The Solid State - Part 1

Objectives

After going through this lesson, the learners will be able to understand the following:

- Describe general characteristics of solid state
- Distinguish between amorphous and crystalline solids
- Classify crystalline solids on the basis of the nature of binding forces

Contents Outline

- Introduction
- General Characteristics of Solid States
- Classification of Solids
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    - Ionic solids
    - Metallic Solids
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Introduction

What is Matter?

- Matter is everything around us. Matter can occupy space and has mass.
- Matter can exist in three states, namely, solid, liquid and gas. The most stable state of a given substance depends upon the given conditions of temperature and pressure and their net opposing effect. Intermolecular forces tend to keep the molecules (or atoms or ions) closer, whereas thermal energy tends to keep them apart by making them move faster. At sufficiently low temperature, the thermal energy become low and intermolecular forces bring them so close that they cling to one another and occupy fixed positions. These can still oscillate about their mean positions and the substance exists in solid state.

General Characteristic of Solid State

- They have definite volume and shape.

- Intermolecular distances are short.
- Intermolecular forces are strong.
- The constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
- They are incompressible and rigid.

Some of the physical properties that help to distinguish the three states of matter are summarized in Table 1.

Table 1: Properties of the three states of matter

S. No.	Property	Solids	Liquids	Gases
1.	Shape, volume	Definite shape, volume	Definite volume but no definite shape. It takes the shape of the container in which it is kept	No definite shape and volume
2.	Density	High	Lower than solids but higher than that of gases.	Low
3.	Mutual forces of attraction between molecules	Strongest	Weaker than those in solids	Almost negligible
4.	Type of motion possessed by molecules	Vibratory	Vibratory and Rotatory	Mainly translatory
5.	Compressibility	Least compressible	Slightly higher compressibility	High compressibility
6.	Examples	Metals, glass, wax, butter, diamond	Water, alcohol	N_2, CO_2, O_2

Classification of Solids

Amorphous and Crystalline Solids

Solids can be classified as crystalline or amorphous on the basis of the nature of order present in the arrangement of their constituent particles. A crystalline solid usually consists of a large number of small crystals, each of them having a definite characteristic geometrical shape. In a crystal, the arrangement of constituent particles (atoms, molecules or ions) is ordered. It has a long range order which means that there is a regular pattern of arrangement of particles which repeats itself periodically over the entire crystal. Sodium chloride and quartz are typical examples of crystalline solids. An amorphous solid (Greek amorphous = no form) consists of particles of irregular shape. The arrangement of constituent particles (atoms, molecules or ions) in such a solid has only short range order. In such an arrangement, a regular and periodically repeating pattern is observed over short distances only. Such portions are scattered and in between the arrangement is disordered. The structures of quartz (crystalline) and quartz glass (amorphous) are shown in Fig1 (a) and (b), respectively.

