6

SOLIDS

This is a 10 days unit

After completing this lesson, you will be able to:

- Define lattice energy.
- Describe simple properties of solids e.g., diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on kinetic molecular theory.
- Differentiate between amorphous and crystalline solids.
- Describe properties of crystalline solids like geometrical shape, melting point, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature.
- Use oxygen and sulphur to define allotropes.
- . Name three factors that affect the shape of an ionic crystal
- Explain the low density and high heat of fusion of ice.
- Define and explain molecular and metallic solids.
- Explain the significance of the unit cell to the shape of the crystal using NaCl as an example.
- Name three types of packing arrangements and draw or construct models of them
- Differentiate between ionic, covalent, molecular and metallic crystalline solids.

Reading

INTRODUCTION

The characteristics of the solid state are that the substance has definite shape. Due to the strongest inter-molecular forces existing between the molecules, it is little affected by changes in temperature and pressure. Glasses and amorphous materials are the exceptions where there is no orderly arrangement of atoms. Such solids are called super-cooled liquids. Other solids have complete regularity of their atomic and molecular structures. Such solids are called crystals.

It is observed that some kind of forces exists between the ions, atoms or molecules which keep them together in a crystalline solid. This gives a definite shape, rigidity and mechanical strength to the solids. Such forces are called inter-ionic inter-molecular and inter-atomic forces. These forces are of different types in different solids. As a result the solids have different physical properties.

6.1 KINETIC MOLECULAR INTERPRETATION OF SOLIDS

Kinetically the crystalline solids can be interpreted as follows:

i. **Attractive Forces:**

The attractive forces among the molecules are maximum due to closest packing of the molecules.

ii. **Rigidity:**

The molecules in solids are closely packed. Therefore their movement is restricted (limited). As a result they are rigid in nature. The molecules cannot move due to maximum attractive forces between them. However, molecules vibrate about their mean position.

iii. **High density:** $d = \frac{m}{v}$

The molecules of a crystalline solid are closely packed. As a result, molecules of solid occupy minimum volume. As density is inversely proportional to volume, therefore high density will be observed due to the minimum volume existing between the molecules.

iv. **Collision:**

As there is no translational movement of particles in a solid, therefore, there are no collisions among the molecules.

v. **Kinetic Energy:**

There is negligible translational and rotational kinetic energy in solid molecules. However they can vibrate about their mean positions. So molecules of solid possess only vibrational K.E.

vi. **Geometric Shape:**

The crystalline solids have definite distinctive geometrical shape. It is due to the definite and orderly arrangement of atoms, ions or molecules in three dimensional shape.

6.1.1 Properties of Solids

Some simple properties of solids are diffusion, compression, expansion, motion of molecules, spaces between them, intermolecular forces and kinetic energy based on Kinetic Molecular Theory.

Explanation of Properties

i. **Diffusion:**

The diffusion depends upon velocity of molecules. As the movement of the molecules is very slow, therefore, the diffusion will be minimum. Had there been diffusion in solids? The centuries old buildings would have collapsed in no time.

ii. **Compression (Effect of Pressure):**

There is practically no effect of pressure on solids as the molecules are very closely packed together.

The effect of pressure on solids is expressed in terms of compressibility (β). This is defined as, "The decrease in volume per unit volume when the pressure is increased by one atmosphere." $\beta = \frac{\Delta V}{V}$, 1atm

iii. **Expansion:** (Temperature)

The solids expand when heated i.e. their volume increases. This is because the increase of temperature decreases the intermolecular attractive forces. As a result, the volume increases.

The co-efficient of expansion (α) is defined as "the increase in volume per unit volume when the temperature is increased by 1 °C." When a solid is heated, its geometric shape

$\alpha = \frac{\Delta V}{V}$, 1°C

The student should be also guided to recall the information.

changes until at a certain temperature, it changes into the liquid form. The temperature at which a solid, changes into the liquid form is called Melting Point of the solid."

iv. Motion of Molecules:

There is no translational and rotational motion due to presence of strong intermolecular forces in the crystalline solid, as the molecules are already closely packed together. However the molecules can vibrate about their mean position.

v. Intermolecular Forces:

In solids, the intermolecular forces are maximum in between the particles. These are held together in fixed positions by strong attractive force. They can vibrate only about their fixed positions.

vi. Kinetic Energy Based Upon Kinetic Molecular Theory:

According to the Kinetic Molecular Theory, the attractive forces between the solid particles are maximum. This is due to minimum distance between them and, therefore, molecules do not possess translation and ~~vibrational~~ rotational kinetic energies. However, they can vibrate about their mean positions. So they possess vibrational kinetic energy.

6.2 TYPES OF SOLIDS:

There are two types of solids:

> **Do You Know**
>
> Metallic glasses are new amorphous materials composed of metallic alloys atomic with disordered atomic structure.

i. Amorphous Solids:

The solids which have no definite geometric shape are called amorphous solids e.g. glass, rubber, dust etc.

ii. Crystalline Solids:

The solid, which have a definite regular and three-dimensional geometric shape are called crystalline solids. Some crystalline solids have certain molecules of water of crystallization e.g. $CuSO_4.5H_2O$, $Na_2SO_4.10H_2O$.

