stains from the cloth.
- iv) Sodium sulphate is added to prevent the caking of the detergent powder.
- v) Enzymes are added to break down some stains caused by biological substances like blood and vegetable juice.



Notes

- vi) Certain chemicals that give out a pleasant smell are also added to make the clothes fragrant after they are washed with detergents.

3. Cleansing action of soap

A soap molecule contains two chemically distinct parts that interact differently with water. It has one **polar end**, which is a *short head* with a carboxylate group ($-\text{COONa}$) and one **non-polar end** having the *long tail made of the hydrocarbon chain*.

The polar end is **hydrophilic (Water loving)** in nature and this end is attracted towards water. The non-polar end is **hydrophobic (Water hating)** in nature and it is attracted towards dirt or oil on the cloth, but not attracted towards water. Thus, the hydrophobic part of the soap molecule traps the dirt and the hydrophilic part makes the entire molecule soluble in water.

When a soap or detergent is dissolved in water, the molecules join together as clusters called 'micelles'. Their long hydrocarbon chains attach themselves to the oil and dirt. The dirt is thus surrounded by the non-polar end of the soap molecules (Figure 11.3). The charged carboxylate end of the soap molecules makes the micelles soluble in water. Thus, the dirt is washed away with the soap.

Advantages of detergents over soaps

Detergents are better than soaps because they:

- can be used in both hard and soft water and can clean more effectively in hard water than soap.
- can also be used in saline and acidic water.
- do not leave any soap scum on the tub or clothes.
- dissolve freely even in cool water and rinse freely in hard water.
- can be used for washing woollen garments, whereas soap cannot be used.
- have a linear hydrocarbon chain, which is biodegradable.
- are active emulsifiers of motor grease.
- do an effective and safe cleansing, keeping even synthetic fabrics brighter and whiter.

Biodegradable and Non-biodegradable detergents:

a) Biodegradable detergents:

They have straight hydrocarbon chains, which can be easily degraded by bacteria.

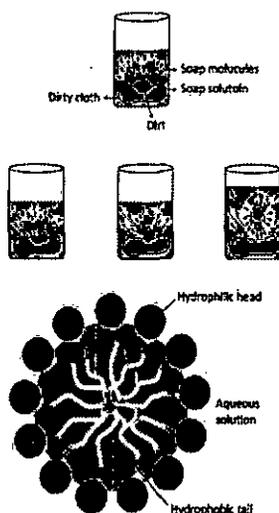


Figure 11.3 Cleansing action of soap



b) Non-biodegradable detergents:

They have highly branched hydrocarbon chains, which cannot be degraded by bacteria.

Disadvantages of Detergents

1. Some detergents having a branched hydro-carbon chain are not fully biodegradable by micro-organisms present in water. So, they cause water pollution.
2. They are relatively more expensive than soap.

4. Comparison between soap and detergents

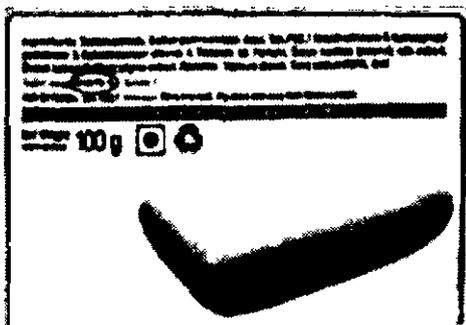
Soap	Detergent
It is a sodium salt of long chain fatty acids.	It is sodium salts of sulphonic acids.
The ionic part of a soap is $\text{-COO}^- \text{Na}^+$.	The ionic part in a detergent is $\text{-SO}_3^- \text{Na}^+$.
It is prepared from animal fats or vegetable oils.	It is prepared from hydrocarbons obtained from crude oil.
Its effectiveness is reduced when used in hard water.	It is effective even in hard water.
It forms a scum in hard water.	Does not form a scum in hard water.
It has poor foaming capacity.	It has rich foaming capacity.
Soaps are biodegradable.	Most of the detergents are non-biodegradable.

Soap

- It is a sodium salt of long chain fatty acids.
- The ionic part of a soap is $\text{COO}^- \text{Na}^+$
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- It forms a scum in hard water.
- It has poor foaming capacity.
- Soaps are biodegradable.

Detergent

- It is sodium salts of sulphonic acids.
- The ionic part in a detergent is $\text{SO}_3^- \text{Na}^+$.
- It is prepared from hydrocarbons obtained from crude oil.
- It is effective even in hard water.
- Does not form a scum in hard water.
- It has rich foaming capacity.
- Most of the detergents are non-biodegradable.





Polymers

A Polymer is a giant molecule formed by inter molecular linkage between same or different types of smaller molecules called monomers. If a large number of monomers (A) are linked together then the polymer is represented as

$(-An -) - (-A - A - A - A - A) n$ is a polymer of the monomer of (A).

For example, polyethene $(-CH_2 - CH_2)_n$ is a polymer of the monomer ethylene ($CH_2 = CH_2$).

Polymer is a high molecular mass molecule formed by linking up of two or more small molecules called monomers. Monomers are the small molecule which is capable of linking amongst them to form big molecules called polymers. In some polymers more than one type of monomers combines with each other to give the polymer.