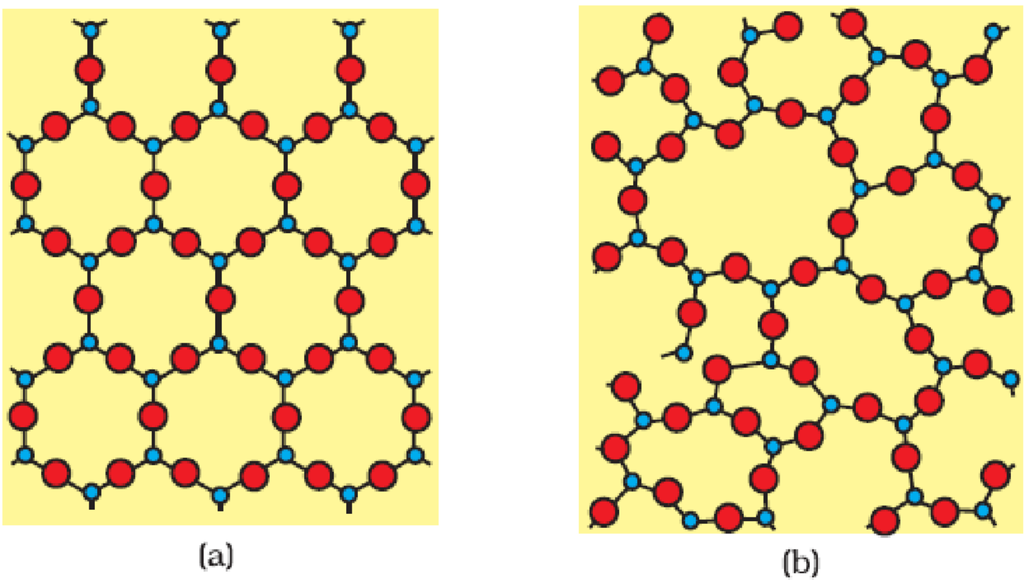

Fig. 1: Two dimensional structure of (a) quartz and (b) quartz glass

Quartz is a form of SiO_2 (silica). It has tetrahedral SiO_4 (silicate) units which are orderly arranged in crystalline quartz as shown (Fig. 1, a). When SiO_2 is melted and the melt is cooled, it forms quartz glass which is amorphous in nature. In this state, the SiO_4 units are present in random order. The structure of amorphous solids is similar to that of liquids as they can also flow at extremely slow rate. Glass, rubber and plastics are typical examples of amorphous solids. Due to the differences in the arrangement of the constituent particles, the two types of solids differ in their properties.

Properties of crystalline solid

- The crystalline solids have definite regular geometry because of regular arrangement of the constituent particles. They are said to exhibit a long range order. The crystalline solids have definite characteristic shape.
- The crystalline solids have sharp melting points. Therefore, crystalline solids have definite enthalpy of fusion.
- Crystalline solids can be cleaved along definite planes. When cut with a sharp edged tool (e.g. knife) they split into two pieces and the newly generated surfaces are plain and smooth.
- Crystalline solids are **anisotropic** in nature. It is because the arrangement of constituent particles is regular and ordered along all the directions. Therefore, the value of any physical property (electrical resistance or refractive index) would be different along each direction.

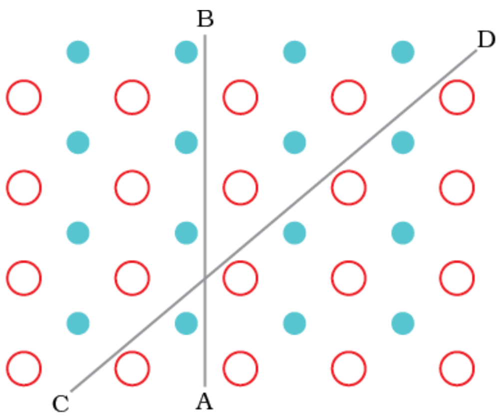

Fig. 2: Anisotropy in crystals is due to different arrangement of particles along different directions

Properties of Amorphous solids

- Amorphous solids do not have any regular arrangement of the constituent particles. They may have short range orders. The amorphous solids have irregular shapes.
- They do not have a sharp melting point. They gradually soften over a range of temperatures. They do not have definite enthalpy of fusion.
- When cut with a sharp edged tool they cut into two pieces with irregular surfaces.
- Amorphous solids are **isotropic** in nature. It is because the arrangement of constituent particles is irregular along all the directions. Therefore, the value of any physical

property (electrical resistance or refractive index) would be the same along each direction.

Some Interesting Facts

- On heating they become crystalline at some temperature. Some glass objects from ancient civilisations are found to become milky in appearance because of some crystallisation.
- These are called **pseudo solids or supercooled liquids** because like liquids, they have a tendency to flow. Therefore, glass panes fixed to windows or doors of old buildings are invariably found to be slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Uses of Amorphous solids

Amorphous solids such as glass, rubber and plastic find many uses in our daily lives because of their unique characteristics. For example,

- Inorganic glasses are used in construction, house ware, laboratory ware, etc .
- Amorphous silicon is the best photovoltaic material for converting the sunlight into electricity.
- Rubber is also an amorphous solid which is used in making tyres, shoe soles, etc.
- A large number of plastics are used in making articles of daily use.
- The differences between amorphous and crystalline solids are summarized in Table 2.

Table 2: Distinction between Crystalline and Amorphous Solids

Property	Crystalline solids	Amorphous solids
Shape	Definite characteristic geometrical shape	Irregular shape
Melting point	Melt at a sharp and characteristic temperature	Gradually soften over a range of temperature
Cleavage property	When cut with a sharp edged tool, they split into two pieces and the newly	When cut with a sharp edged tool, they cut into two pieces with irregular surfaces

	generated surfaces are plain and smooth	
Enthalpy of fusion	They have a definite and characteristic enthalpy of fusion	They do not have definite enthalpy of fusion
Anisotropy	Anisotropic in nature	Isotropic in nature
Nature	True solids	Pseudo solids or super cooled liquids
Order in arrangement of constituent particles	Long range order	Pseudo solids or super cooled liquids only short range order.