6.2.1 Differences between Amorphous and Crystalline Solids

1) In the crystalline state, the crystals possess definite geometrical structure e.g. NaCl is cubic in nature. In the amorphous state the solids do not have definite geometrical structure e.g. glass.
2) There is a complete regularity of arrangement of atoms, ions or molecules in a crystalline solid whereas the atoms, ions or molecules are not arranged in a regular manner in amorphous solids.
3) The crystalline substance has a sharp Melting Point while the amorphous solid do not have sharp Melting Point and gradually soften on heating. They may be called as super-cooled liquids e.g. glass, plastic etc.
4) In a crystalline substance, water molecules are a part of crystal e.g. $FeSO_4.7H_2O$, $CuSO_4.5H_2O$ etc while the amorphous substances have no such water of crystallization.

The student should be guided to remember information.

5) In some cases, the colour of a crystalline substance is due to water of crystallization e.g. $CuSO_4.5H_2O$ is blue. The colour of crystals fades away in $CuSO_4.5H_2O$ when it is heated.

6) The amorphous solid is a solid which soften on heating ultimately they become mobile over a wide range of temperatures while the crystalline substances have no such property.

Crystal lattice → X-Ray of Crystal

6.3 PROPERTIES OF CRYSTALLINE SOLIDS

Some important properties of crystalline solids are described here:

Geometrical Shape:

Almost all the crystalline solids have a definite, distinctive geometrical shape because the molecules have fixed positions. Therefore they cannot move appreciably. Moreover the solids have orderly arrangement of atoms, ions or molecules in three dimensional space e.g. NaCl is cubic in nature.

Melting Point:

Pure crystalline solids have sharp melting point. When a solid is heated, the atoms, ions or molecules present in a solid start vibrating at higher frequency and transfer their kinetic energy throughout the solid. At the melting point, their vibrational energies become so much that they leave their fixed positions simultaneously and become a liquid.

(Break down)

Cleavage Planes:

A crystalline solid contains atoms, ions or molecules closely packed to each other. When some external pressure is applied to it, it changes into small crystals of the same size and shape as that of the original one.

The breaking up of larger crystals into smaller one with identical size and shape is called cleavage. The plane which contains the direction of cleavage is called cleavage plane.

e.g (i) $NiSO_4.6H_2O$ crystal can be cleaved easily provided cleavage is parallel to the surfaces.

(ii) The cleavage of $NaNO_3$ and $(CH_3COO)_2Ca$ is easy. It is parallel to the surface.

(iii) Mica can be cut easily parallel to the layers.

Habit of a Crystal:

Almost all the solids have particular no. of faces under identical conditions e.g. NaCl is cubic with six faces. But if an impurity is present, the solid material changes its structure because new faces are produced in addition to the original one.

The shape of a crystal in which it usually grows is called habit of a crystal. For example cubic crystals of sodium chloride are obtained from its aqueous solution. If the conditions are changed, the shape of crystal also changes. If 10% urea is present in aqueous solution of sodium chloride, octahedral crystals of sodium chloride are obtained.

v. **Crystal Growth:**

The crystal growth takes place when the heated solution of a substance is allowed to cool in a slow manner. The outer appearance or shape of the crystals depends on how it is prepared and under what condition e.g. a crystal with cubic structure may develop into a cube, a flat plate or a long needle like structure, under different conditions. The size of a crystal is controlled by its rate of growth. A slowly growing crystal has large size.

vi. **Anisotropy:**

A crystalline substance is a built up of small units all having the same geometrical form. But although a crystal is homogeneous, it possesses different properties in different directions. It is because crystal has different arrangements in different directions e.g. graphite exist in the form of layers, so it is conductor in one direction, parallel to layers but insulator across the layers.

A substance which shows different intensity of properties in different directions is called anisotropic and this property as anisotropy. *e.g.* Refractive index, co-efficient of thermal expansion, electrical and thermal conductivities give different intensity of properties in different directions. e.g. Mica can be cut parallel to the layers but difficult to cut in some other plane.

vii. **Symmetry:**

There are certain crystalline substances which after rotation to certain angles give similar edges, corners or faces at definite distances in definite directions. The rotational operation which brings the crystals into its original appearance is called symmetry of element; e.g. if a regular cube is rotated about its axis at an angle of 90°, the identical face is obtained. On rotating to 180°, a second identical face and at 360°, four identical faces are observed. An axis containing four identical faces is called four-fold axis of rotation. The process through which the crystal was brought back to its identical position is called symmetry operation.

An imaginary plane passing through a crystal that divides a crystal into two identical halves is called plane of symmetry. The symmetry elements that occur in a crystal are plane of symmetry, centre of symmetry, axis of symmetry and angle of symmetry.

viii. **Isomorphism:**

There are certain substances which are similar in shape. Different crystalline substances having the same crystalline shapes are called Isomorphs, and this phenomenon is called isomorphism; due to having same ratio of atoms.

e.g. (i) $ZnSO_4$ and $NiSO_4$ are isomorphism because both have the same crystalline shape i.e. orthorhombic. isomorphs have same atomic ratio.

(ii) Ag_2SO_4 and Na_2SO_4 are hexagonal. (Atomic ratio= 2:1:4)

(iii) $CaCO_3$ and $NaNO_3$ are Rhombohedral. (Atomic ratio= 1:1:3)

The student should be guided to recognize the information

xiv. **Polymorphism:**

The substance existing in more than one crystalline form is called polymorphous substance and the phenomena as polymorphism.

e.g. 1. NaCl is found in cubic and octahedral forms.