Types of Polymers

Depending upon the nature of the repeating structural units (monomers), polymers are divided into two broad categories viz., homopolymers and copolymers

(a) Homopolymer

A polymer formed from only one kind of monomers is called homopolymer.

Polyethene $(-CH_2 - CH_2 -)_n$ is an example of homopolymer.

(b) Copolymer

A polymer formed from more than one kind of monomer units is called copolymer or mixed polymer. For example, Buna-S rubber which is formed from 1, 3-butadiene ($CH_2 = CH - CH = CH_2$) and styrene ($C_6H_5 - CH = CH_2$) is an example of copolymer.

Polymerization

The process by which the monomers get linked up is called polymerization.

Polymerization is represented as : $M + M \rightarrow M_2$ (Dimer) $M + M + M \rightarrow M_3$ (Trimer) $M + M + M + M \rightarrow M_4$ (Polymer) $M + M + M + M + M \rightarrow M_5$ (Polymer) $M + M + M + M + M + M \rightarrow M_6$ (Polymer) where M stands for the monomer

Types of Polymerization

Depending upon the mode of reaction, polymerisation is classified as : (a) addition polymerization and (b) condensation polymerization. (a) Addition Polymerization : This process involves the addition of monomer units to themselves to form a growing chain by a chain reaction mechanism. It is for this reason that the process is also known as chain growth polymerization. Addition polymerization is achieved by adding a catalyst (known as initiator), which provides some reactive species like free radicals. For example benzoyl peroxide provides free radical 'benzyl' to initiate the chain polymerization reaction. $6 \text{ C}_6\text{H}_5\text{COO} \cdot \text{C}_6\text{H}_5 \rightarrow 2 \text{C}_6\text{H}_5\text{CO} \cdot \text{C}_6\text{H}_5$ (or R)

Classification of polymers

The polymers can be classified in a number of ways. Some of these are discussed below for a systematic investigation of their properties and uses.



(a) Classification of Polymers on the Basis of Origin.

On the basis of origin, polymers are classified as :

1. Natural polymers Chemistry in Everyday Life
2. Synthetic polymers
 1. Natural Polymers : The polymers obtained from nature (plants and animals) are called natural polymers. Starch, cellulose, natural rubber, proteins, etc. are some examples.
 2. Synthetic Polymers : The polymers which are prepared in the laboratories are called synthetic polymers. These are also called man-made polymers. Polyethene, PVC, nylon, Teflon, Bakelite, terylene, synthetic rubber, etc. are common examples.

(b) Classification of Polymers on the Basis of structure

On the basis of structure of polymers, these can be classified as :

1. Linear polymers
2. Branched chain polymers
3. Cross-linked polymers.
 1. Linear polymers : These are polymers in which monomeric units are linked together to form linear chains. These linear polymers are well packed and therefore, have high densities, high tensile (pulling) strength and high melting points. For example, polyethylene, nylons and polyesters are examples of linear polymers.
 2. Branched chain polymers : These are polymers in which the monomers are joined to form long chain with side chains or branches of different lengths. These branched chains polymers are irregularly packed and therefore, they have lower tensile strength and melting points than linear polymers. For example, low density polyethene, glycogen, starch, etc.
 3. Cross-linked polymers : These are polymers in which long polymer chains are cross-linked together to form a three dimensional network. These polymers are hard, rigid and brittle because of the network structure.

(c) Classification of Polymers on the Basis of Method of Polymerisation

On the basis of method of polymerisation the polymers are classified as :

1. Addition polymer: A polymer formed by direct addition of repeated monomers without the elimination of any small molecule is called addition polymer. In this type, the monomers are unsaturated compounds and are generally derivatives of ethene. The addition polymers have the same empirical formula as their monomers. Examples are polyethene, polypropylene and polyvinyl chloride, etc.
2. Condensation polymer: A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, alcohol, etc. is called condensation polymer. In this type, each monomer generally contains two functional groups. For example, nylon - 66 is obtained by the condensation of two monomers; hexa methylenediamine and adipic acid with the loss of water molecules.



Notes

SUMMARY

Polymers, the high molecular mass macrosized molecules consisting of repeating units of monomers of synthetic or natural origin. Synthetic polymers are classified with respect to their composition, mode of polymerization and nature of molecular forces. Polymerization is classified into two categories (i) addition polymerization (ii) condensation polymerization. Addition polymers are formed by addition of large number of monomers without the elimination of any smaller molecules. Condensation polymers are formed by elimination of smaller molecules such as H_2O , NH_3 etc. Natural rubber is a linear polymer of isoprene, and is vulcanized by heating with sulphur, which forms cross link between different chains. Vulcanized rubber has much improved physical properties. Synthetic rubbers are usually obtained by copolymerization of an alkene and 1,3-butadiene derivatives. Synthetic polymers due to their inertness to degradation have created environmental problems. Since biopolymers degrade enzymatically, synthetic biodegradable polymers having functional groups such as ester, amide etc. have potential use as sutures, implants, drug release materials, are developed as alternatives. For example, PHBV, PLA, etc. constitute such materials.

EXERCISE

MCQ

1. Which of the following statements is not correct.
 - (i) Some antiseptics can be added to soaps.
 - (ii) Dilute solutions of some disinfectants can be used as antiseptic.
 - (iii) Disinfectants are antimicrobial drugs.
 - (iv) Antiseptic medicines can be ingested.