Answer the following questions

1. Crystalline solids exhibit __________ i.e. they have different physical properties in different directions.

   Ans: Anisotropy

2. There is a _____________ range order in amorphous solids.

   Ans: Short

3. Quartz is __________ while glass is ____________

   Ans: Crystalline, amorphous

4. Amorphous solids have tendency to flow although very slowly therefore they are called _________solids or ________ liquids.

   Ans: Pseudo, Supercooled

5. Crystalline solids have ______ melting point.

   Ans: Sharp

6. Some glass objects from ancient civilizations are found to become milky in appearance . It is due to ____________

   Ans: Crystallisation

7. Anisotropy is a strong evidence for the existence of ___________arrangement in crystalline solids

   Ans: Ordered

8. NaCl and KNO_3 are _____________ solids while plastic and glass are ____________ solids .

   Ans: Crystalline, Amorphous

9. ____________ solids undergo irregular cleavage.

   Ans: Crystalline, Amorphous

Answer

1. Anisotropy
2. Short
3. Crystalline, amorphous
4. Pseudo, Supercooled
5. Sharp
6. Crystallisation
7. Ordered
8. Crystalline, Amorphous
9. Crystalline, Amorphous

Classification of Crystalline Solids

The crystalline solids can be classified into the following four types depending upon the nature of intermolecular forces operating in them.

- Molecular solids
- Ionic solids
- Metallic solids
- Covalent or network solids

Molecular Solids

These are crystalline substances in which the constituent particles are molecules. The molecules are held together by dispersion forces or London forces, dipole-dipole forces or hydrogen bonds. These are further subdivided into the following categories:

- *Non polar molecular solids*: They comprise either atoms, for example, argon and helium or the molecules formed by non polar covalent bonds for example H_2, Cl_2 and I_2. In these solids, the atoms or molecules are held by weak dispersion forces or London forces about which you have learnt in Class XI. These solids are soft and non-conductors of electricity. These solids have the following characteristics:
    - They have low melting points.
    - They are generally soft.
    - They are usually in liquid or gaseous state at room temperature and pressure.

- They are non-conductors of electricity because they consist of neutral molecules in solid as well as in dissolved state.

- *Polar molecular solids*: The molecules of substances like HCl, SO_2, etc. are formed by polar covalent bonds. The molecules in such solids are held together by relatively stronger dipole-dipole interactions. Solid SO_2 and solid NH_3 are some examples of such solids. These solids have the following characteristics:
  - These solids are soft.
  - They are non-conductors of electricity.
  - They have low melting and boiling points. But their melting and boiling points are higher than those of non-polar molecular solids.
  - Because their melting and boiling points are not very high, most of these are gases or liquids under room temperature and pressure conditions.
- *Hydrogen bonded molecular solids*: The molecules of such solids contain polar covalent bonds between H and F, O or N atoms. Strong hydrogen bonding binds molecules of such solids like H_2O (ice). These solids have the following characteristics:
  - They are generally volatile liquids or soft solids under room temperature and normal pressure conditions.
  - They are non-conductors of electricity.
  - Their melting and boiling points are generally higher than those of non polar molecular solids and polar molecular solids.

Ionic Solids

Ionic solids consist of positively and negatively charged ions arranged in a regular manner throughout the solid. The ions are held together by strong coulombic (or electrostatic) forces. These solids have the following characteristics:

- Ionic solids are very **hard and brittle** because the ions in the compound are held rigidly in place in a lattice due to the strong electrostatic forces of attraction in between the cations and anions. **Brittleness** is due to the fact that when large enough force is applied along a certain plane, this causes the ions to shift along that layer, displacing that layer with respect to others. This brings charges closer which causes repulsion. This repulsion shatters the crystal lattice of the ionic compound.
- They have very high melting and boiling points.
- They are poor conductors of electricity and therefore, are insulators in solid state because the ions are not free to move about. However, in the molten state or when

dissolved in water (aqueous solution), the ions become free to move about and they conduct electricity.

- They have high enthalpies of vaporisation.
- Ionic crystals are soluble in water and also in other polar solvents. They are insoluble or very slightly soluble in non-polar solvents such as benzene, carbon tetrachloride and carbon disulphide.

The common examples of ionic crystals are: salts like NaCl, KNO_3, LiF, Na_2SO_4, etc.