2. $CaCO_3$ is trigonal when present as calcite and orthorhombic when present as aragonite.

3. HgI_2 is orthorhombic (yellow form) and tetragonal in red form.

xx. **Allotropy (allotrope – Greek-allos (other), tropia (turning): (forms)**

An element may exist in different crystalline forms. These forms are called Allotropes and this phenomenon is called allotropy.

e.g. (i) C (as diamond) ________ in cubic form.

(ii) C (as graphite) ________ in hexagonal form.

xxi. **Transition Temperature:**

The temperature at which more than one forms of a given substance can exist in equilibrium is called transition temperature. Above and below this temperature only one polymorph or allotrope can exist.

No	Substance	Crystalline form	Transition temperature
1	Tin (grey) Tin (white)	Orthorhombic Tetragonal	18 °C
2	Sulphur	Monoclinic Ortho rhombic	95.6 °C
3	KNO_3	Orthorhombic Rhombohedral	128.5 °C

Allotropes of Oxygen

Dioxygen (O_2) and Trioxygen (O_3 or Ozone) are considered to be the two forms of oxygen obtained by the absorption of certain amount of heat from atmosphere.

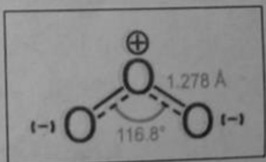


Figure 6.4: Shape of an ozone molecul

$$3O_2 \rightleftharpoons 2O_3, \qquad \Delta H = 142\ kJ\ mole^{-1}$$

The student should be guided to list given information.

Explanation to form Allotropes

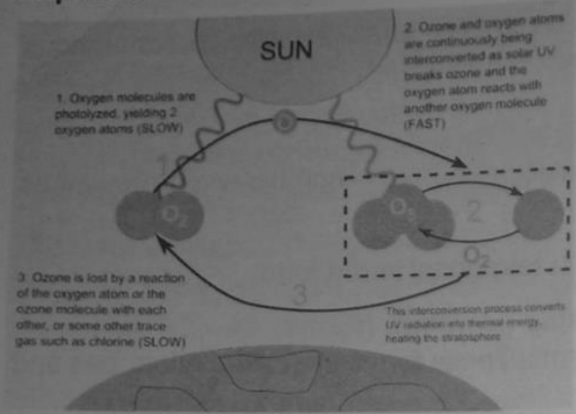


Figure 6.5 How ozone protects earth

Certain amount of heat is absorbed by dioxygen to form trioxygen i.e. ozone, the ultraviolet (U.V) light in the form of energy brings about photo-chemical reactions. These reactions can convert oxygen (O_2) to ozone (O_3). Since the conversion is spontaneous and one directional, therefore, it is called monotropic (moving in one direction). It has been found that the maximum concentration of ozone is (about 10 ppm) (parts per million), occurs 24-30 Km from the surface of the earth. Thus oxygen has two allotropic forms which are irreversible.

Structures

Oxygen molecule O = O has a sigma (σ) bond and a Pi-bond (π) between the two atoms. In ozone molecule, there is an angle of 117° between the bonds as indicated.

The ozone layer in the stratosphere (one of the layer of atmosphere) is shown below.

The allotropes of oxygen are of two types:

(i) Oxygen (O_2) (ii) Ozone (O_3)

Ozone has a characteristic smell, in concentration above 1000 ppm, it is causes health hazards.

Allotropes of Sulphur

Sulphur exists in four allotropic forms which are:

i. **Rhombic Sulphur (α-Sulphur):** It is bright yellow in colour and stable below 96°C. It is crystalline in nature and made up of S_8 molecules.

ii. **Monoclinic Sulphur (β-Sulphur):** It is a crystalline solid and stable between 96°C and 119°C. It is converted to Rhombic Sulphur at room temperature.

$$2H_2S_{(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} + 2S_{(s)} \text{ (amorphous solid)}$$

iii. **Plastic Sulphur (γ-Sulphur):** It is a super cooled form of sulphur. If yellow sulphur is heated to boiling and poured into liquid water, it will roll up and produce yellow ribbons resembling plastic like material. It is not considered to be a true allotrope of sulphur because it is soft and elastic in nature and insoluble in H_2S.

iv. **Amorphous Sulphur:** It has irregular crystalline shape which may be called as Amorphous. It is not found in the free state. It may be prepared by passing H_2S gas through water for a long time. The saturated solution of H_2S so obtained is exposed to air. Amorphous sulphur so produced has almost white colour.

6.4 CRYSTAL LATTICE:

The regular arrangement of the particles of a crystalline solid at the microscopic level produces characteristic shapes of crystals. The position of the particles in a crystalline solid is represented by a Lattice. An array of points representing the arrangement of particles (atoms, ions or molecules) in three dimensional spaces is called crystal lattice.

The external shape of a crystal depends upon the conditions of crystallisation. It may be different in one form or the other e.g. NaCl is cubic at ordinary conditions but octahedral in the presence of urea as impurity. But the internal structure is the same with basic structural unit. This unit describes the pattern by which the particles are arranged in a crystal. Primarily a crystal depends upon,

- Shape of the unit cell.
- Contents of the unit cell.