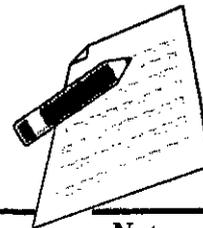
Solution: Option (iv) is the answer.

2. Which is the correct statement about birth control pills?
 - (i) Contain estrogen only.
 - (ii) Contain progesterone only.
 - (iii) Contain a mixture of estrogen and progesterone derivatives.
 - (iv) Progesterone enhances ovulation.

Solution: Option (iii) is the answer.

3. Which statement about aspirin is not true
 - (i) Aspirin belongs to narcotic analgesics.
 - (ii) It is effective in relieving pain.
 - (iii) It has an anti-blood-clotting action.
 - (iv) It is a neurologically active drug.

Solution: Option (i) is the answer.



4. The most useful classification of drugs for medicinal chemists is _____.
- (i) based on chemical structure.
 - (ii) on the basis of drug action.
 - (iii) on the basis of molecular targets.
 - (iv) on the basis of the pharmacological effect.

Solution: Option (iii) is the answer.

5. Which of the following statements is correct?
- (i) Some tranquilisers function by inhibiting the enzymes which catalyse the degradation of noradrenaline.
 - (ii) Tranquilisers are narcotic drugs.
 - (iii) Tranquillizers are chemical compounds that do not affect the message transfer from nerve to the receptor.
 - (iv) Tranquilisers are chemical compounds that can relieve pain and fever.

Solution: Option (i) is the answer.

Review Questions

1. What is the difference in between soaps and detergents?
2. Write the cleansing action of soap sand detergents.
3. Write the names of two anti-oxidants.
4. Which type of soap and detergents are biodegradable?
5. What is saponification?
6. Explain the difference between chain growth and step growth polymerization.
7. Define the terms thermosetting and thermo-plastics. Give one example of each.
8. What is a copolymer. Give one example.



Notes

19

ENVIRONMENTAL CHEMISTRY

- Understand the concept of environment.
- Discuss the types of environmental pollution.
- Discuss the concept of environmental chemistry.
- Discuss the causes of environmental pollution.
- Discuss the measures taken to prevent environment pollution.

Objective of the Chapter:

The basic objective of this chapter is to throw some light on the initial concepts of environmental chemistry so that the types and causes of environment pollution can be learned.

Introduction

Earth is composed of numerous minute substances and particles which are involved in reactions leading to the formation of new ones. Hence, the earth is said to be a closed system and the energy comes and leaves the planet, of which most of the mass stays here. This means that all the elements on this planet are continuously recycling within the environment.

For example, consider free oxygen molecules that were floating in the atmosphere yesterday and it might be the part of someone's hamburger the next day. It's all up to the chemists to study these cycles and to watch their movements.

Hence, the *Environmental Chemistry* can be defined as:

The field of chemistry that deals with the study of reactions, sources, transport, effects, along with the fates of all the chemical species present in the soil, water, and the air environments, and also the effects of technology thereon.

- Environmental chemistry is the scientific study of the biochemical and chemical phenomena that occur in natural places.
- Environmental chemistry is a study that is more than air, water, soil, and chemicals. This field uses various techniques of biology, maths, genetics, engineering, hydrology, toxicology, etc. that will help to fetch an answer to all the questions related to the environment.
- Environmental chemistry also contains aspects of analytical chemistry, physical chemistry, organic chemistry & inorganic chemistry as well as more diverse areas, such as epidemiology, public health, biochemistry, biology, & toxicology.
- Environmental chemists are responsible for finding how the unpolluted environment functions and to find ways of sustainable development which do not harm the environment.

One component which a lot of environmental chemists come across are contaminants and a good portion of our environment is a victim of contamination.

Contamination

Environmental Chemistry Facts

Aluminium can be continually recycled, as in forever. Recycling 1 aluminium can save enough energy to run at least three hours of our TV's. Every year 80 trillion cans of aluminium are used by humans.

The chemical industry is usually associated with fluxes of polluted waste. There are, however, many other sources of water chemical pollution, including transport, agriculture, power plants and household chemicals like detergents! In fact, the chemical industry's waste streams are now strictly controlled and treated before they are released into the environment.

Chemical weathering means a chemical transformation or degradation, which usually occurs when the chemical is released into the environment. In the air, weathering is due to a combination of processes that all results in reducing the air concentration of pollutants.

Chemical water contamination can cause severe long-term problems. The consequences of acute chemical emissions on air, however, are typically short-term-but they may still be devastating.

Contamination of the environment takes place when there are unwanted chemical substances present in the atmosphere. In fact, environmental chemistry mainly deals with the study of these unwanted substances and their effects.

Some contaminants of the environment are mentioned below.

- **Small contaminants:** Small contaminants are those metal particles that can be easily measured and controlled. These particulate contaminants can be monitored by the process of abrasion, fatigue and silting.
- **Chemical Contaminants:** These are the pollutants that are produced by the process of chemical reactions. They contaminate the water and soil, and those are arsenic, nitrate, fluoride, manganese atom, iron, etc.
- **Gaseous contamination:** This type of pollution occurs through pollution of the gaseous atmosphere by the components such as sulphur, chlorine, bromine, etc.
- **Microbial contamination:** This is known to be one of the dangerous types of contamination as it does not only affect the environment but also the living system within it. The cause for this is microbes such as the yeast, bacteria, mould, fungi, protozoa, virus, or the toxins and by-products.