Metallic Solids

In metallic crystals, the constituent particles are positive ions (called kernels) immersed in a sea of mobile electrons. The electrons in metallic crystals are mobile and are evenly spread throughout the crystal. Each metal atom contributes one or more electrons towards this sea of mobile electrons. These free mobile electrons are responsible for high electrical and thermal conductivities of metals. When an electric field is applied, these electrons flow through the network of positive ions. Similarly, when heat is supplied to one portion of metal, the thermal energy is uniformly spread throughout the crystal by free electrons. The forces present between the metal ions are metallic bonds. The main characteristic of metallic crystals are:

- Metallic crystals may be hard or soft.
- They are good conductors of heat and electricity.
- They have metallic luster and colour in certain cases.
- They are malleable and ductile. Due to malleable nature, they can be beaten into sheets and drawn into wires.
- They have moderate enthalpies of fusion.

The examples of metallic crystals are common metals such as nickel, copper and alloys.

Covalent or Network Solids: In covalent crystals, the constituent particles are non-metal atoms which are linked to the adjacent atoms by covalent bonds throughout the crystal. There is a continuous network of covalent bonds forming a giant three dimensional structure. They are also called giant molecules. Covalent bonds are strong and directional in nature. Therefore, the atoms in these solids are held very strongly at their positions. Their main characteristics are:

- The covalent crystals are hard.
- They have extremely high melting points.
- They are poor conductors of electricity and are insulators.

The common examples of covalent crystals are: diamond, Carborundum (silicon carbide), quartz (SiO_2), boron nitride (BN), etc. Diamond is a three-dimensional network solid. In diamond each carbon atom has four covalent bonds with surrounding atoms. This effectively makes each crystal one giant molecule held together by covalent bonds. This structure makes diamond chemically very non-reactive, very hard and electrical insulator.

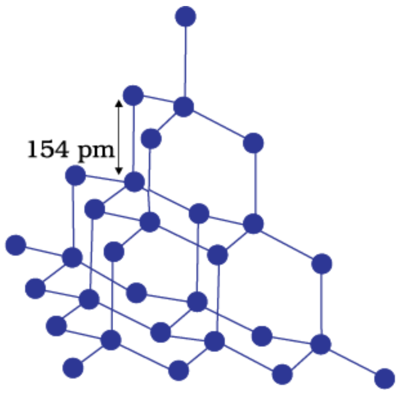

Fig. 3: Network structure

Graphite is soft and a conductor of electricity. Its exceptional properties are due to its typical structure (Fig. 4). Carbon atoms are arranged in different layers and each atom is covalently bonded to three of its neighbouring atoms in the same layer. The fourth valence electron of each atom is present between different layers and is free to move about. These free electrons make graphite a good conductor of electricity. Different layers can slide one over the other. This makes graphite a soft solid and a good solid lubricant.

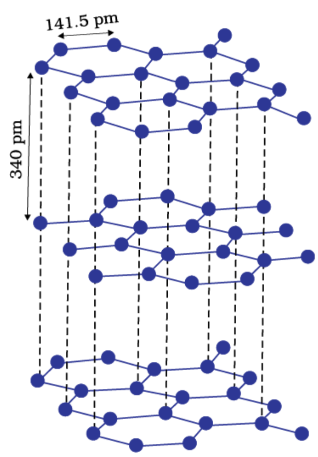

Fig. 4: Structure of graphite of diamond

The key points of different types of crystalline solids are summarized in Table 3.

Table 1.2: Different Types of Solids

Type of Solid	Constituent Particles	Bonding/ Attractive Forces	Examples	Physical Nature	Electrical Conductivity	Melting Point
(1) Molecular solids (i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4, H_2, I_2, CO_2	Soft	Insulator	Very low
(ii) Polar		Dipole-dipole interactions	HCl, SO_2	Soft	Insulator	Low
(iii) Hydrogen bonded		Hydrogen bonding	H_2O (ice)	Hard	Insulator	Low
(2) Ionic solids	Ions	Coulombic or electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	Insulators in solid state but conductors in molten state and in aqueous solutions	High
(3) Metallic solids	Positive ions in a sea of delocalised electrons	Metallic bonding	Fe, Cu, Ag, Mg	Hard but malleable and ductile	Conductors in solid state as well as in molten state	Fairly high
(4) Covalent or network solids	Atoms	Covalent bonding	SiO_2 (quartz), SiC, C (diamond), AlN,	Hard	Insulators	Very high
			$C_{(graphite)}$	Soft	Conductor (exception)	