The atoms, molecules or ions in a crystal are repeated in a systematic manner. **The smallest unit of volume of a crystal, which shows all the properties of its pattern, is called a unit cell.** This is a basic structural unit of a crystal. The systematic arrangement of atoms in a crystal is called lattice. It represents the structure of any substance.

A lattice is of three types:

- Three dimensional lattice.
- Two dimensional lattice.
- One dimensional lattice.

6.4.1 Unit Cell and Shape of NaCl

We can explain significance of unit cell to the shape of crystal using NaCl as an example.

The unit cell is primarily concerned with the shape of the crystalline substance. Keeping in view the shape of the crystal, its structure can be identified. Let us take the example of NaCl.

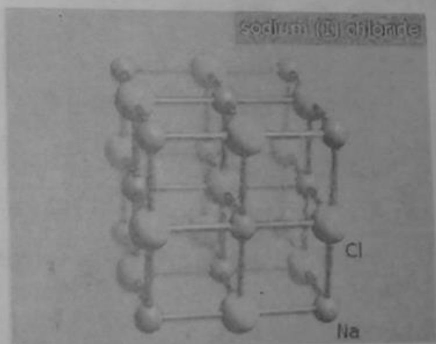


Figure 6.6: Structure of NaCl Crystal

i. **Location of ions:** In NaCl, each Na^{+1} ion is surrounded by 6 Cl^{-1} ions and vice versa. The size of Cl^{-1} ion is bigger than Na^{+1} ion because Cl^{-1} ion has 18 electrons and Na^{+1} ion has 10 electrons.

ii. **Co-ordinate Number:** The number of negative ions which contact a unit positive ion is called it's co-ordinate number. In NaCl each Na^{+1} ion contacts with 6 Cl^{-1} ions at the corner of a regular octahedron. So the co-ordination number of Na^{+1} ion is 6. Similarly co-ordination number of Cl^{-1} ion is also 6. The distance between all Na^{+1} ions and Cl^{-1} ion is the same.

iii. **No. of NaCl in Each Unit Cell:** In NaCl there are 8 Cl^{-1} ions at each corner of the cube. Each Cl^{-1} ion is shared among eight unit cells. Each face shares with two unit cells. So the number of Cl^{-1} ion in each unit cell can be calculated.

(a) Calculation of Cl^{-1} ions:

(i) No of unit cells = 8.

No of Cl^{-1} ions at each corner of cube = 8

Number of Cl^{-1} ions in one unit cell at the corner = $\frac{8}{8} = 1$

(ii) Total number of Cl^{-} ions at the Corner of a regular octahedron = 6

No of unit cells containing each face = 2

No of Cl^{-1} ion in each unit cell at face centers= $= \frac{6}{2} = 3$

Total number of Cl^{-1} ion in each unit cell = 1 + 3 = 4 Cl^{-1}

(b) Calculation of Na^{+1} ions:

Na^{+1} ions are present at the edges.

No of edges present in the cube = 12

Number of unit cells of Na^{+1} ions = 4

No of Na^{+1} ion present in each edge = $\frac{12}{4}$ = 3 Na^{+1}

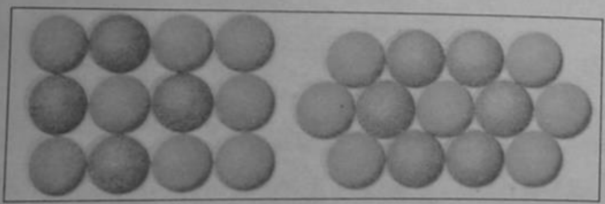
Na^{+1} ion present in the centre = 1 Na^{+1}

Total number of Na^{+1} ions = 3 + 1 = 4 Na^{+1} ions

So each unit cell consists of 4 Na^{+1} ions and 4 Cl^{-1} ions.

Hence 4 Na^{+1} + 4 Cl^{-1} = 4 NaCl can be written.

6.4.2 Types of Packing Arrangements



(a) An open packing (b) Close packing

Fig. 6.7: Packing spheres in two dimensions

The structure of metals can be explained when the atoms are packed together. The atoms in metals are considered as spheres of identical size. The closest packing is the most efficient arrangement of spheres of identical size and to fill available spaces. In which each sphere touches six neighbouring spheres (in green) as shown in (fig 6.7).

(b) Close Packing

This layer is shown in figure 6.8 as the bottom layer (layer A). When we place spheres in the second layer (layer B) each added sphere will rest in the hollow above a void or hole in the bottom layer. The spheres of the second layer will produce two types of voids. (i) a tetrahedral hole which falls above a sphere in the bottom layer. (ii) an octahedral hole, it falls above a void in the bottom layer.

...should be guided to employ the knowledge to illustrate the information.

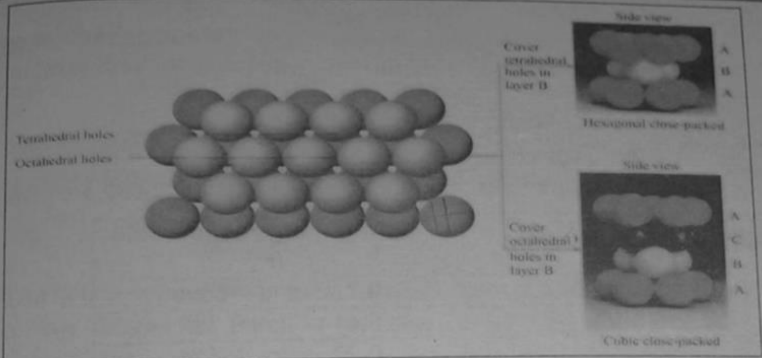


Fig. 6.8: Close-packing of spheres in three dimension

In adding a third layer of spheres (layer C), there are two possibilities.