Applications of Environmental Chemistry

Some applications of environmental chemistry are mentioned below.

- Environmental Chemistry studies the risk factors of all the chemicals in-depth to get a solution for the safety purpose of the environment.
- It is applied in the study of new products and their effects on the environment.
- Environmental Chemistry is used in the method of protection of groundwater which is polluted by soil, dust, and the waste particles.
- It is useful for the protection of surface water from the contaminants through the process of sedimentation, bacteriological, and radiation.
- The quality of the soil is protected by the methods of environmental chemicals such as by the use of indicators like ecotoxicological and chemical.
- Impervious surfaces inside cities like the parking lots, rooftops & roads are prone to build up unwanted pollutants such as motor oil, gasoline, nutrients and sediment (soil), hydrocarbon compounds, metals.
- Environmental chemistry is applied in the Waste Management and Cleaner Production.





Notes

Environmental Pollution

Any undesirable change in our environment that has harmful effects on plants, animals and human beings is called environmental pollution.

Environmental pollution is usually caused by the addition of waste products of human activity to the environment. The substances which cause pollution of environment are called pollutants. The pollutants may be solids, liquids or gaseous substances present in significant concentration in the environment. Our environment becomes polluted day by day, by the increased addition of industrial and domestic wastes to it. The air we breathe, the water we drink and the place where we live in, are highly contaminated.

The pollutants are classified as bio-degradable and non-biodegradable pollutants.

i. Bio-degradable pollutants :

The pollutants which can be easily decomposed by the natural biological processes are called bio-degradable pollutants. Examples: plant wastes, animal wastes etc.

ii. Non bio-degradable pollutants :

The pollutants which cannot be decomposed by the natural biological processes are called Non bio-degradable pollutants. Examples: metal wastes (mainly Hg and Pb), D.D.T., plastics, nuclear wastes etc., These pollutants are harmful to living organisms even in low concentration. As they are not degraded naturally, it is difficult to eliminate them from our environment.

Atmospheric Pollution

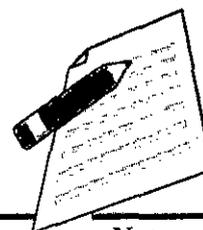
Earth's atmosphere is a layer of gases retained by the earth's gravity. It contains roughly 78% nitrogen, 21% oxygen, 0.93% argon, 0.04% carbon dioxide, trace amounts of other gases and little amount of water vapour. This mixture is commonly known as air.

Earth's atmosphere can be divided into different layers with characteristic altitude and temperature. The various regions of atmosphere are given in table 15.1.

Table 15.1 Regions of atmosphere

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Region	Altitude from earth's surface	Temperature range	Gases/ species present
Troposphere	0-10 km	15°C to -56°C	N ₂ , O ₂ , CO ₂ , H ₂ O (vap)
Stratosphere (ozonosphere)	10-50 km	-56°C to -2°C	N ₂ , O ₂ , O ₃ , O atoms
Mesosphere	50-85 km	-2°C to -92°C	N ₂ , O ₂ , N ₂ ⁺
Thermosphere	85-500 km	-92°C to 1200°C	O ₂ , O ⁺ , NO ⁺ , e ⁻



Troposphere :

The lowest layer of the atmosphere is called the troposphere and it extends from 0 – 10 km from the earth surface. About 80% of the mass of the atmosphere is in this layer. This troposphere is further divided as follows.

i) Hydrosphere:

Hydrosphere includes all types of water sources like oceans, seas, rivers, lakes, streams, underground water, polar icecaps, clouds etc. It covers about 75% of the earth's surface. Hence the earth is called as a blue planet.

ii) Lithosphere:

Lithosphere includes soil, rocks and mountains which are solid components of earth.

iii) Biosphere:

It includes the lithosphere, hydrosphere and atmosphere integrating the living organisms present in the lithosphere, hydrosphere and atmosphere.

Types of environmental pollution

Atmospheric pollution is generally studied as tropospheric pollution. Different types of atmospheric pollutions are

- (1) Air pollution
- (2) Water pollution
- (3) Soil pollution.

Air pollution

Any undesirable change in air which adversely affects living organisms is called air pollution. Air pollution is limited to troposphere and stratosphere. Air pollution is mainly due to the excessive discharge of undesirable foreign matter into the atmospheric air.



Fig 15.1 Air Pollution

Types of air pollutants

Air pollutants may exist in two major forms namely, gases and particulates.

1. Gaseous air pollutants

Oxides of sulphur, oxides of nitrogen, oxides of carbon, and hydrocarbons are the gaseous air pollutants.



a. Oxides of Sulphur

Sulphur dioxide and sulphur trioxide are produced by burning sulphur containing fossil fuels and roasting sulphide ores. Sulphur dioxide is a poisonous gas to both animals and plants. Sulphur dioxide causes eye irritation, coughing and respiratory diseases like asthma, bronchitis, etc.