(Source: Table: 1.2 page no: 6 Ch-1 NCERT Textbook of Class 12 chemistry part-1 Edition 2021-22)

Summary

- There are three states of matter.
- The stable state of matter is decided by the net effect of intermolecular attraction and thermal energy.
- In solids thermal energy is low and intermolecular forces of attraction are strong.
- Solids have definite mass, volume and shape and they are incompressible and rigid.
- On the basis of the nature of arrangement of constituent particles, solids are classified as crystalline and amorphous.
- Crystalline solids have regular arrangement of constituent particles over a long range. They have sharp melting points, definite enthalpy of fusion and are anisotropic in nature.
- Amorphous solids do not have regular arrangement of constituent particles, therefore, they have short range order. They do not have sharp melting points and they are isotropic in nature.

- Depending upon the nature of intermolecular forces operating in them, the crystalline solids can be classified into following four types as Molecular solids, Ionic solids, Metallic solids and Covalent or network solids
- In molecular solids, constituent particles are molecules held together by dispersion forces or London forces, dipole-dipole forces or hydrogen bonds.
- Molecular solids are further classified as non polar molecular solids, polar molecular solids and hydrogen bonded molecular solids
- Ionic solids consist of positively and negatively charged ions arranged in a regular manner throughout the solid held together by strong coulombic (or electrostatic) forces.
- In metallic crystals, the constituent particles are positive ions (called kernels) immersed in a sea of mobile electrons.
- In covalent crystals, the constituent particles are non-metal atoms which are linked to the adjacent atoms by covalent bonds throughout the crystal.

Answer the following questions:

1. 1. Classify following solids into molecular, ionic, metallic and covalent.
   P_4O_{10} , Graphite, Brass , Ammonium Phosphate , SiC , Rb , I_2 , LiBr , P_4 , Si
   Ans: Molecular solid - P_4O_{10}, I_2, P_4 ; Covalent solid- Graphite, SiC, Si; Metallic solid- Brass, Rb; Ionic solid- Ammonium Phosphate, LiBr

2. Classify the following solids as metallic, molecular, amorphous, covalent or ionic.
   (i) SO_2 (ii) Diamond (iii) I_2 (iv) MgO (iv) Ag (v) Quartz (vi) Ar
   Ans: Metallic solid – Ag; Covalent solid – Quartz ; Molecular solids - I_2, Ar, SO_2 ; Ionic solids – MgO

3. What are-(i) Molecular solids (ii) Metallic solids.
   i. **In molecular solids, the individual molecules are the constituents which are held together by van der Waals forces of attraction. e.g. I_2.**
   ii. **Metallic solids consist of positive ions(kernels) in a sea of electrons. The metal atoms are held together by metallic bonds. e.g. Ag, Cu.**

4. Name the force of attraction between the atoms or molecules in solid argon, solid CO_2 .

Dispersion forces

5. Identify the type of solid
   a. There is a solid A which is soft and an insulator. It is a _______ solid.
      Molecular
   b. A solid which conducts electricity only in molten or aqueous solution .It is ________ solid.
      Ionic
   c. A solid which is very hard and an insulator. It is _______ solid.
      Covalent
   d. A solid is hard but brittle . It is _________ solid .
      Ionic
   e. A solid which is a good conductor of heat and electricity . It is ________ solid.
      Metallic

6. Find the odd one out

a) Sulphur , argon , solid CO_2 , **diamond**

b) NaCl , KNO_3 ,**SiC** , Na_2SO_4

c) Teflon, polyurethane , polyvinyl chloride , **naphthalene**

Answer

1. Molecular solid - P_4O_{10}, I_2, P_4 ; Covalent solid- Graphite, SiC, Si; Metallic solid- Brass, Rb; Ionic solid- Ammonium Phosphate, LiBr
2. Metallic solid – Ag; Covalent solid – Quartz ; Molecular solids - I_2, Ar, SO_2 ; Ionic solids – MgO

3. (i) In molecular solids, the individual molecules are the constituents which are held together by van der Waals forces of attraction. e.g. I_2.
   (ii) Metallic solids consist of positive ions(kernels) in a sea of electrons. The metal atoms are held together by metallic bonds. e.g. Ag, Cu.

4. Dispersion forces
5. Identify the type of solid

a. Molecular
b. Ionic
c. Covalent
d. Ionic
e. Metallic

6. Find the odd one out

a) Diamond, all others are molecular solids

b) SiC, all others are ionic solid

c) Naphthalene, all others are amorphous solids