(a) If tetrahedral holes are covered, the third layer is identical to the bottom layer. This arrangement is called hexagonal close-packing (hcp) arrangement. This pattern of arrangement is usually written as ABAB or 1212.

(b) In contrast, if we cover the octahedral holes, the third layer is not identical with the bottom layer. This is called the cubic closed packing (ccp) arrangement. It is usually written as ABCABC or 123123.

6.5.1 The Factors that Affect the Shape of an Ionic Solid

There are three factors which affect the shape of an ionic crystal.

Electrostatic Forces of Attractions:

The ionic solids are composed of cations and anions. They are held together through strong electrostatic forces of attraction forming a well defined geometric shape e.g. formation of NaCl.

Sodium loses one electron to be converted to Na^{+1} ions.

$$\underset{(2,8,1)}{Na} - 1e^{-1} \longrightarrow \underset{(2,8)}{Na^{+1}} \quad \text{(A cation is fomed)}$$

$$\underset{(2,8,7)}{Cl} + 1e^{-1} \longrightarrow \underset{(2,8,8)}{Cl^{-1}} \quad \text{(A anion is fomed)}$$

These ions combine together due to strong electrostatic force.

$$Na^{+1} + Cl^{-1} \longrightarrow NaCl \qquad \Delta H = -787\ kJ\,mole^{-1}$$

It is an exothermic reaction. To form a crystal lattice of NaCl, each Na^{+1} ion is surrounded by 6 Cl^{-1} ions and each Cl^{-1} ion is surrounded by $6Na^{+1}$ ions. As a result a cubic structure of ionic solid of NaCl is formed.

The student may be guided to distinguish between different facts and figures.

2. **Radius Ratio:**
The structure and shape of an ionic solid depends upon the radius ratio of cations and anions e.g. NaCl and CsF have the different geometry because the radius ratio is different in both the cases.

$$\text{Radius ratio} = \frac{\text{radius of cation}}{\text{radius of anion}}$$

The structure and Limiting radius ratio of certain crystalline substances are given below:

No	Shape of ionic solid	Limiting radius radio r^{+1}/r^{-1}
1	Body centred cubic	0.732 and above
2	Octahedral	0.414 to 0.732
3	Tetrahedral	0.22 to 0.414
4	Triangular	0.15 to 0.22

Thus knowledge of radius ratio consisting of cations and anions can give a good idea of the shape of crystal. And ionic compound with radius ratio greater than 0.732 will have Body centred cubic structure e.g. ~~Na~~ Cs Cl.

The radius ratio of an ionic compound with octahedral structure should be in between 0.414 and 0.732. Similarly a tetrahedral structure is formed if the radius ratio is in between 0.22 to 0.414.

The Radius Ratio of the following ionic crystals are:

1. NaCl = 0.522 – Octahedral arrangement or cubic structure.
2. CsCl = 0.93 – Body centred cubic arrangement.
3. ZnS = 0.40 – Tetrahedral arrangement.

3. **Poor Conductivity:**
The ionic crystals do not conduct electricity in the solid state. The shape of the crystals remains as such. However when a solvent (H_2O) is added to the ionic solid e.g NaCl, the crystal lattice is broken and the ionic solid changes into cation and anion. This is because the crystal lattice is broken due to high dielectric constant of water. In other words the shape of the crystal is ruptured.

$$NaCl_{(s)} \xrightarrow{\text{water}} Na^{+1}_{(aq)} + Cl^{-1}_{(aq)}$$

Thus the ions are solvated.

6.5.2 LATTICE ENERGY:

It may be defined on the basis of chemical reactions which may be exothermic or endothermic. The lattice energy can be defined in two ways.

- The amount of heat or energy released when gaseous ions of opposite charges combine to give one mole of a crystalline ionic compound is called lattice energy.

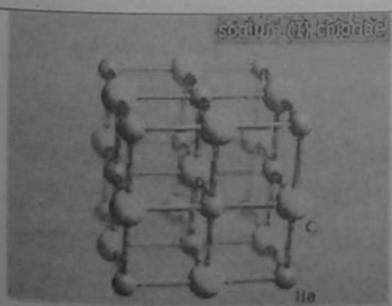
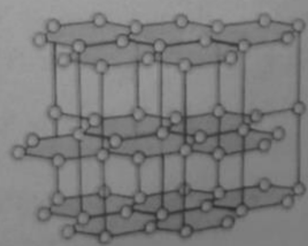
e.g. $Na^{+1}_{(g)} + Cl^{-1}_{(g)} \longrightarrow NaCl_{(s)} \Delta H = -787 \text{ kJ mole}^{-1}$

- The amount of energy required to break one mole crystal lattice into its gaseous ions is called lattice energy.

e.g. $NaCl_{(s)} \longrightarrow Na^{+}_{(g)} + Cl^{-}_{(g)} \qquad \Delta H = +787 \text{ kJ mole}^{-1}$

2) The lattice energy of the ions depends upon their size and charge of the ions. Lattice energy decreases with the increase in the size of the ions, (whether cations or anions), the packing of oppositely charged ions become less and less tight. Lattice energy increases with increasing ionic charge.