Sulphur dioxide is oxidised into more harmful sulphur trioxide in the presence of particulate matter present in polluted air.



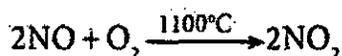
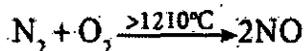
SO₃ combines with atmospheric water vapour to form H₂SO₄, which comes down in the form of acid rain.



Some harmful effects of acid rain will be discussed in section 15.3

b. Oxides of nitrogen

Oxides of nitrogen are produced during high temperature combustion processes, oxidation of nitrogen in air and from the combustion of fuels (coal, diesel, petrol etc.).



The oxides of nitrogen are converted into nitric acid which comes down in the form of acid rain. They also form reddish brown haze in heavy traffic. Nitrogen dioxide potentially damages plant leaves and retards photosynthesis. NO₂ is a respiratory irritant and it can cause asthma and lung injury. Nitrogen dioxide is also harmful to various textile fibres and metals.

c. Oxides of carbon

The major pollutants of oxides of carbon are carbon monoxide and carbon dioxide.

(i) Carbon Monoxide

Carbon monoxide is a poisonous gas produced as a result of incomplete combustion of coal or firewood. It is released into the air mainly by automobile exhaust. It binds with haemoglobin and forms carboxy haemoglobin which impairs normal oxygen transport by blood and hence the oxygen carrying capacity of blood is reduced. This oxygen deficiency results in headache, dizziness, tension, loss of consciousness, blurring of eye sight and cardiac arrest.

(ii) Carbon dioxide

Carbon dioxide is released into the atmosphere mainly by the process of respiration, burning of fossil fuels, forest fire, decomposition of limestone in cement industry etc.



Green plants can convert CO_2 gas in the atmosphere into carbohydrate and oxygen through a process called photosynthesis. The increased CO_2 level in the atmosphere is responsible for global warming. It causes headache and nausea.

(d) Hydrocarbon

The compounds composed of carbon and hydrogen only are called hydrocarbons. They are mainly produced naturally (marsh gas) and also by incomplete combustion of automobile fuel.

They are potential cancer causing (carcinogenic) agents. For example, polynuclear aromatic hydrocarbons (PAH) are carcinogenic, they cause irritation in eyes and mucous membranes.

2. Greenhouse effect and Global warming:

In 1987, Jean Baptiste Fourier a French mathematician and scientist coined the term "Greenhouse Effect" for trapping of heat in the atmosphere by certain gases.

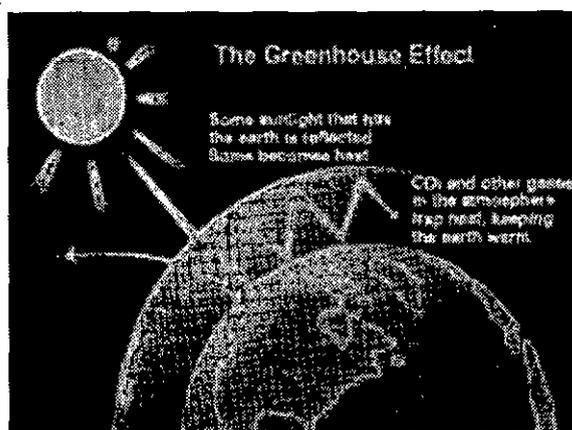


Fig 15.2 Greenhouse effect

The earth's atmosphere allows most of the visible light from the Sun to pass through and reach Earth's surface. As Earth's surface is heated by sunlight, it radiates part of this energy back toward space as longer wavelengths (IR).

Some of the heat is trapped by CH_4 , CO_2 , CFCs and water vapour present in the atmosphere. They absorb IR radiation and effectively block a large portion of earth's emitted radiation. The radiation thus absorbed is partly reemitted to earth's surface. Therefore, the earth's surface gets heated up by a phenomenon called greenhouse effect.

Thus Greenhouse effect may be defined as the heating up of the earth surface due to trapping of infrared radiations reflected by earth's surface by CO_2 layer in the atmosphere". The heating up of earth through the greenhouse effect is called global warming.

Without the heating caused by the greenhouse effect, Earth's average surface temperature would be only about -18°C (0°F). Although the greenhouse effect is a naturally occurring phenomenon, it is intensified by the continuous emission of greenhouse gases into the atmosphere.

During the past 100 years, the amount of carbon dioxide in the atmosphere increased by roughly 30 percent and the amount of methane more than doubled. If these trends continue, the average global temperature will increase which can lead to melting of polar



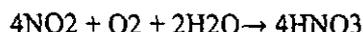
Notes

ice caps and flooding of low-lying areas. This will increase incidence of infectious diseases like dengue, malaria etc.

3. Acid Rain

Rain water normally has a pH of 5.6 due to dissolution of atmospheric CO₂ into it. Oxides of sulphur and nitrogen in the atmosphere may be absorbed by droplets of water that make up clouds and get chemically converted into sulphuric acid and nitric acid respectively as a result of pH of rain water drops to the level 5.6, hence it is called acid rain.

Acid rain is a by-product of a variety of sulphur and nitrogen oxides in the atmosphere. Burning of fossil fuels (coal and oil) in power stations, furnaces and petrol, diesel in motor engines produce sulphur dioxide and nitrogen oxides. The main contributors of acid rain are SO₂ and NO₂. They are converted into sulphuric acid and nitric acid respectively by the reaction with oxygen and water.



