SOLID STATE

Kumud Bala

As we look around, most of things we see are solid substances rather than liquids and gases. Solids are the substances which have definite volume and definite shape. In terms of kinetic molecular model, solids have regular order of their constituent particles (atoms molecules or ions). Solids are characterized by the state of matter in which particles are closely packed and held together by strong intermolecular attractive force, therefore, they are present at fixed positions. The properties of the solids not only depend upon the nature of the constituents but also on their arrangements and types of forces which hold the constituent particles together in a tightly packed arrangement.

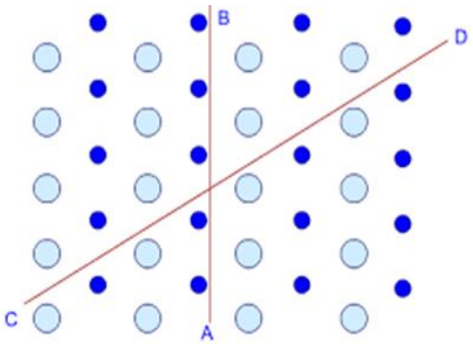
Properties of solids:

1. In solid state the particles are not able to move randomly.
2. They have definite shape and volume.
3. Solids have high density.
4. Solids have high and sharp melting points which depends on the strength or value of binding energy.
5.They are almost incompressible.
6. They show very slow diffusion.

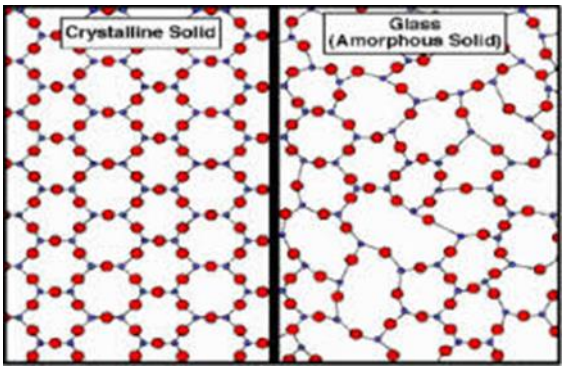
Solids can be classified on the basis of nature of order present in the arrangement of constituent particles (atoms, ions and molecules) into two types:

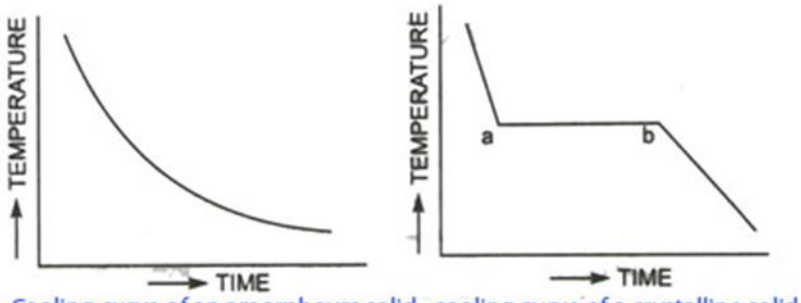
(i) crystalline solids: Substance whose constituent particles (atoms, ions or molecules) are arranged in a definite geometric pattern in three-dimensional space are called crystalline solid.
(ii) amorphous solids: (Greek word amorphous = no form)

Property	**Crystalline solids**	**Amorphous solids**
1. Shape	They have definite and regular geometrical form.	They do not have definite and regular geometrical form.
2. Order in arrangement of constituent particles	They have regular arrangement of the constituent particles. They are said to exhibit long range order.	They do not have regular arrangement of the constituent particles. They may have short range order.
3. Melting point	They have sharp and characteristic melting point.	They do not have sharp melting point. They gradually soften over a range of temperature.
4. Cleavage property	When cut with a sharp-edged tool, they split into two pieces and the newly generated surfaces are plain and smooth .	When cut with a sharp-edged tool, they split into two pieces with irregular surfaces.
5. Anisotropy and isotropy	They are anisotropic and have different physical properties in different directions.	They are isotropic and have same physical properties in all directions.
6. Enthalpy of fusion	They have a definite and characteristic enthalpy of fusion.	They do not have definite enthalpy of fusion.
7. Nature	They are true solids.	They are pseudo solids and supercooled liquids
8. Cooling curve	Discontinuous	Continuous
9. Examples	copper, silver, iron, NaCl, ZnS, KNO_3	glass, rubber, plastics, etc.