6.3 Comparison of Ionic and Covalent Crystals

Difference Between	
Ionic Crystals (Solid)	**Covalent Crystals**
1. An ionic crystal is formed due to the transference of electrons to the other e.g. NaCl formation. The cations and anions formed are held together through strong electrostatic forces of attractions.	1. The crystalline solids in which atoms of similar or dissimilar elements are held together in a network of single bond are known as covalent crystals e.g. diamond etc.
2. Formation of NaCl $\underset{(2,8,1)}{Na} - e^{-1} \longrightarrow \underset{(2,8)}{Na^{+1}}$ (cation) $\underset{(2,8,7)}{Cl} + e^{-1} \longrightarrow \underset{(2,8,8)}{Cl^{-1}}$ (anion) $Na^{+1} + Cl^{-1} \longrightarrow NaCl$	2. Covalent crystals are of two types: (i) When covalent bonds give giant molecules e.g. diamond, SiC (Silicon carbide) (ii) When atoms join together by sharing of electrons. As a result separate layers are formed e.g. graphite.
 Sodium Chloride crystal	 Graphite crystal

3.	They are non-conductors of electricity in the solid state. However they conduct electricity in the molten or solution form.	3.	They are bad conductors of electricity with the exception of graphite.
4.	They have definite geometric shape.	4.	They have definite shape and oriented in three directions with a network structure.
5.	They are non-directional in nature.	5.	They have open structures due to the valences of atoms directed in definite directions.
6.	They do not exist in the form of molecules due to their ionic nature.	6.	They may be called as molecules due to their covalent nature. e.g. S_8, P_4, ice.

6.5.4 Low Density and high Heat of Fusion of Ice

i. Low density of ice

When the temperature is decreased the molecules come close to each other. As a result the intermolecular attractive forces increase. However some empty spaces are developed in the ice. As a result about 9% more space than liquid water is produced. As $d = \frac{m}{v}$, that is density is, inversely proportional to volume, the increase in volume decreases the density. That is why ice floats over water.

Application of Low Density in Real Life

In cold countries when temperature is decreased to 0°C, water in ponds and lakes freezes. The ice formed stays on the top. This layer of ice acts as insulator for further heat loss. A thick layer of ice is formed at the top. Fish and plants can survive in the water for months under the thick blanket of ice.

Keeping in view the above discussion, we are forced to believe that the pattern of life for plants and animals would have been totally different in the absence of Hydrogen bonding in water.

ii. High Heat of Fusion of Ice

The quantity of heat required to convert one mole of a solid into liquid is called molar heat of fusion.

e.g. $\text{Ice} \longrightarrow \text{liquid water} \qquad \Delta H_f = 6.02 \text{ kJ mole}^{-1}$

Applications in Real Life

Ice absorbs 333 joules of energy for every gram of ice to melt. It means, if 33.3 k. Joules of energy from the surrounding is absorbed by each of the drink, the temperature of the drink without ice would rise from 0°C to 20°C. The drink containing the ice would remain at 0°C but 100 grams of ice would melt.

6.5.5 Molecular and Metallic Solids

1. **Molecular Solids:**

Definition: The solid substances in which the particles forming the solids are polar or non-polar molecules are called molecular crystals.

e.g. In solidified gases, these are non-polar atoms. Two types of intermolecular forces hold them together.

1. Dipole-Dipole interactions.
2. Van der Waal's forces.

Examples:

1. Crystals with polar molecules e.g. ice, sugar.
2. Crystals with non-polar molecules e.g. I_2, S_8; P_4, CO_2 etc.

Properties:

1. X-ray analysis indicates the regular arrangement of atoms. Thus we get the exact positions of all the atoms.
2. Polar molecular crystals have high m.p. and b.p. as compared to non-polar molecular crystals.
3. They are soft and easily compressible.
4. They are volatile in nature.
5. They are bad conductors of electricity.
6. They have low densities due to weak attractive forces.
7. They are transparent to light.

2. **Metallic Solids:**

Definition: The crystalline solids in which metal atoms are held together by metallic bonds are known as metallic solid e.g. Na, Cu etc.

Explanation (Electron Sea or Electron Gas Theory: Metals are good conductors because the valence electrons are loosely bound. Therefore they can move from one atom to the other. Due to this mobility of electrons, they are considered to conduct electricity. The positively charged portion of the metallic atom is surrounded by electrons in such a way that these electrons serve as an atmosphere of distributed charges. The positively charged particles are immersed in it. Such an atmosphere is called an electron gas or sea. This is shown below:

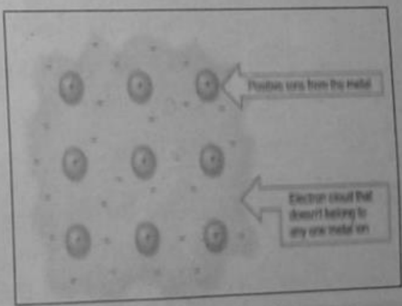


Figure 6.9 An electron sea surrounding cations

There are two forces responsible for the metallic bond.

1) Force of attraction between the electron gas and the positive ions.