Harmful effects of acid rain:

Some harmful effects are discussed below.

- i. Acid rain causes extensive damage to buildings and structural materials of marbles. This attack on marble is termed as Stone leprosy.

$$\text{CaCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$$
- ii. Acid rain affects plants and animal life in aquatic ecosystem.
- iii. It is harmful for agriculture, trees and plants as it dissolves and removes the nutrients needed for their growth.
- iv. It corrodes water pipes resulting in the leaching of heavy metals such as iron, lead and copper into the drinking water which have toxic effects.
- v. It causes respiratory ailment in humans and animals.

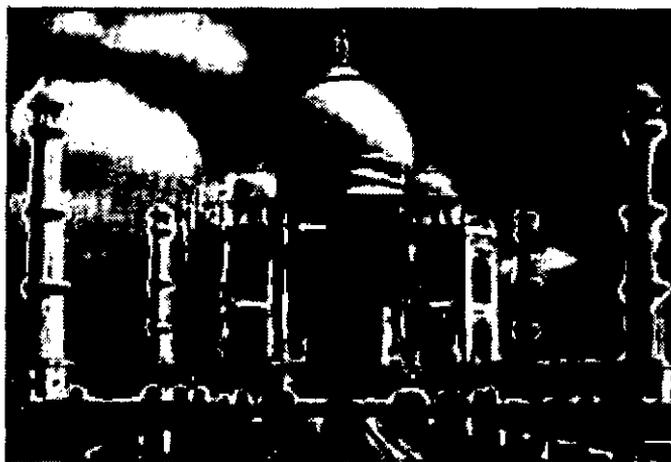
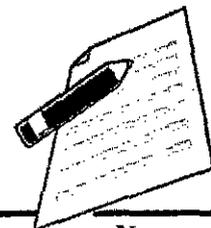


FIG 15. 3. Effect Of Acid Rain On Tajmahal



B. Particulate matter (Particulate pollutants)

Particulate pollutants are small solid particles and liquid droplets suspended in air. Many of particulate pollutants are hazardous. Examples: dust, pollen, smoke, soot and liquid droplets (aerosols) etc.,

They are blown into the atmosphere by volcanic eruption, blowing of dust, incomplete combustion of fossil fuels induces soot. Combustion of high ash fossil fuels creates fly ash and finishing of metals throws metallic particles into the atmosphere.

1. Types of Particulates:

Particulate in the atmosphere may be of two types, viable or non-viable.

a. Viable particulates

The viable particulates are the small size living organisms such as bacteria, fungi, moulds, algae, etc. which are dispersed in air. Some of the fungi cause allergy in human beings and diseases in plants.

b. Non-viable particulates

The non- viable particulates are small solid particles and liquid droplets suspended in air. They help in the transportation of viable particles. There are four types of non-viable particulates in the atmosphere. They are classified according to their nature and size as follows

(i) Smoke

Smoke particulate consists of solid particles (or) mixture of solid and liquid particles formed by combustion of organic matter.

For example, cigarette smoke, oil smoke, smokes from burning of fossil fuel, garbage and dry leaves.

(ii) Dust:

Dust composed of fine solid particles produced during crushing and grinding of solid materials.

For example, sand from sand blasting, saw dust from wood works, cement dust from cement factories and fly ash from power generating units.

(iii) Mists

They are formed by particles of spray liquids and condensation of vapours in air.

For example, sulphuric acid mist, herbicides and insecticides sprays can form mists.

(iv) Fumes

Fumes are obtained by condensation of vapours released during sublimation, distillation, boiling and calcination and by several other chemical reactions.

For example, organic solvents, metals and metallic oxides form fume particles.



Notes

2. Health effects of particulate pollutants:

- i. Dust, mist, fumes, etc., are air borne particles which are dangerous for human health. Particulate pollutants bigger than 5 microns are likely to settle in the nasal passage whereas particles of about 10 micron enters the lungs easily and causes scarring or fibrosis of lung lining. They irritate the lungs and causes cancer and asthma. This disease is also called pneumoconiosis. Coal miners may suffer from black lung disease. Textile workers may suffer from white lung disease.
- ii. Lead particulates affect children's brain, interferes maturation of RBCs and even cause cancer.
- iii. Particulates in the atmosphere reduce visibility by scattering and absorption of sunlight. It is dangerous for aircraft and motor vehicles
- iv. Particulates provide nuclei for cloud formation and increase fog and rain.
- v. Particulates deposit on plant leaves and hinder the intake of CO₂ from the air and affect photosynthesis.

3. Techniques to reduce particulate pollutants

The particulates from air can be removed by using electrostatic precipitators, gravity settling chambers, and wet scrubbers or by cyclone collectors. These techniques are based on washing away or settling of the particulates.

C. Smog

Smog is a combination of smoke and fog which forms droplets that remain suspended in the air.



Fig 15.4 classical smog

Smog is a chemical mixture of gases that forms a brownish yellow haze over urban cities. Smog mainly consists of ground level ozone, oxides of nitrogen, volatile organic compounds, SO₂, acidic aerosols and gases, and particulate matter.