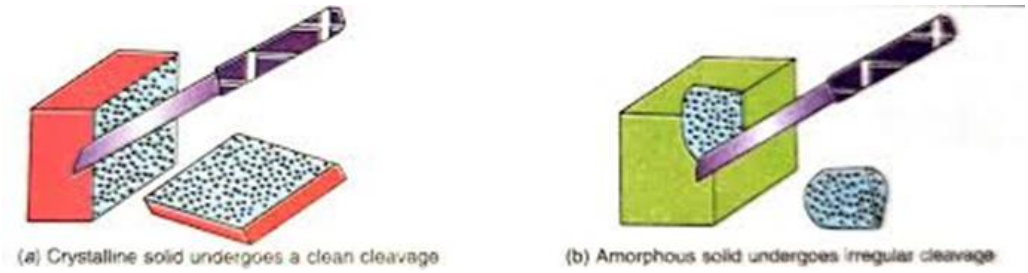


Anisotropy in Crystals





Cooling curve of an amorphours solid cooling curve of a crystalline solid


(a) Crystalline solid undergoes a clean cleavage

(b) Amorphous solid undergoes irregular cleavage

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

1. molecular solids
2. ionic solids
3. metallic solids
4. covalent or network solids

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

(a) Non polar molecular solids: these comprise of atoms, for example argon and helium or the molecules formed by nonpolar covalent bonds. For example, solid hydrogen, solid carbon dioxide, iodine etc. In these

solids, the atoms or molecules are held by week dispersion forces or London forces. These solids have the following characteristics:

(i) they are generally soft.

(ii) they have low melting points and are usually in a liquid or gaseous state at room temperature and pressure.

(iii) they are non -conductor of electricity because they consist of neutral molecules in solid as well as in dissolved state.

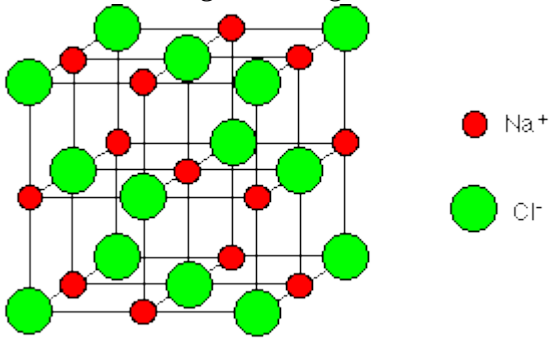
(iv) they are volatile and have low enthalpies of vaporization.

(b) Polar molecular solids: these comprise of molecules of substances formed by polar covalent bonds. For example, solid HCl, solid SO_2, solid NH_3, etc. The molecules in such solids are held together by relatively stronger dipole -dipole forces. These solids are also soft and non- conductors of electricity. They have low melting and boiling point. But their melting and boiling points are higher than those of non -polar molecular solids. Yet most of these are gases or liquids under room temperature and normal pressure conditions. They also have higher enthalpies of vaporization than those of non -polar molecular solids.

(c) Hydrogen bonded molecular solids: The molecules of such solids contain hydrogen bonds between them. For example, in case of solid water (ice), the negative end of one molecule (Oδ-) attracts the positive end of a neighboring molecule ($H^{\delta-}$) forming hydrogen bonding. These solids contain hydrogen bonds between hydrogen and F, O or nitrogen. They are generally volatile liquids or soft solids under room temperature and pressure conditions. They are non -conductor of electricity.

2. Ionic solids: These solid are consist of positively and negatively charged ions arranged in a regular fashion throughout the solid. The ions are held together by strong coulombic or electrostatic forces. Thus, in ionic solids the constituent particles are ions.

The regular arrangement of atoms and molecules extend continuously throughout the crystal. For example, in sodium chloride, Na^+ and Cl^- ions have a definite regular arrangement.