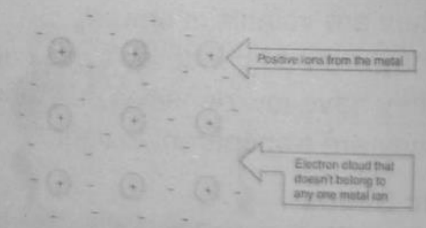
The student should be guided to discuss and explain information.

2) Force of repulsion between positively charged ions. These forces are equal and opposite. Therefore, they counterbalance each other. Thus the metallic atom is neutral as a whole.

Properties:

- They are best conductors of heat and electricity.
- They have lustrous surfaces.
- They are malleable and ductile.
- They have high melting points.

Comparison of molecular crystals and metallic solids

Molecular Crystals	Metallic Solids
1. Those solid substances in which the particles forming the solids are polar or non-polar molecules are called molecular crystals e.g. ice etc.	1. The crystalline solid in which metal atoms are held together by metallic bonds are known as metallic solids e.g. Na, Cu etc.
2. Two types of intermolecular forces hold them together. **(i) Dipole-Dipole interactions (Polar) e.g Ice, Sugar.** **(ii) London dispersion forces (Non-Polar) e.g.** I2, S8, P4 **etc.**	2. In metallic crystals, electron gas theory is involved.  An electron sea surrounding cations
3. They are bad conductors of electricity because they have not free electrons.	3. They are good conductors of electricity due to presence of free electrons.
4. They are not malleable and ductile.	4. They may be malleable and ductile.

6.5.6 Hygroscopic Salts

Some salts absorb moisture from atmosphere. Such salts are called hygroscopic salts. Calcium chloride ($CaCl_2$) has the property of absorption of moisture from the atmosphere. Thus it becomes hygroscopic. The absorption of moisture becomes maximum when there is humidity in air. The water molecules absorbed will become part of crystal of $CaCl_2$ and may be called as water of crystallization such substances are called Hydrates. $CaCl_2$ can absorb a maximum of $2H_2O$. Therefore $CaCl_2$ becomes $CaCl_2 \cdot 2H_2O$. The water of crystallization attached will increase the mass of calcium chloride.

The student should be guided to examine the different aspects of concepts.

HOW TO GET SODIUM CHLORIDE FROM SALINE SOLUTION:

Saline water (NaCl solution) contains water along with certain impurities. If saline water is allowed to freeze in freezing mixture of water, the impurities come up to the surface in the form of ice at -3.4°C leaving behind NaCl. Ice and impurities are removed from the surface leaving behind pure NaCl.

References for additional information

- Frank L. Pilar, Elementary Quantum chemistry.
- Drew H. Wolfe, Introduction to college chemistry.
- Olmsted Williams, Chenistry , The molecular Science.

Exercise

1. **Choose the correct answer (MCQs).**

i. The temperature at which two or more than two types of crystals exist in equilibrium is called.

(a) Melting Point (b) Transition temperature
(c) Eutectic temperature (d) Boiling point.

ii. The solids in which atoms, ions or molecules have random non-repetitive three dimensional arrangements are termed as:

(a) Crystals (b) Glasses
(c) Alloys (d) Amalgams

iii. The nature of bond in diamond is

(a) Ionic (b) Covalent
(c) Molecular (d) Metallic

iv. Crystal Lattice is an arrangement of particles in

(a) One dimension (b) Two dimensions
(c) Three dimensions (d) Four dimensions

v. Lattice energy is also called

(a) Crystal energy (b) Ionization energy
(c) Energy of affinity (d) Bond Energy

vi. When gaseous ions are allowed to form a crystal, energy

(a) is evolved (b) is absorbed
(c) is sometimes absorbed and sometimes released
(d) has no effect

vii. NaF and MgO have both atomic ratio 1:1 in their crystals such property is

(a) Polymorphism (b) Isomorphism
(c) Isotropy (d) Allotropy

viii. Electric current can pass through graphite in one direction but not through other direction of crystal such a property is called

(a) Allotropy (b) Anisotropy

(c) Isomorphism (d) Polymorphism

ix. Iron acts as an electrical conductor due to

(a) Electron cloud (b) Free protons

(c) Free neutrons (d) Free ions

x. A crystal of the purple compound Potassium Permanganate placed at the bottom of a beaker of water and the beaker left until there is no further change. What will be observed?

(a) A uniformly purple solution.

(b) A colourless liquid with the purple crystal unchanged.

(c) A purple layer below a colourless layer.

(d) A colourless layer below a purple layer.

(e) A deep purple layer below a pale purple layer.

xi. Which of the following method is most suitable for obtaining a pure, dry sample of NaCl from a mixture of NaCl and sand?

(a) Shake the mixture with water. Filter and dry the substances on the filter paper.

(b) Shake the mixture with water. Filter and evaporate the filtrate.

(c) Shake the mixture with water and distil off the sand.

(d) Heat the mixture gently and collect the substances which boil off.

xii. What method could be used to obtain copper from mixture of pondered copper and sodium chloride?

(a) Heating the mixture.

(b) Fractional distillation of the mixture.

(c) Passing an electric current through the mixture.

(d) Adding excess water to the mixture and filtering.

xiii. A bottle of copper oxide has been contaminated with some sodium chloride. How can the NaCl be removed from the copper oxide?

(a) Place the mixture in a separating funnel.

(b) Heat the mixture and allow it to cool.

(c) Add water to the mixture and filter.