There are two types of smog. One is Classical smog caused by coal smoke and fog ; second one is photo chemical smog caused by photo chemical oxidants. They are discussed below in detail.



Notes

(i) Classical smog or London smog

Classical smog was first observed in London in December 1952 and hence it is also known as London smog. It consists of coal smoke and fog.

It occurs in cool humid climate. This atmospheric smog found in many large cities. The chemical composition is the mixture of SO_2 , SO_3 and humidity. It generally occurs in the morning and becomes worse when the sun rises.

This is mainly due to the induced oxidation of SO_2 to SO_3 , which reacts with water yielding sulphuric acid aerosol.

Chemically it is reducing in nature because of high concentration of SO_2 and so it is also called as reducing smog.

Effects of classical smog:

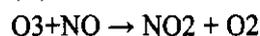
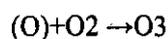
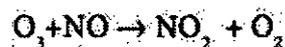
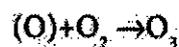
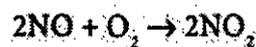
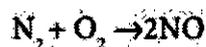
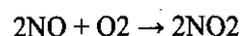
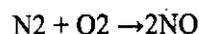
- Smog is primarily responsible for acid rain.
- Smog results in poor visibility and it affects air and road transport.
- It also causes bronchial irritation.

ii) Photo chemical smog or Los Angel Smog

Photo Chemical smog was first observed in Los Angeles in 1950. It occurs in warm, dry and sunny climate. This type of smog is formed by the combination of smoke, dust and fog with air pollutants like oxides of nitrogen and hydrocarbons in the presence of sunlight.

It forms when the sun shines and becomes worse in the afternoon. Chemically it is oxidizing in nature because of high concentration of oxidizing agents NO_2 and O_3 , so it is also called as oxidizing smog.

Photo chemical smog is formed through sequence of following reactions.



NO and O_3 are strong oxidizing agent and can react with unburnt hydrocarbons in polluted air to form formaldehyde, acrolein and peroxy acetyl nitrate(PAN).



Effects of photo chemical smog

The three main components of photo chemical smog are nitrogen oxide, ozone and oxidised hydro carbon like formaldehyde(HCHO), Acrolein (CH₂=CH-CHO), peroxy acetyl nitrate (PAN).

Photochemical smog causes irritation to eyes, skin and lungs, increase in chances of asthma.

High concentrations of ozone and NO can cause nose and throat irritation, chest pain, uncomfortable in breathing, etc.

PAN is toxic to plants, attacks younger leaves and cause bronzing and glazing of their surfaces

It causes corrosion of metals stones, building materials and painted surfaces.

Control of Photo chemical smog

The formation of photochemical smog can be suppressed by preventing the release of nitrogen oxides and hydrocarbons into the atmosphere from the motor vehicles by using catalytic convertors in engines. Plantation of certain trees like Pinus, Pyrus, Querus Vitus and juniparus can metabolise nitrogen oxide.

Types of air pollutants

Air pollutants may exist in two major forms namely, gases and particulates.

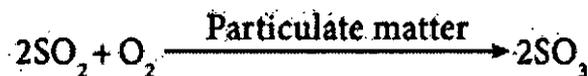
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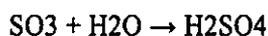
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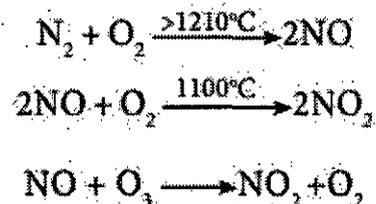


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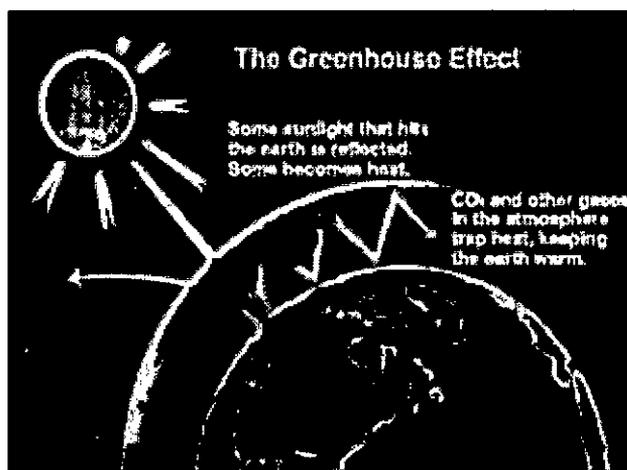


Fig 15.2 Greenhouse effect

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Some of the heat is trapped by CH₄, CO₂, CFCs and water vapour present in the atmosphere. They absorb IR radiation and effectively block a large portion of earth's emitted radiation. The radiation thus absorbed is partly reemitted to earth's surface. Therefore, the earth's surface gets heated up by a phenomenon called greenhouse effect.

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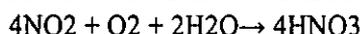
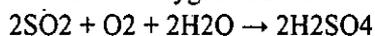
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Notes

Harmful effects of acid rain:

Some harmful effects are discussed below.

- i. Acid rain causes extensive damage to buildings and structural materials of marbles. This attack on marble is termed as Stone leprosy.