In this arrangement, each Na^+ is surrounded by six Cl^- and each Cl^- is surrounded by six Na^+ ions. Similar regular arrangements are also observed in other ionic solids. The main characteristics of ionic crystals are:

(i) ionic solids are very hard and brittle

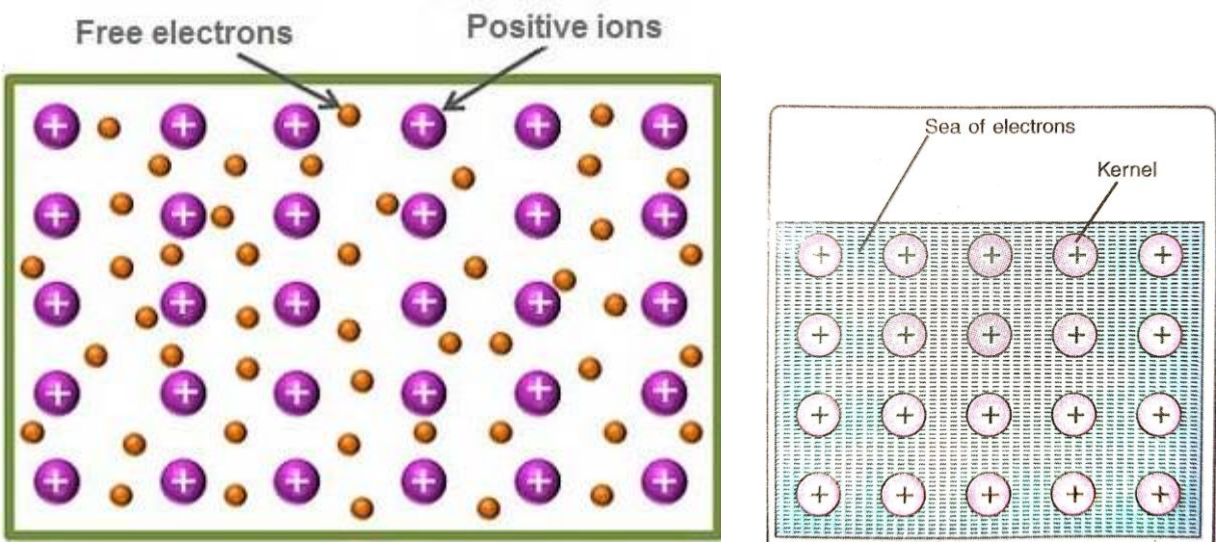
(ii) they have high melting points.

(iii) they are poor conductors of electricity and therefore, are insulators in solid state. This is because, in the solid state, the ions are not free to move about. However, in the molten state, or when dissolved in water, the ions become free to move about and they conduct electricity.

(iv) They have high enthalpy of vaporization.

(v) 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, carbon disulfide. Common examples of ionic crystals are sodium chloride, potassium nitrate, sodium sulphate, etc.

3. Metallic solids or crystals: In metallic solids, the constituents' particles are positive (called kernels) immersed in a sea of mobile electrons.



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

(i) metallic crystals may be hard as well as soft.

(ii) they are good conductors of heat and electricity.

(iii) they have metallic luster and colour in certain cases.

(iv) they are malleable and ductile. Due to malleable nature, they can be beaten into sheets and drawn into wires.

(v) they have moderate enthalpies of fusion. The examples of metallic crystals are common metals such as nickel, copper and alloys.

4. Covalent or network solids or crystals: In covalent crystal the constituent particles are atoms which are linked together by a continuous system of covalent bonds throughout the crystal. In other words,

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 and therefore, atoms in these solids are held very strongly at their position. The important characteristics of covalent crystals are:

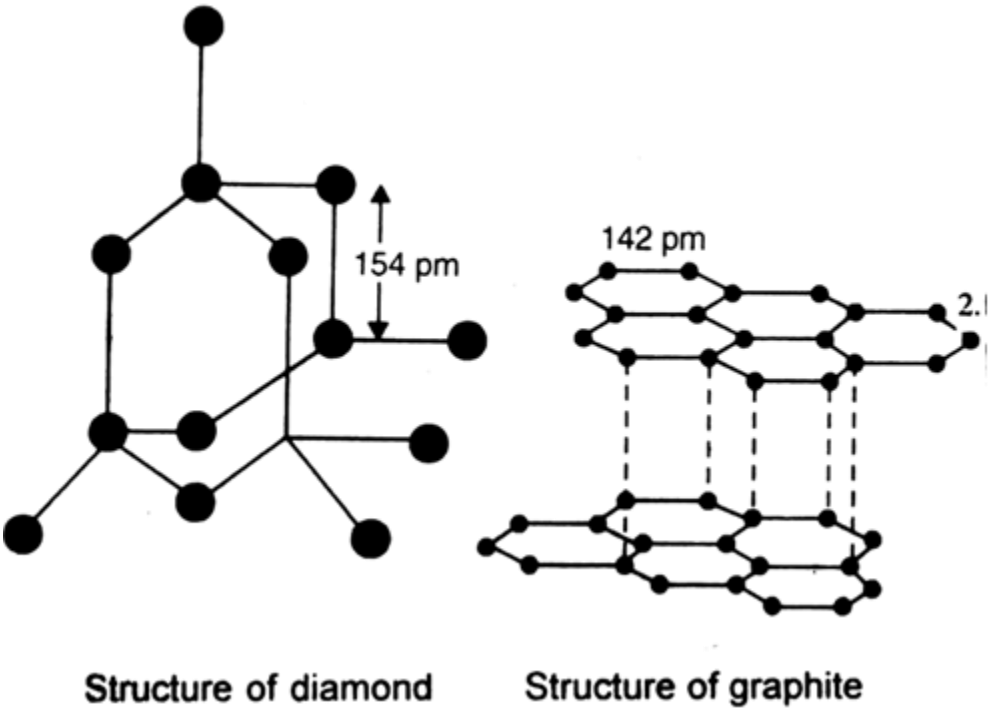
(i) the covalent crystals are hard.

(ii) they have extremely high melting point and may even decompose before melting.

(iii) they are poor conductors of electricity and are insulators.

(iv) they have high enthalpies of fusion.

The common examples of covalent crystals are diamond, carborundum (silicon carbide) quartz (silicon dioxide) boron nitride (BN) etc.



Structure of diamond Structure of graphite

Assignment

1. In which of the following pair, both the crystals are not of the same type.
   (A) ice, solid CO_2 (B) NaCl, BaO (C) SiC, diamond (D) Mg, Ar

2. In which of the following pairs, both the solids belong to same type?
   (A) solid CO_2, ZnS (B) CaF_2, Ca (C) graphite, ice (D) SiC, AlN

3. Graphite is an example of -----
   (A) ionic solid (B) covalent solid (C) molecular solid (D) metallic crystal
4. Which is amorphous solid?

(A) rubber (B) plastic (C) glass (D) all of these

5. Which of the following is an example of covalent solid?
(A) silicon carbide (B) $BaSO_4$ (C) solid CO_2 (D) iodine

6. An example of an ionic crystalline solid is ------
(A) diamond (B) silica (C) LiF (D) iron

7. Which of the following is not the property of crystalline solid?
(A) definite geometry (B) sharp melting point (C) isotropy (D) anisotropy

8. Which of the following is a molecular solid?
(A) MgO (B) AgCl (C) CO_2 (D) Pb

9. Which of the following does not belong to same type of crystal?
(A) quartz (B) SiC (C) iodine (D) diamond

10. Which one is called pseudo solid?
(A) CaF_2 (B) glass (C) NaCl (D) all of these

11. Amorphous solids ------
(A) possess sharp melting points
(B) undergo clean cleavage when cut with knife
(C) do not undergo clean cleavage when cut with knife
(D) possess orderly arrangement over long distances

12. Wax is an example of ----
(A) ionic crystal (B) covalent crystal (C) amorphous solid (D) metallic crystal

13. Crystals which are good conductor of electricity and heat are known as ------
(A) ionic crystals (B) covalent crystal (C) metallic crystals (D) molecular crystals

14. Iodine crystals are ----
(A) metallic crystals (B) ionic crystals (C) molecular crystals (D) covalent crystal

15. Which among the following will show anisotropy?
(A) glass (B) barium chloride (C) wood (D) paper

16. Which is covalent solid?
(A) rubber (B) diamond (C) graphite (D) all of these

Answers

1. (D) 2. (D) 3. (B) 4. (D) 5. (A) 6. (C) 7. (C) 8. (C)
9. (C) 10. (B) 11. (C) 12. (C) 13. (C) 14. (C) 15. (B) 16. (D)