(d) Add aqueous $AgNO_3$ to the mixture.

xiv. Lead and zinc can be separated by distillation because they have different.

(a) Boiling point (b) Densities

(c) Mass numbers (d) Reactivities.

xv. An insoluble solid was dropped into a measuring cylinder containing 50 cm^3 of water. What will be the effect on volume of water?

(a) 15 cm^3 (b) 17 cm^3

(c) 50 cm^3 (d) 65 cm^3

xvi. The results of the accurate weighing of some crystals are as follows:

Mass of weighing bottle empty = 25.652 g

Mass of weighing bottle + crystals = 26.541 g

What is the mass of the crystals?

(a) 0.111 g
(b) 0.889 g
(c) 1.111 g
(d) 1.889 g

xvii. The spontaneous mixing of particles is called:

(a) Evaporation
(b) Sublimation
(c) Diffusion
(d) Boiling

2 Write brief and short answers to the following:

i. Indicate the effect of pressure and temperature on solids.

ii. Differentiate between amorphous solids and crystalline solids.

iii. Write a note on Anisotropy.

iv. What is symmetry, symmetry operations, planes of symmetry and symmetry elements?

v. Write a note on transition temperature?

vi. What do you know by a Unit Cell?

vii. What do you know about Hexagonal Closest Packing?

viii. What do you know about Lattice Energy?

ix. Write a note on Dispersion Effect.

x. There are some changes in matter.

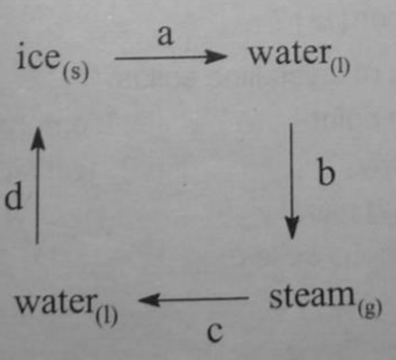
(i) Solids → Liquid
(ii) Liquid → Gas
(iii) Gas → Liquid
(iv) Liquid → Solid

Which of the changes require us to provide energy and which gives out energy?

xi. Explain each of the statements below,

(a) You can smell a fish from across the road.
(b) Sugar dissolves faster in hot water than in cold water.
(c) Condensation occurs on the inside of your windows in winter.

xii. Use the following words to label the changes "a" to "d" condensation, evaporation, freezing, melting.



xiii. Look at the densities in the table below:

No	Element	Density (g/cm^3)
1	Oxygen	0.00133 at room temperature and pressure
2	Sulphur	8.92
3	Potassium	7.14
4	Nitrogen	0.00117 at room temperature and pressure

a) What is the physical state of each element in the above table at 25°C?
b) Give the reason for big differences in the densities of elements shown above?
c) Why is the temperature and pressure important when giving the density of oxygen and nitrogen?

xiv. Explain why the particles in solid ice stick together and those of steam do not (even when they get very close (collision)?

xv. When long bridges are constructed, the roadbed is made in sections with spaces between the sections. Why must be done so?

xvi. Explain each of the following situations in terms of energy produced or used.
(a) You feel cold immediately after getting out of a swimming pool, but you feel comfortably warm when you have dried yourself.
(b) Skin exposed for just a short time to steam can suffer severe burns whereas; skin exposed to hot water for the same length of time suffers only a mild burn or none at all.

xvii. Write notes on (i) Amorphous solids (ii) Crystalline solids.

3 (a) How will you define a crystalline solid?
(b) Explain the kinetic molecular interpretation of a solid, keeping in view the following properties:
(i) Rigidity (ii) Collision (iii) Geometric shape
(iv) Attractive forces

4 Define and explain compressibility (β)?

5 Define the co-efficient of expansion (α)?

6 Describe the following properties of crystalline solids:
(i) Cleavage plane (ii) Melting point (iii) Isomorphism
(iv) Polymorphism (v) Allotropy (vi) Transition temperature

7 Differentiate between the following pairs:
(a) Crystalline solids and amorphous solids.
(b) Lattice and crystal lattice.
(c) Polymorphism and isomorphism.

(d) Hexagonal closest packing and cubic closest packing.
8 (a) Define a unit cell. List the factors on which a unit cell depends?
(b) Explain the structure of NaCl, keeping in view the unit cell?
9 Explain the three factors that affect the shape of an ionic crystal?
10 (a) Define lattice energy and give a particular example?
(b) Explain the low density and high heat of fusion of ice?
11 Compare molecular crystals and metallic crystals.
12 Illustrate the conductivity of a metallic crystal using "electron sea theory".
13 Write a detail note on ionic solids.
14 (a) Define covalent crystals and give their properties?
(b) How will you explain the covalent solids?
(i) When the atoms are jointly held together like diamond.
(ii) When the atoms have separate layers like graphite.
15 Value the significance of a unit cell to tell the shape of a crystal, using NaCl as an example?
16 ✓ Diamond is non-conductor while graphite is conductor in nature. Defend this statement.
17 Explain the kinetic energy of solids, based upon the kinetic molecular theory?
18 How will you explain the use of oxygen and sulphur to define allotropes?
19 ✓ A compound like $CaCl_2$ (calcium chloride) fluctuate in mass from day to day because of humidity. Evaluate this statement Hygroscopic
20 Saline water can be purified by repeated freezing method. Justify it.