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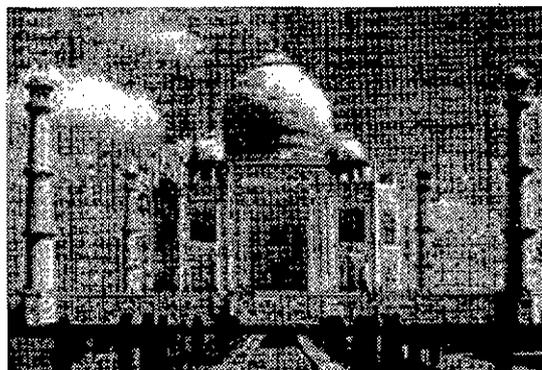


FIG 15. 3. Effect Of Acid Rain On
Tajmahal

Strategies to control environmental pollution

After studying air, water and soil pollution, as responsible individuals we must take responsibility to protect our environment. Think of steps which you would like to undertake for controlling environmental pollution not only in your locality but also in national and international level. We must realize about our environmental threat, focus strongly on this issues and be an eye opener to save our environment. We can think about following strategies to control environmental pollution.

1. Waste management: Environmental pollution can be controlled by proper disposal of wastes.
2. Recycling: a large amount of disposed waste material can be reused by recycling the waste, thus it reduces the land fill and converts waste into useful forms.
3. Substitution of less toxic solvents for highly toxic ones used in certain industrial processes.
4. Use of fuels with lower sulphur content (e.g., washed coal)
5. Growing more trees.
6. Control measures in vehicle emissions are adequate.

Efforts to control environmental pollution have resulted in development of science for synthesis of chemical favourable to environment and it is called green chemistry.



Notes

SUMMARY

Environmental chemistry plays a vital role in environment. Environmental chemistry means scientific study of chemical and bio chemical process occurring in environment. World Environmental Day is celebrated on fifth of June of every year. Environmental pollution is the effect of undesirable changes in the surrounding that have harmful effects on living things. Pollutants are generally classified as rapidly degradable (e.g. discarded vegetables), slowly degradable (e.g. Agriculture waste) and non-bio degradable pollutants (e.g. DDT, plastic materials). Atmospheric pollutions include tropospheric and stratospheric pollution. Troposphere and stratosphere greatly affect the biosphere of the earth due to which the study of pollutions in these regions is most important. Troposphere is the lowest region of atmosphere in which man, animal and plants exist. Gaseous pollutants like SO_x , NO_x , CO , CO_2 , O_3 hydrocarbons and particulate pollutants like dust, mist, fumes, smog cause pollutions in troposphere. When the PH of rain water becomes lower than 5.6 it is called acid rain. Acid rain is a by-product of various human activities that emit sulphuroxides and nitrogen oxides in atmosphere. It damages buildings, statues and other monuments. The acid rain in water reservoir like rivers, ponds adversely affects microbes, aquatic plants and fishes. The process of warming up of earth is known as greenhouse effect or global warming. CO_2 , CH_4 , O_3 , CFC, N_2 and water vapour present in atmosphere act as a greenhouse gases. Heat retaining capacity of greenhouse gases are called Global Warming Potential (GWP). The GWP based sequence of greenhouse gases is as $\text{CFC} > \text{N}_2\text{O} > \text{CH}_4 > \text{CO}_2$.

EXERCISE

MCQ

- The gaseous envelope around the earth is known as atmosphere. The region lying between an altitudes of 11-50 km is _____
 - Troposphere
 - Mesosphere
 - Thermosphere
 - stratosphere**
- Which of the following is natural and human disturbance in ecology?
 - Forest fire**
 - Floods
 - Acid rain
 - Greenhouse effect
- Bhopal Gas Tragedy is a case of _____
 - thermal pollution
 - air pollution**
 - nuclear pollution
 - land pollution



4. Haemoglobin of the blood forms carboxy haemoglobin with
- Carbon dioxide
 - Carbon tetra chloride
 - Carbon monoxide**
 - Carbonic acid
5. Which sequence for greenhouse gases is based on GWP?
- CFC > N₂O > CO₂ > CH₄
 - CFC > CO₂ > N₂O > CH₄
 - CFC > N₂O > CH₄ > CO₂**
 - CFC > CH₄ > N₂O > CO₂
6. Photo chemical smog formed in congested metropolitan cities mainly consists of
- Ozone, SO₂ and hydrocarbons
 - Ozone, PAN and NO₂**
 - PAN, smoke and SO₂
 - Hydrocarbons, SO₂ and CO₂
7. The pH of normal rain water is
- 6.5
 - 7.5
 - 5.6
 - 4.6**
8. Ozone depletion will cause
- forest fires
 - eutrophication
 - bio magnification**
 - global warming
9. Identify the wrong statement in the following
- The clean water would have a BOD value of more than 5 ppm**
 - Greenhouse effect is also called as Global warming
 - Minute solid particles in air is known as particulate pollutants
 - Biosphere is the protective blanket of gases surrounding the earth
10. Living in the atmosphere of CO is dangerous because it
- Combines with O₂ present inside to form CO₂
 - Reduces organic matter of tissues
 - Combines with haemoglobin and makes it incapable to absorb oxygen
 - Dries up the blood**



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Near Indira Bypass, NH-10, Gangtok, East Sikkim- 737102
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